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Insect Sex Attractants

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The review deals with the chemical study of natural attracting substances in insects. Insect attractants have been classified in accordance with structural factors: (1) unsaturated alcohols and their acetates; (2) aliphatic acids; (3) terpene-like substances. The methods of isolation of new attractants, biological tests, proof of individuality, determination of structure, and syntheses have been described in detail. The bibliography includes 140 references.

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I. INTRODUCTION

There are more than a million species of insects in nature. Among this wide variety similar species are encountered, which are almost indistinguishable in their external features. However, in the world of insects there is almost never any crossing of different species. The maintenance of "order" in nature is favoured by a number of refined phenomena involving sight, hearing, and especially smell, which is very highly developed in insects. This enables them to find food, sites for the deposition of eggs, and also individuals of the opposite sex.

The French naturalist Jean Henri Fabre was the first to note at the end of the XIXth century that the female of *Saturnia peri* (L) placed in a cage attracted a large number of males. He carried out experiments with other species of butterflies (moths) and concluded that the female executes vibrations which are propagated in air in the form of waves and are received by the antennae of the male. Later it was established that the information provided by the female is transmitted with the aid of a chemical substance. These substances have been called sex attractants†.

Sex attractants are extremely effective biologically active compounds and are distinguished by high specificity. These properties are of great value for the investigation of practical application of attractants for the purpose of attracting and destroying insects. The application of attractants in the fight against harmful insect species has developed in recent years and already considerable successes have been achieved. The practical importance of attracting substances stimulated the study of the chemical aspects of the problem. At the present time the structures of a number of natural attractants have been established.

The known compounds have definite structural features, which permit the classification of the sex attractants into three groups according to their structures: unsaturated alcohols and their esters, aliphatic acids, and terpene-like compounds. The first group contains the greatest number of the known attractants. It is noteworthy that the acetates of unsaturated aliphatic acids containing between 12 and 16 carbon atoms function as attractants for insects belonging mainly to the order Lepidoptera. No general conclusions concerning the other two groups are at the moment possible because of the insufficiency of factual data. In the present review the authors attempted to arrange the available data systematically in accordance with the structural features discovered.

A number of reviews dealing with sex attractants have been published[3-14], but these are of a descriptive type and the chemical aspects of the problem are touched upon only briefly. Nevertheless the chemical studies on sex attractants are very interesting because of their complexity and specificity. In the present review the authors' aim was to cover the literature data up to 1968 and to elucidate most fully the problems of the chemical nature and syntheses of attractants.

II. UNSATURATED ALCOHOLS AND THEIR ESTERS

1. Attractant of the Silkworm Moth [*Bombyx mori* (L.)]

In the 1940's Butenandt and coworkers began to study the attracting substance produced in the glands in the last two segments of the abdomen of the female silkworm moth. In 1959 they succeeded in isolating the sex attractant and in determining its structure[15,16]. The starting material consisted of the glands of 500 000 females. After a number of operations, shown in Scheme (I), fractions A, B, and C were obtained, which exhibited high activity. After three chromatographic purifications on Kieselguhr and then on silicic acid and repeated recrystallisation, 6 mg of the ester of 4'-nitroazobenzene-4-carboxylic acid was isolated from fraction B. After hydrolysis the substance yielded an alcohol with LE‡ = 10^{-10} μg, which was called bombykol. A further 6 mg of the bombykol ester was obtained from fractions A and C by analogous purification.

The general formula and the molecular weight of the bombykol ester were determined by elemental analysis and ultraviolet spectroscopy. The infrared spectrum showed absorption characteristic of the C–OH group in a primary alcohol, *cis-trans*-conjugated double bonds, and a methylene chain with not less than four carbon atoms. Catalytic

† The compounds secreted by one insect in order to influence another individual of the same species and to induce in the latter definite responses are frequently called "pheromones"[1]. Kirshenblat proposed a classification of such compounds and introduced the term "telergones"[2].

‡ *LE* is the unit of attraction defined as the weight of the substance in 1 ml of the attractant solution in petroleum ether which gives rise to a response in 50% of the males tested.

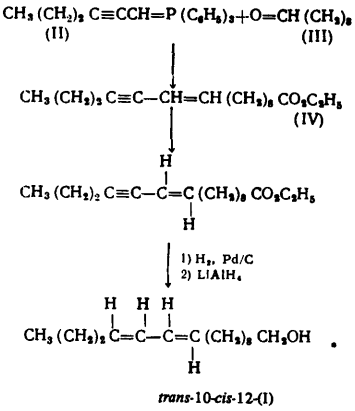
hydrogenation of bombykol yielded cetyl alcohol. The position of the double bonds in the molecule was established by oxidative degradation combined with paper chromatography of the ozonolysis products [17].

The combined data obtained led to the attribution of structure (I) to bombykol:

$$CH_3(CH_2)\underset{(I)}{CH{=}CH{-}CH{=}CH}(CH_2)_8CH_2OH\ .$$

The geometrical configuration of the compound was established by the synthesis of the four possible isomers of compound (I) and the comparison of their physicochemical and biological properties with those of the natural substance [18,19].

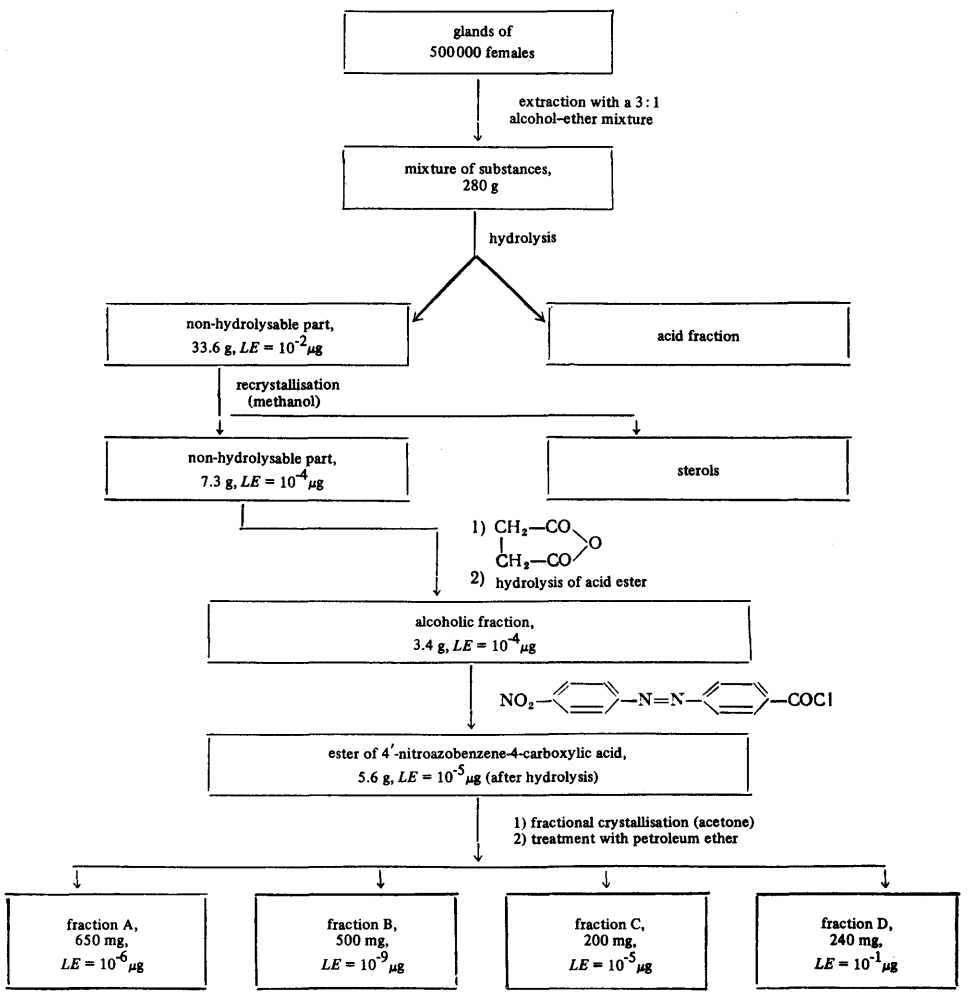
The *trans*-10-*cis*-12-isomer was obtained by the Wittig condensation of hex-2-ynylidenetriphenylphosphorane (II) with the aldehyde (III). This yields a mixture of the *cis*- and *trans*-isomers (IV) in approximately equal proportions. To separate the isomers and also in other syntheses [18,19], repeated crystallisation of the urea complexes was employed. After the hydrogenation of *trans*-(IV) using Lindlar's catalyst and after reduction with lithium aluminium hydride, *trans*-10-*cis*-12-(I) was obtained:



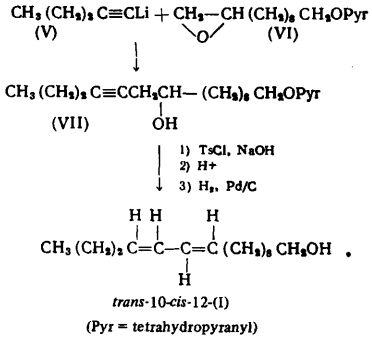
trans-10-*cis*-12-(I)

Scheme I

Isolation of the Natural Sex Attractant of the Silkworm Moth

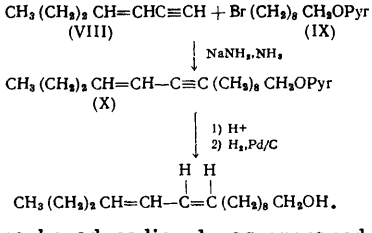


The same isomer was synthesised also by another method using the condensation of the lithium derivative of the pentyne (V) with the epoxide (VI):



After the dehydration of compound (VII), separation of the isomers, removal of the protective groups, and hydrogenation, the *trans*-10-*cis*-12-(I) isomer was obtained. The physicochemical properties of the latter were indistinguishable from those of the compound synthesised by the Wittig condensation.

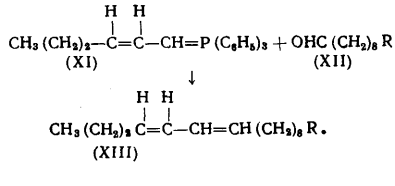
By the reaction of the sodium derivatives of *trans*- and *cis*-hept-3-enyne (VIII) with the tetrahydropyranyl ether of 9-bromononanol (IX), compound (X) was obtained, which after hydrolysis and hydrogenation by Lindlar's method gave respectively the *cis*-10-*trans*-12-(I) and the *cis*,*cis*-10,12-(I) isomers:



Trans,*trans*-hexadecadienol was prepared from *cis*-10-*trans*-12-(I) by photoisomerisation in the presence of iodine [19,9].

After comparing the melting points of the isomers and the natural bombykol, and also the melting points of the esters of 4'-nitroazobenzene-4-carboxylic acid and the ultraviolet and infrared spectroscopic data, the structure of *trans*-10-*cis*-12-hexadecadienol was attributed to bombykol. This was confirmed by comparing the activities of all the isomers in biological tests (Table 1).

Independently of these investigations, other workers [20] described the synthesis of all the isomers of compound (I). Like Butenandt, they employed the Wittig reaction, as one of the methods for the preparation of hexadecadienols:



In compounds (XII) and (XIII) R = $COOCH_3$, CH_2OCOCH_3, COOH, or CH_2OH.

Since it was shown that in the condensation process the configuration of the double bond in compound (XI) does not change, the reaction yields two isomers: *cis*-(XIII) and *trans*-(XIII). The problem of the separation of the isomers of compound (XIII) is greatly facilitated because the corresponding *cis*- and *trans*-acids differ fairly considerably in their solubility in petroleum ether and can be separated by recrystallisation [20]. This method makes it possible to obtain all four isomers.

The condensation of compounds (XIV) and (XV) was employed for the synthesis of the required *trans*-10-*cis*-12-(I), whereby it can be obtained with only a small admixture of the *trans*,*trans*-isomer:

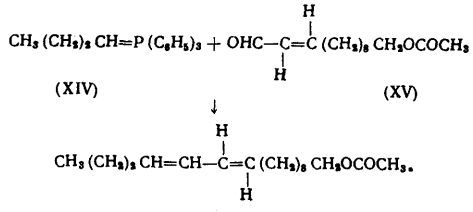
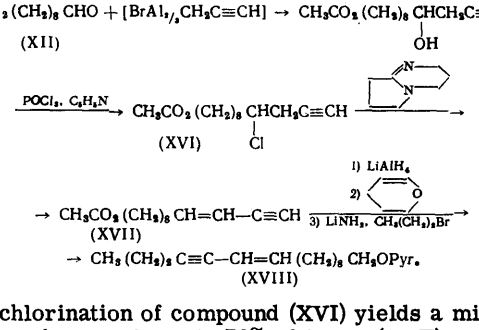


Table 1. Activity of bombykol and four geometrical isomers of a hexadeca-10,12-dienol.

Compound	*LE*, $\mu g\ ml^{-1}$*	*LE*, $\mu g\ ml^{-1}$**
Bombykol	10^{-10}	—
cis,*cis*-Hexadeca-10,12-dienol	1	—
cis-10-*trans*-12-Hexadecadienol	10^{-8}	10^{-5}
trans-10-*cis*-12-Hexadecadienol	10^{-12}	10^{-13}
trans,*trans*-Hexadeca-10,12-dienol	10	10^{3}

* According to Butenandt [19].
** According to Eiter [20].

Furthermore the same isomer of compound (I) was obtained by the following mechanism starting with compound (XII):



Dehydrochlorination of compound (XVI) yields a mixture consisting of approximately 70% of *trans*-(XVII) and 30% of *cis*-(XVII). However, after the reduction of compound (XVII) to the alcohol, protection of the hydroxy-group, and condensation with propyl bromide, mainly *trans*-(XVIII) was obtained. The biological activities of the compounds synthesised [20] differed somewhat from the activities of the isomers described by Butenandt [19] (See Table 1).

2. Attractants of the Gypsy Moth (*Porthetria dispar*).

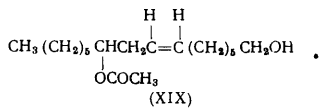
The gypsy moth causes serious damage to woods and fruit trees. After its accidental introduction in the past century into the USA, this insect multiplied rapidly and caused enormous damage in the forests of America. The gypsy moth is fairly widely distributed also in the USSR and periodically damages the forests in various regions.

It has long been known that the female of the gypsy moth attracts the male by means of "smell" and that the extract from the last two segments of the abdomen is a powerful attractant for males[21]. A benzene extract of the female abdomen is employed in the USA to control the numbers of the insects.

The first attempts to isolate the attractant were undertaken by Acree[22-24], who obtained an extract from the glands of 100 000 females and established that the non-hydrolysable fraction is active. By the chromatography of this fraction on magnesium carbonate and magnesium oxide, 12 mg of active but insufficiently pure substance was isolated, which the authors called "gyptol". Subsequently Jacobson et al.[25,26] isolated, using Acree's method[24], 75 mg of an active fraction from 500 000 females, which gave rise to five spots on paper. Only one of these was active. By extracting this spot, they obtained two substances: 3.4 mg of a solid fraction which was active at concentrations of 10^{-2} μg and 20 mg of a highly active liquid (10^{-7} μg in field tests) which fluoresced in ultraviolet light.

The reason for the existence of two natural active compounds has not been definitely established. It is suggested[26] that one of these serves to attract the male from a large distance and the other is necessary to cause it to mate.

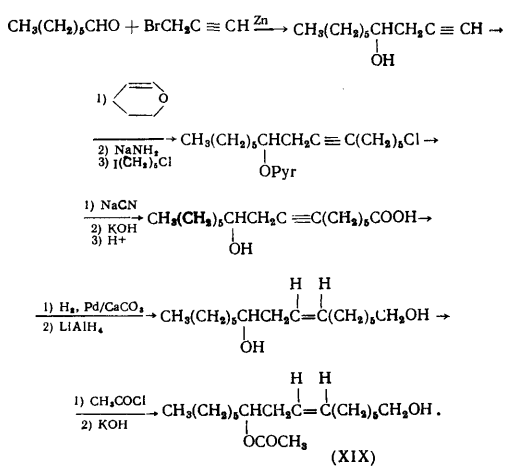
The chemical nature of the solid fraction has not been investigated. The liquid substance is optically active: $[\alpha]_D^{23} = +7.9°$. Its overall formula, $C_{17}H_{32}O_3$ or $C_{18}H_{34}O_3$, was established by elemental analysis. The infrared spectrum indicated the presence in the molecule of a primary hydroxyl, a secondary acetoxy-group, a *cis*-double bond, and a methylene chain with not less than four carbon atoms. Catalytic hydrogenation established the presence of only one double bond; its position and that of the acetoxy-group were demonstrated by oxidative degradation. As a result of these investigations, the attractant was identified as D-*cis*-10-acetoxyhexadec-7-enol (XIX):



(XIX)

Its structure was confirmed by the synthesis of the optically inactive form according to Scheme 2.

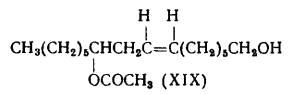
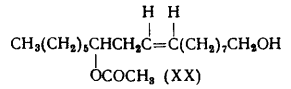
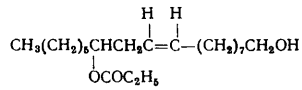
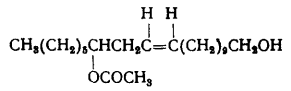
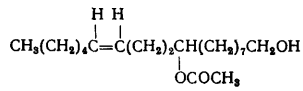
Scheme 2



DL-(XIX) was separated into the individual optical isomers[27]. The D- and L-isomers were identical in all respects, except for the sign of the angle of rotation. Nor did they differ in biological properties.

Gyptol analogues were obtained from the natural hydroxy-acids ricinoleic, (+)-14-hydroxy-*cis*-11-eicosenoic, and (+)-9-hydroxy-*cis*-12-octadecenoic by their reduction to the corresponding alcohols, acylation, and selective hydrolysis of the primary acetoxy-group[28-30] (Table 2).

Table 2. Activity of gyptol and its analogues.

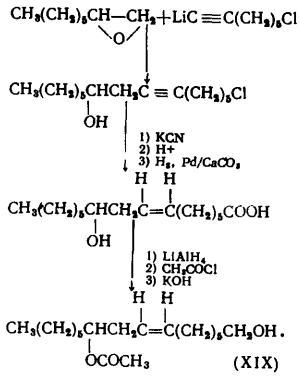
Compound	Activity, μg	
	laboratory	field
 (XIX)	10^{-12}	10^{-7}
 (XX)	10^{-12}	10^{-5}
trans-(XX)	10^{4}	$2.5 \cdot 10^{5}$
	inactive	
	10^{-2}	10
	inactive	

After studying the biological properties of compounds having structures similar to those of gyptol, the authors concluded that the presence of a *cis*-double bond and an acetoxy-group in β-position relative to the double bond is necessary for the activity of the molecule.

The most active analogue [compound (XX)] of the natural attractant was called "gyplure", and, because of the availability of the starting material for its manufacture, found practical application in the USA as a substitute for the benzene extract[31,32]. However, in industrial tests of the gyplure specimen the biological activity proved to be variable and in a number of cases the substance proved to be completely inactive. The authors explain this finding by the impurities produced in the preparation of gyplure under industrial conditions. In the study of this phenomenon it was found[33-35] that certain substances masked the effect of the attractant. For example, it is stated[34] that the presence of 20% of the *trans*-isomer in the highly active compound (XX) makes the latter completely inactive. An admixture of 7% of ricinoleyl alcohol also deactivates the attractant. Other workers[36,37] also note the absence of attracting capacity in gyplure specimens which they obtained by Jacobson's method[28,29]. The natural attractant (gyptol) synthesised[37] according to Scheme 3 also proved to be inactive.

The authors reject the hypothesis that in this case impurities may have masked the biological activity since the structure (XIX) of their compound was confirmed by infrared and NMR spectra. Furthermore, in tests by the electrophysiological method[38,39] of a mixture consisting of one part of the attractant obtained from Jacobson and nine parts of the synthetic substance[37], the mixture proved to be unexpectedly completely active. The reason for the loss of activity by attractants, in particular gyplure, is still not explained.

Scheme 3



(XIX)

Later a number of alcohols containing two conjugated double bonds[40] and also various unsaturated compounds incorporating a secondary acetoxy-group[41] were synthesised. Some of these alcohols, present at low concentrations, attracted insects of the order Lepidoptera. However, their activity was much lower than that of the natural attractant.

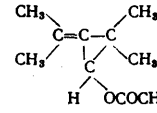
3. Attractant of the American Cockcroach [*Periplaneta americana* (L)]

Wharton and coworkers[42] isolated the active attracting substance from filter paper on which females of the black American cockcroach (*Periplaneta americana*) had been crawling and suggested that the substance was the sex attractant. The authors observed that the substance excites the male and gives rise to a characteristic behaviour of the latter. However, the amounts of attractant obtained (25 μg) were too small to establish fully its structure.

Subsequently Yamamoto[43] and Jacobson et al.[44] employed a method whereby it was possible to obtain the attracting mixture in much greater amounts and developed methods for its preparation. The methods which they proposed consist of the following steps: air was passed through a metal vessel containing about 1000 females of the American cockcroach for a period of nine months. The emerging gas stream was bubbled through a small amount of 0.1% hydrochloric acid and cooled with dry ice in a flask. The resulting condensate was extracted with hexane, the solvent was removed, and the residue was separated on a chromatographic column with silicic acid.

Thus 12.2 mg of pure attractant, consisting of a yellow liquid with a characteristic smell, was obtained from 10 000 females of the American cockcroach[44]. It gave rise to a response in the male even in an amount of 10^{-14} μg.

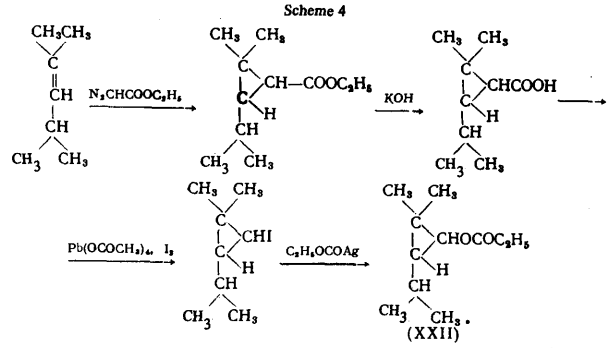
With the aid of elemental analysis, infrared and NMR spectroscopy, and chemical methods, the same authors established the structure of this substance (XXI):



(XXI)

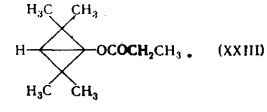
Catalytic hydrogenation of compound (XXI) yielded a substance which was identical with the dihydro-derivative (XXII), which was synthesised as indicated in Scheme 4.

Scheme 4



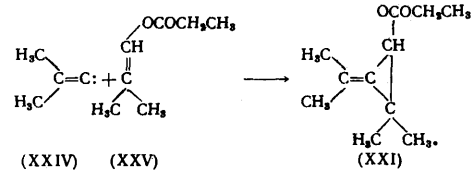
(XXII)

Jacobson's communication[44] attracted the interest of many chemists in different countries. Attempts were made to find methods of synthesis of compound (XXI) and its analogues[45-50]. Thus Day and coworkers[45] obtained compound (XXI) as one of the products of the reaction of 3-methylbuta-1,2-dienyl propionate with diazopropane followed by photolysis. The ester synthesised had the structure suggested by Jacobson for compound (XXI), but according to the NMR spectrum it differed appreciably from the natural attractant and was biologically inactive. On the basis of these data, Day and Whiting[45] suggested that the initially proposed structure for compound (XXI) is erroneous and that the bicyclobutane structure (XXIII) is more likely:



(XXIII)

Recently Wakabayashi[50] described a new synthesis of compound (XXI). The principal idea underlying the synthesis was the use of the reaction of the carbene (XXIV) with the enol ester (XXV):



(XXIV) (XXV) (XXI)

The carbene, formed in the reaction of dibromo-2-methylpropene with magnesium in tetrahydrofuran, was allowed to react with 2-methylpropenyl propionate (XXV) and gave the required product (XXI) in 18% yield. The latter had the same infrared and NMR spectra and the same gas–liquid chromatographic elution time as the substance obtained by Day and Whiting[45].

The absence of biological activity of the synthetic compound (XXI) confirms the earlier data[45] concerning its non-identity with the natural attractant.

Additional studies carried out by Jacobson and Beroza[51], who admitted that the initial structure (XXI) which they established for the sex attractant was erroneous, showed high instability of the natural compound. The crude attractant decomposes even in the cold in several days. However, in an atmosphere of nitrogen in a dilute hydrocarbon solution it can be stored at low temperatures for six months. The authors suggest[51] that compound (XXI) readily undergoes a complex rearrangement, the mechanism of which is still unknown. Thus the structure of the sex attractant of the American cockcroach requires revision.

4. The Sex Attractant of the Pink Bollworm Moth (*Pectinophora gossypiella*)

The pink bollworm moth causes considerable damage in the cotton industry. Its caterpillar, the pink bollworm, feeds on the seeds and seed filaments. All the countries in the world lose 20–25% of their cotton crop because of the pink bollworm. In the Soviet Union this variety of the insect is not widespread.

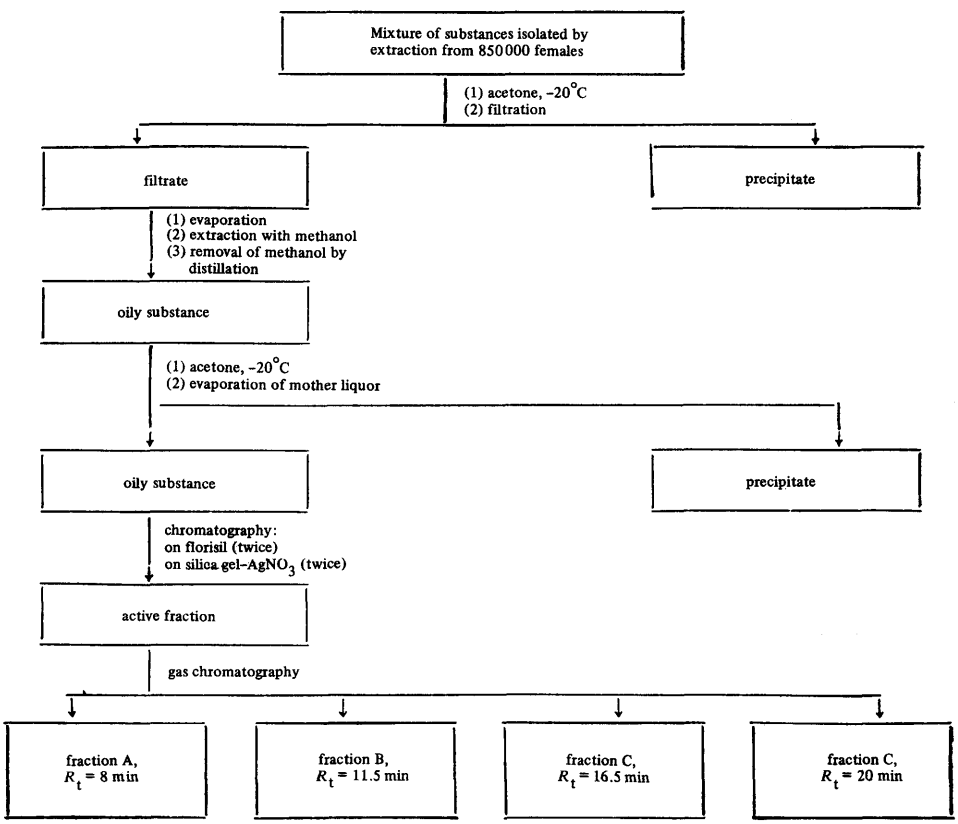
The first mention of the presence of an attractant in the females of the pink bollworm moth was made in 1957.[52] Then the characteristic behaviour of the male during mating was described[53]: excited flight, rapid wing vibration, and curving of the abdomen. A similar response was produced by an extract from the terminal segments of the female abdomen[53,54]. Such extracts were used to trap males under field conditions[54].

In 1966 the pure attractant of the pink bollworm moth was isolated and its structure was established[55]. The publication of this study is evidence of considerable progress in the chemistry of attractants. The authors, who had at their disposal 1.6 mg of the compound, established its complete structure, the investigation lasting only 2–3 years. The isolation of the sex attractant from the extract obtained from the whole bodies of 850 000 two days old females was carried out in accordance with Scheme 5.

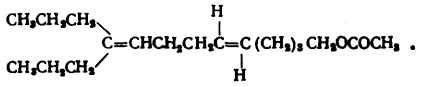
Only fraction B exhibited biological activity and was used to identify the attractant. The structure was established with the aid of physicochemical methods alone. The infrared spectrum demonstrated the presence in the molecule of a primary acetoxy-group, a *trans*-double bond, and a long methylene chain. The presence of a branched skeleton was demonstrated by means of the chromatography of the hydrogenation product[56]. The ultraviolet spectrum did not show the absorption characteristic of conjugated double bonds. Mass spectroscopy established the overall formula of the compound ($C_{18}H_{32}O_2$) and the molecular weight. These investigations suggested that the attractant is an acetate of a primary alcohol with 16 carbon atoms and has branched structure.

Scheme 5

Isolation of the Sex Attractant of Pectinophora gossypiella



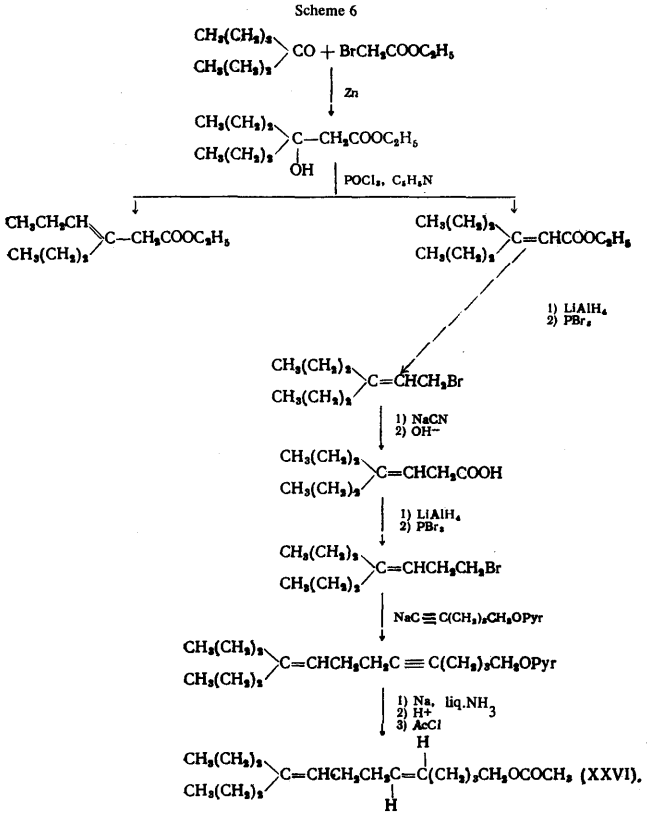
Additional NMR spectroscopic data showed that the sex attractant is *trans*-10-propyltrideca-5,9-dienyl acetate (XXVI):



(XXVI)

The structure of the attractant was confirmed by synthesis (Scheme 6) with a 0.2% yield of the final substance. The authors called compound (XXVI) "propylure" and stated that this is in fact the first natural substance with propyl branching.

Scheme 6

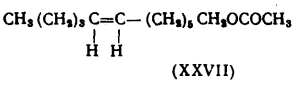


At the present time yet another method of synthesising "propylure", including a number of consecutive reactions in accordance with Scheme 7, is known.

Another cotton pest, the cotton leafworm moth [*Alabama argillacea* (Hübner)], secretes about 0.1 μg of the pheromone. A concentrate containing one tenth of this amount gives rise to a typical response in the males[57]. After the purification of the concentrate by thin-layer and gas chromatography, a substance was obtained with properties characteristic of a hydrocarbon with about 20 carbon atoms.

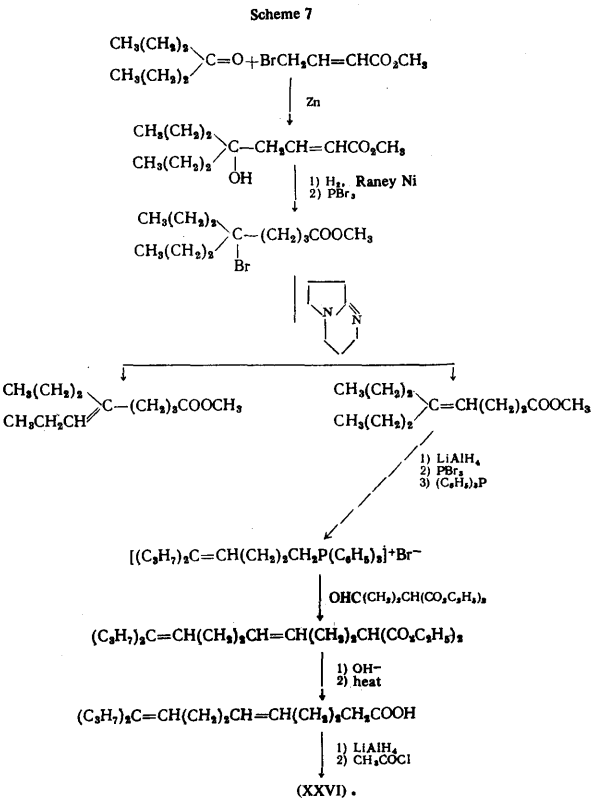
5. The Attractant of the Cabbage Looper (*Trichoplusia ni*)

The presence of a sex attractant in the females of the cabbage looper (*Trichoplusia ni*) became known thanks to the work of Ignoffo et al.[58] and Shorey[59]. In 1966 Berger[60] isolated by extraction with methylene chloride from 2500 females of the cabbage looper about 200 mg of a yellow oil containing the pheromone. The crude extract was separated from the major part of the lipids by chromatography on silicic acid, which yielded about 10 mg of a highly active substance; this, however, still contained impurities. Further purification by gas chromatography led to the isolation of the pure compound. Physicochemical methods and the chemical properties of the compound led to the determination of the structure of the attractant as *cis*-dodec-7-enyl acetate (XXVII).



(XXVII)

Scheme 7

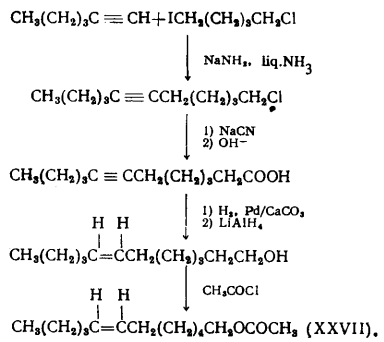


The proposed structure (XXVII) was confirmed by synthesis with an overall yield of product of 28%. The attractant was synthesised according to Scheme 8.

1-Chloroundec-6-yne (XXVII), obtained by the action of hex-1-yne and sodamide on 1-chloro-5-iodopentane in liquid ammonia, was converted into dodec-7-ynoic acid by treatment with sodium cyanide and subsequent hydrolysis. After the reduction of the triple bond in the presence of Lindlar's catalyst to a *cis*-double bond and of the carboxy-group with lithium aluminium hydride to an alcoholic group, a high yield of an unsaturated alcohol, *cis*-dodec-7-enol, was obtained. On acetylation of the hydroxy-group with acetyl chloride, the alcohol was converted into *cis*-dodec-7-enyl acetate (XXVII).

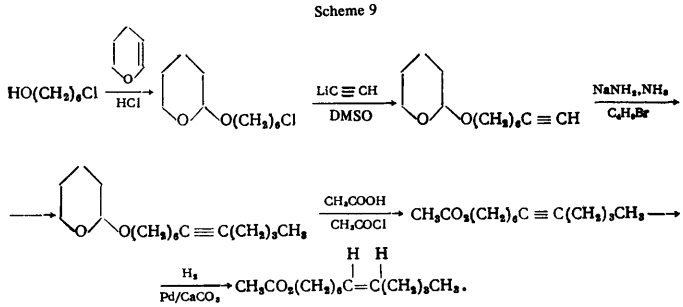
According to the infrared spectrum, the gas chromatographic elution time, and the physicochemical constants, the compound synthesised is identical with the natural attractant. The amounts of both the natural and the synthetic compounds showing the minimal biological activity are the same: 0.1 $\mu g\ ml^{-1}$.

Scheme 8



Green et al.[61] synthesised *cis*- and *trans*-dodec-7-enyl acetates by two different procedures. The method pf preparation of the *cis*-isomer (XXVII) is clear from Scheme 9 quoted below.

Scheme 9



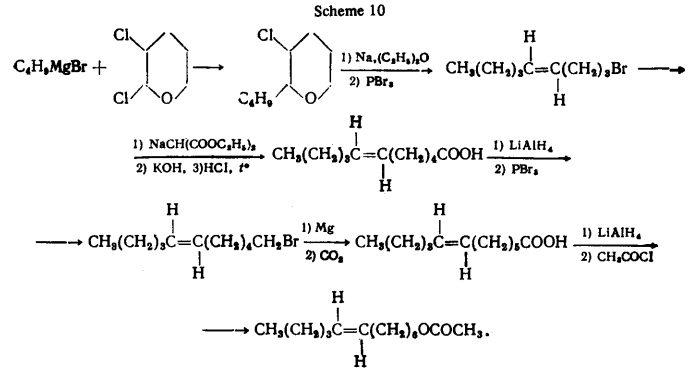
The synthesis of the *trans*-isomer according to Scheme 10 has the advantage that the final product is obtained without an admixture of the *cis*-form. The same workers and also Toba et al.[62] confirmed the high biological activity of the *cis*-acetate (XXVII) under both laboratory and field conditions. Synthetic analogues[61,63-65] of the natural attractant such as oct-7-ynyl, dodec-7-ynyl, *cis*-oct-7-enyl, *cis*-dec-7-enyl, *trans*-dodec-7-enyl, *cis*-dodec-5-enyl, *trans*-dodec-5-enyl, *cis*-dodec-9-enyl, dodecyl, and *cis*-tetradec-7-enyl acetates and the alcohols *cis*-dec-7-enol and dodecanol are weakly active or altogether inactive.

Thus the conditions necessary for the activity of the attractants of the cabbage looper are the presence of a straight twelve atom carbon chain, a *cis*-double bond in position 7, and an acetoxy-group in position 1. The failure of even one of these requirements leads to a sharp reduction or complete loss of the biological activity of the attractant.

6. Attractants of the Trinidad Butterfly (*Lycorea ceres ceres*)

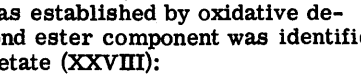
The males of the tropical butterfly of the subfamily Danainae have two organs, called androconia, which can be projected from the abdomen. During the "nuptial games" the male secretes the odorous substance through the androcones. The female attracted by the substance during the flight pursues the male.

Scheme 10



The data on the chemical nature of the substances secreted by the male moth are fewer than those of the attractants produced in the female organism. However, recently the chemical composition of the secretion of the male Trinidad butterfly (*Lycorea ceres ceres*) became known[66]. Extraction of the hairs removed from the androconia of several hundred males yielded a mixture which contained three substances according to gas–liquid chromatographic data. Adsorption chromatography of the extract from 100 males yielded two fractions: about 2.8 mg of the ester fraction and about 10 mg of the carbonyl fraction. The ester fraction was separated by preparative gas–liquid chromatography into two ester components. The infrared spectrum of one of these showed absorption characteristic of the acetate, which did not change on catalytic hydrogenation. On the basis of the mass spectra, the formula $C_{16}H_{33}OCOCH_3$ was proposed in the above investigations. The structure was confirmed by comparison with a cetyl acetate specimen.

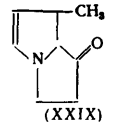
The second substance was investigated by infrared and mass spectroscopy. It was shown that it is the acetate derived from an alcohol with a molecular weight of 310, which corresponds to an unsaturated or monocyclic alcohol with 18 carbon atoms. Catalytic hydrogenation gave stearyl acetate. Comparison of the spectroscopic and chromatographic data for the compound isolated and oleyl acetate revealed a considerable similarity. The position of the double bond in the chain was established by oxidative degradation. Thus the second ester component was identified as *cis*-octadec-11-enyl acetate (XXVIII):



(XXVIII)

A synthetic specimen of compound (XXVIII) was obtained by the reduction of methyl *cis*-octadec-11-enoate with lithium aluminium hydride and acetylation of the resulting alcohol.

The unknown substance was isolated from the carbonyl fraction by vacuum sublimation. The study of the infrared, NMR, and mass spectra of this substance and a number of known compounds similar to the carbonyl component led to formula (XXIX) for the latter:



(XXIX)

The structure of the compound was confirmed by synthesis, which included the cyclisation of *N*-cyanoethyl-3-methylpyrrole[67]. The specimen obtained was identical with compound (XXIX) according to infrared, ultraviolet, NMR, and mass spectra, but it did not have the sweetish smell characteristic of the natural compound. Possibly this smell is due to traces of impurities[66]. The structure of compound (XXIX) differs sharply from that of the pheromones of the moth of this species and also from those of the attractant described earlier, but it is fairly similar to the structure of a number of plant alkaloids[68]. It is suggested[66] that compound (XXIX) is not produced in the insect organism but is introduced with the food or is derived from compounds obtained from the food.

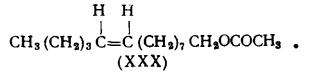
The males of another Danainae species, *Danaus gilippus berenice*, also produce an odorous secretion, which is exuded through androconia[69]. However, the chemical nature of their pheromones is still unknown.

7. Attractant of the Fall Armyworm Moth (*Spodoptera frugiperda*)

Various species of *Spodoptera frugiperda* secrete a substance which stimulates the male to mate. The substance is concentrated in the terminal segments of the abdomen. Each female produces approximately 0.01 μg of the odorous secretion[70,71].

The structure of the attractant secreted by *Spodoptera frugiperda* has now been established[72]. The terminal segments of 135 000 unmated females 3–5 days old were used for the isolation. The mixture (55 ml) obtained from the extract was separated by column and repeated thin-layer chromatography into a number of fractions. The active fractions were selected with the aid of a biological test. The final purification was achieved by preparative gas chromatography. In this way 900 mg of the pure attractant was obtained.

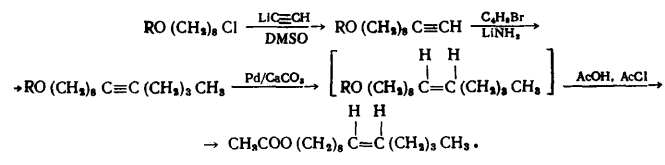
The infrared spectrum showed an absorption characteristic of the acetyl carbonyl group and a *cis*-double bond. The ultraviolet spectrum did not contain any absorption characteristic of conjugated bonds. The presence of an ester group was confirmed by alkaline hydrolysis, which resulted in complete disappearance of biological activity. On acetylating the hydrolysis product, the activity was restored. Catalytic hydrogenation yielded tetradecanol. The position of the double bond was established by ozonolysis. These investigations led to the identification of the attractant as *cis*-tetradec-9-enyl acetate (XXX)[72]:



(XXX)

Compound (XXX) was obtained from myristoleic (tetradecenoic) acid by reduction with lithium aluminium hydride and acetylation. The synthetic substance was active at a concentration of 3×10^{-12} g.

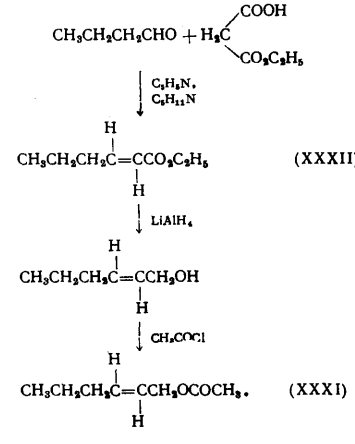
In addition, the complete synthesis of *cis*-tetradec-9-enyl acetate, based on the condensation dec-1-yn-10-ol with butyl bromide, has been described[73]:



Jacobson and Harding[74] suggested that *cis*-tetradec-9-enyl acetate be obtained using as the starting material the commercial preparation of dodec-7-enyl acetate—the attractant of *Trichoplusia ni*.

8. The Attractant of the Giant Water Beetle [*Belostoma indica vitalis* or *Lethocerus indicus* (Lep)]

The giant water beetle is a large insect approximately 7 cm long and 4 cm wide. It lives in ponds in South East Asia, Africa, and South America. The males have two tubes about 4 cm long on the abdomen. Through these the giant water beetles secrete approximately 0.02 ml of a transparent liquid with a cinnamon smell. In Southern Asia it is used as a spice in food. This liquid is probably the sex pheromone of the male[75]. Butenandt investigated the attractant of the giant water beetle[75]. To obtain the substance, he removed the glands from the male and squeezed the secretion from them. In this way he managed to secure 3 ml of the liquid. It was established by chemical reactions that the attractant is an acetate ester. The alcoholic component characterised as the 4′-nitroazobenzenecarboxylate ester[76], was found to be an unsaturated alcohol $C_6H_{11}OH$. The position of the double bond was determined by oxidative degradation. Thus it has been established that the main component of the secretion of the giant water beetle is *trans*-hex-2-enyl acetate (XXXI). This structure is confirmed by the synthesis of compound (XXXI) based on butyraldehyde and the half-ester of malonic acid. The ester (XXXII) formed on condensation was reduced to the alcohol with lithium aluminium hydride and acetylated:



(XXXII)

(XXXI)

III. ALIPHATIC ACIDS

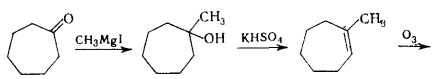
1. Attractants of the Honey Bee [*Apis mellifera* (L.)]

The complex life of the beehive is probably regulated and controlled by many pheromones having different purposes. At the present time at least several such compounds, produced by the queen and worker bees, are known. In 1959 Butler[77] showed that the secretions of the queen bee contain a pheromone which prevents the laying of eggs by the worker bees and the growth of new queens. This substance was isolated[78-81] and proved to be *trans*-9-oxodec-2-enoic acid. The studies carried out by Gary[82] provided the experimental proof of the existence of volatile sex attractants in the queen bee. The secretions of the mandibular glands of the queen enable the drones to find it during the nuptial fight. It was shown[81] that the scent attracting the drones is mainly due to 9-oxodecenoic acid. 9-Hydroxydecenoic acid accompanying it is only weakly active with respect to drones—it is responsible for the stabilisation of the swarm.

The practical and theoretical interest in the discovery of the pheromones of bees led over a short period of time to a number of independent investigations of the synthesis of *trans*-9-oxodec-2-enoic acid[79,86-92] (XXXIII), the biologically similar *cis*-isomer[93], and 9-hydroxydecenoic acid[80-91].

Among the methods described for the preparation of compound (XXXIII), the elegant synthesis from cycloheptanone[84,85] and the relatively simple synthesis, yielding compound (XXXIII) in large (of the order of 50–100 g) amounts, from glutaric aldehyde[90,91] are noteworthy.

When methylmagnesium iodide is allowed to act on cycloheptanone, 1-methylcycloheptanol is obtained, its dehydration over potassium hydrogen sulphate yielding 1-methylcycloheptene. Treatment with ozone with subsequent degradation of the ozonide yields 7-oxo-octanal, the condensation of which with malonic acid in pyridine gives after decarboxylation and purification 9-oxodecenoic acid in 20% yield:



$$\rightarrow CH_3C(CH_2)_5CHO \xrightarrow[C_5H_5N]{CH_2(COOH)_2} CH_3C(CH_2)_5CH{=}CHCOOH.$$

(XXXIII)

In another method glutaric aldehyde is converted by the Wittig reaction into the methyl ester of 2-formylhept-7-enoic acid (XXXIV):

$$OHC(CH_2)_3CHO + (C_6H_5)_3P{=}CHCOOCH_3 \rightarrow OHC(CH_2)_3CH{=}CHCOOCH_3.$$

(XXXIV)

The resulting ester (XXXIV) can be converted into the acid (XXXIII) in two ways:

(a) XXXIV $+ CH_3COCH_3 \xrightarrow{C_5H_{11}N\cdot CH_3COOH} CH_3COCH{=}CH(CH_2)_3CH{=}CHCOOCH_3 \rightarrow$

$$\xrightarrow[2)\ Na_2CO_3]{1)\ H_2;\ Pd/C} CH_3CO(CH_2)_5CH{=}CHCOOH.$$

(XXXIII)

(b) XXXIV $+ HC{\equiv}CCH_2Br \xrightarrow[Al]{Zn} HC{\equiv}CCH_2CH(OH)(CH_2)_3CH{=}CHCOOCH_3 \rightarrow$

$$\xrightarrow[HgSO_4,\ 2HgO]{1)\ H_2SO_4} CH_3COCH{=}CH(CH_2)_3CH{=}CHCOOCH_3 \rightarrow$$

$$\xrightarrow[2)\ Na_2CO_3]{1)\ H_2,Pd/C} CH_3CO(CH_2)_5CH{=}CHCOOH.$$

(XXXIII)

The *cis*- and *trans*-isomers are isolated by crystallisation from the mixture of 9-oxodecenoic acids. It is interesting that a considerable amount of 10-hydroxydec-2-enoic acid was detected in the food received by the queen[94]. The biochemical role of this acid is still not completely clear, but its bactericidal, fungicidal[95], and anti-tumour[96] properties are already known. The synthesis of this compound has also been worked out in detail[87,89,97-100].

In addition to *trans*-9-oxodecenoic and 9- and 10-hydroxydecenoic acids, a large number of carboxylic acids were also isolated from the queen bee extract and from the royal jelly. Thus nonanoic, decanoic, dec-2-enoic, *p*-methoxybenzoic, 9-oxodecanoic, 9-hydroxydecenoic, *p*-hydroxybenzoic, decane-1,10-dicarboxylic (sebacic), dec-2-ene-1,10-dicarboxylic, adipic, pimelic, and suberic acids in the form of their methyl esters and phenylacetic and phenylpropionic acids have been found and identified[80]. In addition there remain unidentified[80] a further 17 peaks, detected by the gas chromatography of the acid fraction of the royal jelly. Aromatic acids are frequently encountered in nature in many tissues and probably do not play a specific role in bees. On the other hand, the majority of the aliphatic acids isolated have a chain with ten carbon atoms. This situation is scarcely fortuitous. Members of this series of acids may be biogenetically related, constituting the units of a single series of reactions in the living organisms. However, their biochemical role and interrelations have not been adequately investigated.

2. The Attractant of the Black Carpet Beetle [*Attagenus megatoma* (Fabricius) or *Attagenus piceus* (Olivier)]

The attractant of the black carpet beetle was recently isolated and identified[101,102]. The active substance was found in the acid fraction of the extract from 30 000 females. After purification by adsorption and gas–liquid chromatography, the methyl ester of an unknown acid was isolated by three gas-chromatographic purifications.

The structure of the acid was established solely by physicochemical methods. The molecular weight and the general formula of the compound ($C_{15}O_{26}H_2$) were obtained with the aid of the mass spectrum. The infrared spectrum indicates the presence in the molecule of a carbonyl group, conjugated double bonds having the *cis*,*trans*-configuration, and a methylene chain. The ultraviolet spectrum confirmed the presence of a conjugated diene system.

The NMR spectrum confirmed the spectroscopic data. On the basis of these studies, the esterified attractant of the black carpet beetle could be identified as one of the two *cis*,*trans*-isomers of methyl tetradeca-3,5-dienoate (XXXV):

$$CH_3(CH_2)_7CH{=}CH{-}CH{=}CHCH_2COOCH_3.$$

(XXXV)

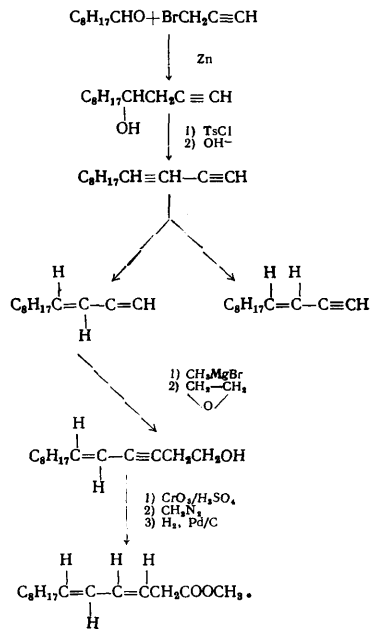
The geometrical configuration of the compound was established by synthesising the two isomers and comparing their physicochemical properties. Methyl *trans*-3-*cis*-5-tetradecadienoate was obtained by the method devised for the synthesis of methyl *trans*-3-*cis*-5-tridecanoate[103]. The *cis*-3-*trans*-5-isomer (XXXV) was synthesised according to Scheme 11.

The synthetic *trans*-3-*cis*-5-isomer (XXXV) had the same spectroscopic and chromatographic properties as the natural compound, while the *cis*-3-*trans*-5-isomer showed considerable differences in the infrared and NMR spectra. Therefore the structure of the *trans*-3-*cis*-5-tetradecadienoic acid was attributed to the compound. The response of the male to the synthetic substance was somewhat weaker than to the extract from the female. The authors suggest that[102] the extract might contain other active components, which were lost during isolation.

3. Attractant of the Sugar-beet Wireworm [*Limonius californicus* (Mann)]

The sugar-beet wireworm is a widespread pest on sugar-beet, potatoes, onions, and other crops. Its larvae live and develop in the soil on the roots of the plants, which makes the fight against them difficult. The adult insects crawl out on the surface of the earth in the spring for a brief period of mating. It was noted[104] that each female may attract a large number of males. Lilly[105] showed that this attraction is due to the sex pheromones produced by the female.

Scheme 11



In paper chromatographic experiments using a mixture of ethanol and ammonia (95 : 5) the alcoholic extract of the abdomens gave a spot with $R_f = 0.85$, which attracted the males under laboratory conditions.

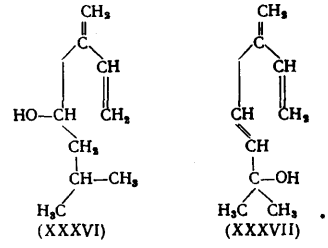
In his latest work Lilly[106] stated that he succeeded in isolating and identifying the sex attractant of the females. It proved to be n-valeric acid. The biological activities of synthetic n-valeric acid and the natural attractant were the same.

The female of the wireworm *Limonius canus* (Le Conte) also secretes a sex attractant[107] which gives rise to a response in the males when present in an amount equivalent to 0.005 of the total substance secreted by one female. According to preliminary data, the pheromone is a carboxylic acid.

IV. TERPENE-LIKE COMPOUNDS

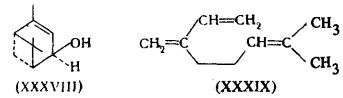
1. Attractant of the bark beetle (*Ips confusus*)

The males of the bark beetle bore passages in coniferous trees and produce a brown powder (a mixture of wood particles and excrement) which contains pheromones[108]. The powder attracts both sexes, especially females. A mass attack by the beetles due to the presence of these pheromones frequently results in the destruction of the tree. In biological tests an appreciable response of the female was obtained with the substance from the benzene extract corresponding to 3×10^{-8} g of the powder[108]. A highly active fraction[108] of pheromones was obtained in a yield of 0.0007% (relative to the weight of the initial powder) from 3 kg of the powder derived from 21 000 males by extraction, vacuum distillation, and gas chromatography. Nonanal, geranyl acetate, and two terpene alcohols, (XXXVI) and (XXXVII), hitherto not described in the literature were obtained from this fraction:



(XXXVI) (XXXVII)

Apparently nonanal and geranyl acetate are impurities. It is not known whether the terpene alcohols (XXXVI) and (XXXVII) are of plant origin or metabolic products of the beetles. Subsequently (-)-2-methyl-6-methyleneoct-7-en-4-ol (XXXVI), detected previously, and two other terpene alcohols,



(XXXVIII) (XXXIX)

were isolated[109] from 4.5 kg of the powder produced by the males of *Ips confusus*. The structures of compounds (XXXVI), (XXXVIII), and (XXXIX) were established by physicochemical methods and confirmed by synthesis.

In laboratory biological tests compounds (XXXVI), (XXXVIII), and (XXXIX) were inactive[109] in amounts of 1000, 20, and 100 μg respectively. At the same time a mixture of 1 μg of compound (XXXVI) with 0.01 μg of compound (XXXVIII) and a mixture of 1 μg of compound (XXXVI) with 1 μg of compound (XXXIX) gave rise to a typical response by the beetles.

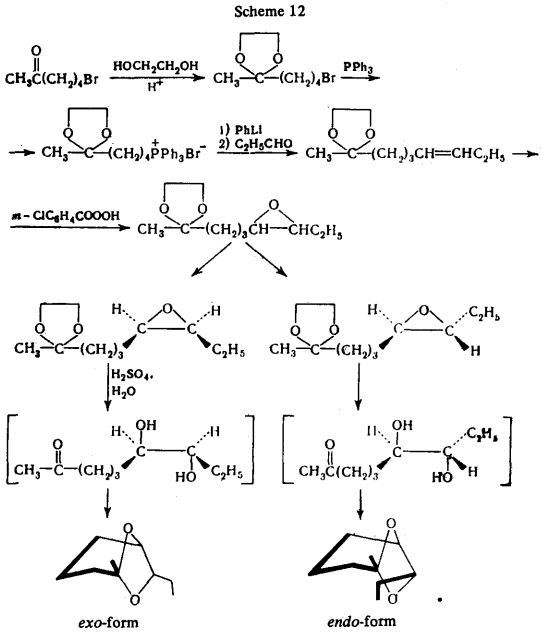
Tests under field conditions showed[110] that the most active is a mixture of compounds (XXXVI), (XXXVIII), and (XXXIX), which caused the appearance of 14 males and 18 females during 20 min (average per day). A mixture of compounds (XXXVI) and (XXXIX) attracted only the females. The individual compounds and their other combinations attracted only a few isolated insects.

An interesting and unexpected observation was made[110] that compound (XXXVI) and also its mixture with compound (XXXVIII) attracted *Ips latidens*. The addition of 0.1 μg of compound (XXXIX) to a mixture of 2 μg of compound (XXXVI) with 0.1 μg of compound (XXXVIII) greatly reduced the attraction of *Ips latidens*, but greatly enhanced the attraction of *Ips confusus*. The unusual synergistis system obtained by the addition of compound (XXXIX) to a mixture of compounds (XXXVI) and (XXXVIII) the attractive properties in relation to *Ips latidens* and enhances them in relation to *Ips confusus*.

Recently the structure of the sex attractant secreted by *Dendroctonus brevicomis* [western pine beetle (Ed. of Translation)] has become known[111]. The concentrate of the active substance was isolated from the brown powder. The pure

substance was obtained by column and gas–liquid chromatography. The study of the spectroscopic and chemical properties of the compound isolated established that it has the structure of a cyclic ketal. It was shown by the synthesis of *exo*- and *endo*-7-ethyl-5-methyl-6,8-dioxabicyclo[3,2,1]-octane (Scheme 12) and by comparison of the synthetic substances with the natural specimen that the attractant, which was called brevicomin, is the *exo*-form of the above compound. It is interesting that similar cyclic structures are rare among natural compounds.

Scheme 12



In the study of the biological activity it was shown that, as in the synergistic phenomenon observed for the attractants of *Ips confusus* [109], certain inactive natural fractions enhance the activity of brevicomin.

Another pest on conifers in which a sex attractant was detected, is the introduced pine sawfly [*Diprion similis* (Hartig)]. In 1960 Coppel et al.[112] noted that the unfertilised females of the introduced pine sawfly attract a large number of males under field conditions. Extraction of the filter paper on which the females of this species had been crawling followed by purification using preparative chromatography led to the isolation[113] of a concentrate containing as its main component the sex attractant of the female. This compound proved to be entirely stable. Thus it did not change at 100°C over a period of 5 h and lost its biological activity only at 180°C after 2 h. Recently Casida and coworkers[114] stated that, having modified Jamamoto's procedure[43] for the collection of the sex attractant of the American cockcroach (*Periplaneta americana*), they succeeded in isolating the fraction of the attractant of the introduced pine sawfly in greater amounts and contaminated to a smaller extent than in the isolation by earlier methods. Nevertheless the inadequate purity of the compound obtained precluded final conclusions concerning its structure.

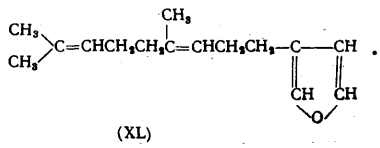
2. Pheromones Causing a Response of Fear or Defence

In social insects (ants, bees) a "chemical language" is fairly highly developed. Apart from the already known functions of attraction, these insects must have a means of communication with one another. There are a number of substances with the aid of which social insects communicate danger, indicate the direction to sources of food, mark their trail in order to return to the nest, etc.

A fairly large number of fear-inducing pheromones, secreted by various species of ants, are known at the present time. Frequently the response of ants to the same compounds is different depending on their concentration in air. Substances which when present in high concentrations give rise to a fear response, for example, at low concentrations attract the working individual.

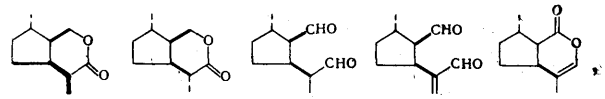
Most species of ants secrete formic and acetic acids which act as repellents. Some species secrete a mixture of acetic, propionic, and isovaleric acids[115]. The West African black ant *Crematogaster* (*Atopogyne*) *africana* (Mayr) emits a characteristic smell when alarmed. It was established[116] that the smell is due to hex-2-enal, which acts as a repellent. The same compound is secreted as a repellent by the cockcroach *Eurucotis floridana*[117].

The ant *Lasius fuliginosus* secretes a substance which causes the excitation of this species but is toxic to other ants. Its active component is dendrolasine[118] (XL):



(XL)

The pheromones of ants of various species of the genus *Iridomyrmex* and *Dolichoderus* have now been fairly well investigated. Thus it has been established[119–121] that the ants *Iridomyrmex detectus*, *I. humilis*, and *I. nitidus* secrete iridomyrmecin (XLI), isoiridomyrmecin (XLII), iridodial (XLIII), and isodihydronepetalactone:



(XLI) (XLII) (XLIII) (XLIV) (XLV)

Dolichodial (XLIV) was found in the secretion of the ant *Dolichoderus acanthoclinea* Clarki[122,123]. These compounds belong to the class of cyclopentanoid monoterpenes, since they are biogenetically related to terpenes[115]. 2-Methylhept-2-en-6-one, 2-methylheptan-4-one, 4-methylhexan-2-one, and 4-methylheptan-3-one, secreted by ants of various species, also have a terpene-like structure[115,124]. It is interesting that the structure of compounds (XLI) and (XLIV) closely resemble those of substances isolated from plant sources, in particular from *Nepeta cataria*[125], namely nepetalactone (XLV) and its analogues.

Together with completed investigations, studies have also been made where so far only the presence of attractants has been established in insects such as the moth of the tobacco hornworm [*Protoparce sexta* (Johannson)][126,127], the moth of the tobacco budworm [*Heliothis veriscens* (F.)][128], the moth of the lesser peach tree borer [*Synanthodon pictipes* (Grote and Robinson)][129], the beetles [*Rhopaea* (Ed. of Translation)] (Coleoptera: Scarabaeidae)[130], cockroaches (*Pycnoseelus suri* and *Nauphoeta cinerea*)[131,132], the apple fly (*Opius alloeus*)[133], the moth of the lesser apple worm[134], the moth of the sugarcane borer [*Diatraca saccharilis*

(F.)][135], the ambrosia beetle [*Trypodendron lineatum* (Oliv.)][136], the Angoumois grain moth *Sitotroga cerealella* (Oliv.)[137], the red cotton bug *Dysdercus cingulatus*[138], the California red scale *Aonidiella aurantii*[139], and the leaf roller *Argurotaenia velutinana*[140]. It is to be expected that further studies in the field of attractants will yield interesting and practically important results.

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