Insect Attractants of Natural Origin

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1 Introduction and Scope

During the past decade, the interdisciplinary investigations of biologists and chemists have established the importance and complexity of chemosensory communication amongst many marine and land animals.[1] The insect world has been the subject of the most intense study and many facets of insect behaviour have been shown to be regulated by chemical stimuli. The current outcry over indiscriminate use of insecticides has provided much of the motivation for this work since the species-specificity and high potency of many naturally occurring chemosensory substances hold great promise for manipulation and control of insect populations.

The objectives of this review are to offer a current and critical survey of the most widely studied area, namely insect attraction. We define an insect attractant as a compound or mixture of compounds which stimulates in an insect a behavioural response of orientation and locomotion to the source of the attractant. This definition is necessarily a convenient oversimplification of an incompletely understood biological process in which other factors can play an important contributing role in producing behavioural responses.

Natural insect attractants fall broadly into two categories: (i) secretions of insect origin which produce responses for mating, aggregation, and foraging within a single species: the term 'pheromone' applies to this type of intra-species attractant; (ii) volatile constituents of plant- or animal-hosts utilized by insects in searching for food and egg-laying (oviposition) sites.

Wilson[2] has classified pheromones and related stimuli into two distinct types, termed 'releasers' and 'primers'. A releaser pheromone elicits an immediate behavioural response upon reception, and insect pheromone attractants fall within this category. In contrast, primer pheromones cause physiological changes which ultimately result in a behavioural response, *e.g.* the pregnancy block induced in mice by the odour of strange males. A consideration of primer stimuli is outside the scope of this review.

A great number of pheromone and host attractants have been reported in the

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[1] 'Communication by Chemical Signals', ed. J. W. Johnston, jun., D. G. Moulton, and A. Turk, Appleton Century Crofts, New York, 1970.

[2] E. O. Wilson, *Science*, 1960, **149**, 1064.

entomological literature[3] but the number of chemical identifications is comparatively small. This survey is primarily concerned with insect attractants of which the chemical identity has been rigorously established, and where the synthetic material has been successfully field-tested. Recent advances in the techniques of microscale structure elucidation which have enabled rapid progress in this field are presented. Brief discussions are devoted to artificial lures discovered by the screening of synthetic compounds, and to the practical and economic uses of insect attractants. Other types of insect secretions, *e.g.* mating aphrodisiacs, defence secretions employed to repel predators, alarm pheromones secreted by social insects to warn a colony of attack, are not considered here.

In a research field which engenders the most formidable practical difficulties, it is inevitable that a number of structural hypotheses are erroneous. Indeed, several discrepancies are currently manifest in the literature and mention is made of such instances.

2 Sex Attractant Pheromones

A. Function.—A sex attractant pheromone is secreted externally by an adult insect to stimulate attraction over a distance of a member of the opposite sex of the same species. At short range the pheromone arrests the insect and induces copulatory movements. This method of intra-species communication over a distance may be vital for the species survival of low-density populations of some non-social insects.

The sex pheromone may comprise one or more components, and is secreted by the virgin adult in many cases soon after emergence from the pupae. In species where mating occurs only once, pheromone production ceases after copulation.[4]

B. Lepidoptera (Moths and Butterflies).—Whereas most species of butterfly (superfamily Papilionoidea) appear to rely upon a visual system of communication over a distance, many of the moth species that have been studied rely upon the production of sex pheromones by the female of the species. Secretion of sex pheromones by males of some lepidopterous species during the courtship stage has been reported, but these are now considered to act as 'aphrodisiacs' to aid in stimulating and arresting females.[5] Such aphrodisiacs are effective only at short range and are not considered further here. However, mention must be made of one of the male pheromones of the greater wax moth, *Galleria mellonella*

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[3] M. Jacobson, 'Insect Sex Attractants', Wiley (Interscience), New York, 1965; M. Jacobson, N. Green, D. Warthen, C. Harding, and H. H. Toba, in 'Chemicals Controlling Insect Behaviour', ed. M. Beroza, Academic Press, New York, 1970, p. 3; K. Eiter, *Fortschr. Chem. org. Naturstoffe*, 1970, **28**, 204; C. G. Butler, ref. 1, p. 37.

[4] C. F. Soo Hoo and R. J. Roberts, *Nature*, 1965, **205**, 724; M. L. Bobb, *J. Econ. Entomol.*, 1964, **57**, 829; C. G. Butler, ref. 1, p. 40.

[5] M. Birch, *Animal Behaviour*, 1970, **18**, 310; J. Meinwald, W. R. Thompson, and T. Eisner, *Tetrahedron Letters*, 1971, 3485 and references cited therein; C. G. Butler, ref. 1, p. 42.

Table 1 *Sex attractants for males of the Lepidoptera*
(*a*) *Sex pheromone attractants—identity rigorously proven*

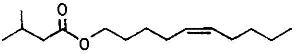
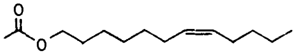
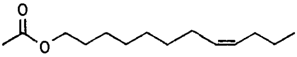
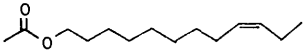
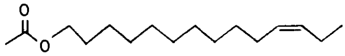
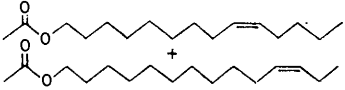
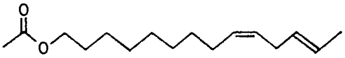
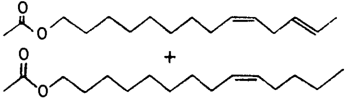
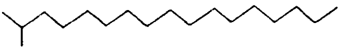
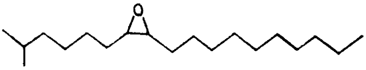
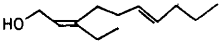
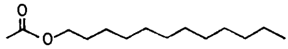
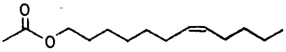
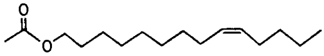
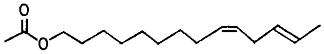
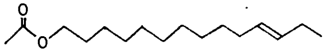
Structure	*Insect Species*	
4 2 0 2 4 6 8 10 12 14 16 18		
	Pine emperor moth (*Nudaurelia cytherea cytherea*)	*a*
	Cabbage looper moth (*Trichoplusia ni*)	*b*
	Oriental fruit moth (*Grapholitha molesta*)	*c*
	Grape berry moth (*Paralobesia viteana*)	*d*
	Red-banded leaf roller (*Argyrotaenia velutinana*)	*e*
	Oblique-banded leaf roller (*Choristoneura rosaceana*)	*f*
	European corn-borer *Ostrinia nubilalis*, Iowa)	*g*
	Tortricid moths (*Adoxophyes orana and A. fasciata*)	*h*
	Indian meal moth (*Plodia interpunctella*) Almond moth (*Cadra cautella*)	*i*
	Southern armyworm moth (*Prodenia eridania*)	*j*
	Silkworm moth (*Bombyx mori*)	*k*
	Tiger moths (7 species) (*Artiidae*)	*l*
	Gypsy moth (*Porthetria dispar*)	*m*
4 2 0 2 4 6 8 10 12 14 16 18		

Table 1 (*continued*)

(*b*) *Proposed sex pheromone attractant structures—awaiting successful and unambiguous field testing*

Structure	*Insect Species*	*Ref.*
4 2 0 2 4 6 8 10 12 14 16 18		
	Codling moth (*Laspeyresia pomonella*)	*n*
	False codling moth (*Argyroploce leucotreta*)	*o*
	*Pseudoplusia includens*, *Radiplusia ou*, *Autographia biloba*.	*p*
	Autographa californica	*q*
	Fall armyworm moth (*Spodoptera frugiperda*)	*r*
	Mediterranean flour moth (*Anagasta kuehniella*)	*s*
	Beet armyworm moth (*Spodoptera exigua*)	*t*
4 2 0 2 4 6 8 10 12 14 16 18		

(c) Sex attractrants identified by the EAG method

4 2 0 2 4 6 8 10 12 14 16 18		
	Codling moth (*Laspeyresia pomonella*)	*u*
	Larch bud moth (*Zeiraphera diniana*)	*v*
4 2 0 2 4 6 8 10 12 14 16 18		

(*a*) H. E. Henderson, F. L. Warren, O. P. H. Augustyn, B. V. Burger, D. F. Schneider, (in part) P. R. Boshoff, and H. S. C. Spies, and H. Geertsema, *J.C.S. Chem. Comm.*, 1972, 686; (*b*) R. S. Berger, *Ann. Entomol. Soc. Amer.*, 1966, **59,** 767; (*c*) W. L. Roelofs, A. Comeau, and R. Selle, *Nature*, 1969, **224,** 723; (*d*) W. L. Roelofs, J. P. Tette, E. F. Taschenberg, and A. Comeau, *J. Insect Physiol.*, 1971, **17,** 2235; (*e*) W. L. Roelofs and H. Arn, *Nature*, 1968, **219,** 513; (*f*) W. L. Roelofs and J. P. Tette, *Nature*, 1970, **226,** 1172; (*g*) J. A. Klun and T. A. Brindley, *J. Econ. Entomol.*, 1970, **63,** 779; (*h*) Y. Tamaki, N. Noguchi, T. Yushima, C. Hirano, K. Honma, and H. Sugawara, *Kontyu*, 1971, **39,** 338; Y. Tamaki, H. Noguchi, T. Yushima, and C. Hirano, *Appl. Ent. Zool.*, 1971, **6,** 139; C. M. Meijer, F. J. Ritter, C. J. Persoons, A. K. Minks, and S. Voerman, *Science*, 1972, **175,** 1470; (*i*) Y. Kuwahara, C. Kitamura, S. Takahashi, H. Hara, S. Ishii, and H. Fukami, *Science*, 1971, **171,** 801; U. E. Brady, J. H.

which has been shown to be n-undecanal.[6] This is reported to perform the dual role of attraction of females over a distance and provision of a stimulus at short range for copulation.

The study of lepidopterous sex attractants was pioneered by Butenandt *et al.*,[7] who identified a pheromone of the female silkworm moth *Bombyx mori* as hexadeca-*trans*-10,*cis*-12-dien-1-ol in 1961 after some twenty years of painstaking research. This remarkable accomplishment was achieved with only 12 mg of pheromone extracted from some half-million virgin females, and without the aid of modern sophisticated instrumentation.

Table 1(a) lists the structures of sex pheromone attractants which have been rigorously proven by isolation and structure elucidation by chemical and spectroscopic methods, and have been confirmed by successful attraction in the field using a synthetic sample of the pheromone. Some cases which await successful and unambiguous field-testing are listed in Table 1(b).

Recent research has provided a more rapid method of sex attractant identification involving the screening of candidate compounds by electrophysiological study of the responses of insect antennae. This 'electroantennogram' technique (abbreviated as EAG) is frequently used as a bioassay method, and its applications are fully discussed in Section 8. Combined field and EAG screening programmes have allowed recognition of sex attractants for a number of species, and a recent review[8] provides an excellent discussion of results for over eighty lepidopterous species, together with taxonomic correlations. However, it is dangerous to assume that a highly potent sex attractant is the natural pheromone until identity has been established by chemical or spectroscopic means. Table 1(c) contains two examples of sex attractants identified by the EAG method for which there exists supporting chemical evidence of identity with a natural pheromone.

Most lepidopterous sex attractants so far identified are monoene or diene straight-chain fatty alcohols or acetates of C_{12} or C_{14} chain length. The most

[6] H. Röller, K. Biemann, J. S. Bjerke, D. W. Norgard, and W. H. McShan, *Acta Ent. Bohemoslov.*, 1968, **65**, 208.

[7] See Table 1, ref. *k*.

[8] W. L. Roelofs and A. Comeau, Proceedings of the Second International Congress on Pesticide Chemistry, IUPAC, Tel Aviv, 1971, p. 91.

Tumlinson, R. G. Brownlee, and R. M. Silverstein, *ibid.*, 1971, **171**, 802; (*j*) M. Jacobson, R. E. Redfern, W. A. Jones, and M. H. Aldridge, *Science*, 1970, **170**, 542; R. E. Redfern, E. Cantu, W. A. Jones, and M. Jacobson, *J. Econ. Entomol.*, 1971, **64**, 1570; (*k*) A. Butenandt, R. Beckman, and D. Stamm, *Z. physiol. Chem.*, 1961, **324**, 84; (*l*) W. L. Roelofs and R. T. Carde, *Science*, 1971, **17**, 684; (*m*) B. A. Bierl, M. Beroza, and C. W. Collier, *J. Econ. Entomol.*, 1972, **65**, 659; (*n*) L. M. McDonough, D. A. George, B. A. Butt, J. M. Ruth, and K. R. Hill, *Science*, 1972, **177**, 177; (*o*) J. S. Read, F. L. Warren, and P. H. Hewitt, *Chem. Comm.*, 1968, 729; (*p*) R. S. Berger and T. D. Canerday, *J. Econ. Entomol.*, 1968, **61**, 452; (*q*) H. H. Shorey, L. K. Gaston, and J. S. Roberts, *Ann. Entomol. Soc. Amer.*, 1965, **58**, 600; (*r*) A. A. Sekul and A. N. Sparks, *J. Econ. Entomol.*, 1967, **60**, 1270; (*s*) Y. Kuwahara, H. Hara, S. Ishii, and H. Fukami, *Agric. and Biol. Chem. (Japan)*, 1971, **35**, 447; (*t*) U. E. Bradey and M. C. Ganyard, *Ann. Entomol. Soc. Amer.*, 1972, **65**, 898; (*u*) W. L. Roelofs, A. Comeau, A. Hill, and G. Milicevic, *Science*, 1971, **174**, 297; (*v*) W. L. Roelofs, R. Carde, G. Benz, and G. von Salis, *Experientia*, 1971, **27**, 1438.

diverse structural types encountered to date occur in the superfamily Noctuoidea where, in addition to unsaturated fatty alcohols and acetates, a hydrocarbon and an epoxide have been found. The sex pheromone of the pine emperor moth, *Nudaurelia cytherea cytherea*, is novel both for its short chain length and its 3-methylbutanoate ester moiety.[9]

For the majority of species where pheromone structures have been identified, only one compound is necessary to attract males. However, several instances have been recognized where two compounds are essential to elicit attraction, for example, the tortricid moths (*Adoxophyes* species),[10] and the southern armyworm moth (*Prodenia eridania*).[11] In the case of the latter, attraction to synthetic pheromones in the field has been reported to be relatively poor, but it is possible that this may have been the result of a formulation problem.

Two groups have reported research into the attractant of the codling moth *Laspeyresia pomonella*. Roelofs *et al.* suggest that dodeca-*trans*-8,*trans*-10-dien-1-ol [Table 1(c)] may be a natural pheromone on the basis of EAG and field screening experiments.[12] McDonough *et al.* report the presence of *cis*-2,-*trans*-6,7-methyl-3-propyl-deca-*cis*-2,*trans*-6-dien-1-ol [Table 1(b)] as one of at least seven natural pheromones,[13] but were unable to confirm the presence of Roelof's attractant. Comparative field-testing experiments may resolve this problem.

The proposed structures for the sex pheromones of both the false codling moth *Argyroploce leucotreta*[14] and the fall armyworm moth *Spodoptera frugiperda*[15] are suspect because the synthetic compounds fail to produce convincing attraction in the field.

The structure (1; 'propylure') first proposed[16] for the pheromone of the pink bollworm moth *Pectinophora gossypiella* now appears to be incorrect. In field-testing, propylure and various formulations in conjunction with its reputed natural synergist *NN*-diethyl-*m*-toluamide (Deet) were found to be markedly less potent than compound (2; 'hexalure'), discovered by screening experiments, which possesses a more conventional sex attractant structure.[17] Jacobson *et al.* assigned structure (3; 'gyptol') to the sex pheromone of the gypsy moth *Porthetria dispar*, and reported that its homologue (4; 'gyplure') was also very active as a sex attractant.[18] However, this work has been subsequently shown to be erroneous and the reputed biological activity ascribed to a highly potent

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[9] See Table 1, ref. *a*.

[10] See Table 1, ref. *h*.

[11] See Table 1, ref. *j*.

[12] See Table 1, ref. *u*.

[13] See Table 1, ref. *n*.

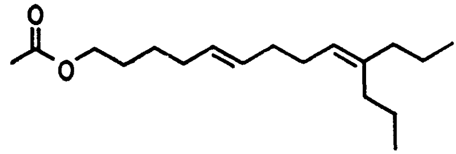
[14] See Table 1, ref. *o*.

[15] See Table 1, ref. *r*.

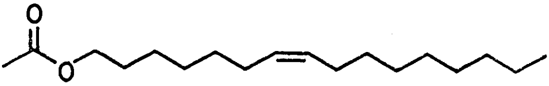
[16] W. A. Jones, M. Jacobson, and D. F. Martin, *Science*, 1966, **152**, 1516; W. A. Jones, and M. Jacobson, *ibid.*, 1968, **159**, 99.

[17] J. C. Keller, L. W. Sheets, N. Green, and M. Jacobson, *J. Econ. Entomol.*, 1969, **62**, 1520.

[18] M. Jacobson, M. Beroza, and W. A. Jones, *J. Amer. Chem. Soc.*, 1961, **83**, 4819; M. Jacobson and W. A. Jones, *J. Org. Chem.*, 1962, **27**, 2523; R. M. Waters and M. Jacobson, *J. Econ. Entomol.*, 1965, **58**, 370.

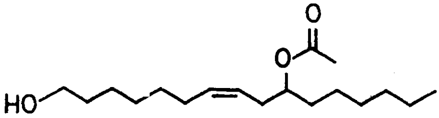


(1) propylure

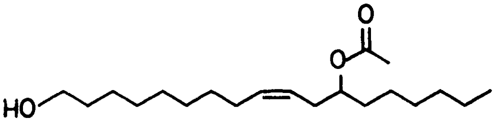


(2) hexalure

contaminant.[19] The situation has recently been clarified by the identification and successful field-testing of *cis*-7,8-epoxyoctadecane [Table 1(a), 'disparlure'].[20]



(3) gyptol



(4) gyplure

The practical difficulties involved in the investigation of the biogenesis of lepidopterous sex attractants have not been surmounted to date. It is significant in this context that many species do not feed as adults and lipid catabolism is a plausible route for attractant biosynthesis.

C. Sex Attractants of Other Orders.—In comparison with the Lepidoptera, far fewer sex attractants have been identified in other orders. Those which have been identified and confirmed by field-testing are listed in Table 2.

The sole identification of a dipterous pheromone is of that produced by the female housefly, *Musca domestica*.[21] 'Muscalure' (*cis*-9-tricosene) is far less potent than many other known sex attractants but its ease of synthesis offers promise for use as a lure.

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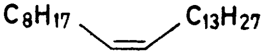
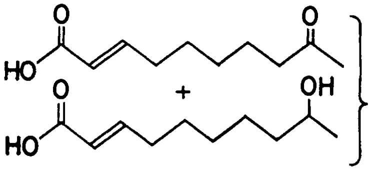
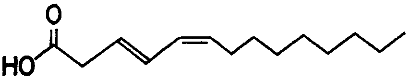
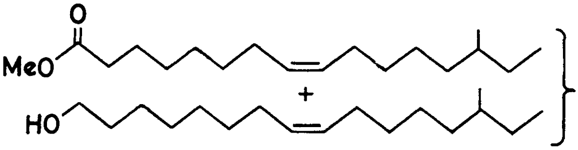
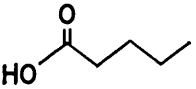
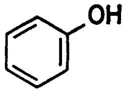
[19] M. Jacobson, R. M. Waters, and M. Schwarz, *J. Econ. Entomol.*, 1970, **63**, 943.
[20] See Table 1, ref. *m*.
[21] See Table 2, ref. *a*.

Table 2 *Sex pheromone attractants for males of non-lepidopterous species*

Structure	*Insect Species*	*Ref.*
	Diptera: Housefly (*Musca domestica*)	*a*
	Hymenoptera: Honeybee (*Apis mellifera*) and related species	*b*
	Coleoptera: Black carpet beetle (*Attagenus megatoma*)	*c*
	Dermestid beetle (*Trogoderma inclusum*)	*d*
	Sugar beet wireworm (*Limonius californicus*)	*e*
	Grass grub beetle (*Costelytra zealandica*)	*f*

(*a*) D. A. Carlson, M. S. Mayer, D. L. Silhacek, J. D. James, M. Beroza, and B. A. Bierl, *Science*, 1971, **174,** 76; (*b*) C. G. Butler and E. M. Fairey, *J. Apicult. Res.*, 1964, **3,** 65; (*c*) R. M. Silverstein, J. O. Rodin, W. E. Burkholder, and J. E. Gorman, *Science*, 1967, **157,** 85; (*d*) J. O. Rodin, R. M. Silverstein, W. E. Burkholder, and J. E. Gorman, *Science*, 1969, **165,** 904; (*e*) M. Jacobson, C. E. Lilly, and C. Harding, *Science*, 1968, **159,** 208; (*f*) R. F. Henzell and M. D. Lowe, *Science*, 1970, **168,** 1005.

Among the Hymenoptera, the honeybees provide an example of social insects where an extremely complex pheromone system has evolved.[22] The so-called 'queen substance', one component of which is 9-oxodec-*trans*-2-enoic acid, of the honeybee functions as both a primer and releaser pheromone. In the hive it regulates ovary development of workers and also queen replacement. During the mating flight, the queen substance, together with the 9-hydroxy-derivative, acts as a sex attractant for the drones. Furthermore, cohesion of swarms is co-ordinated by an interplay of the secretions of two castes: the pheromones of the queen together with the Nassanoff gland secretions of the workers.[23] It is

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[22] Ref. 1, p. 35.

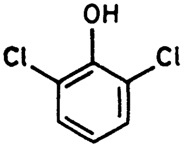
[23] R. A. Morse and R. Boch, *Ann. Entomol. Soc. Amer.*, 1971, **64,** 1414.

noteworthy that queens of some species of termites are reported to utilize 9-oxodec-*trans*-2-enoic acid as a pheromonal secretion.[24] It is likely that secondary pheromones operate in conjunction with queen substance in specific behavioural contexts.

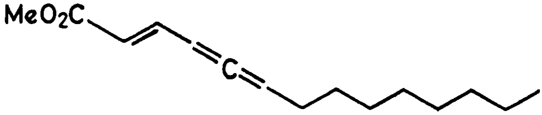
The sex pheromone attractants of the beetles (Coleoptera) are structurally diverse and may be produced by the male or female of the species. The female stored-product beetles (*Trogoderma* and *Attagenus* species) utilize fatty alcohols or acids, and unidentified secondary pheromones are also suspected to be involved.[25] The attractant of the sugar beet wireworm *Limonius californicus* is reported to be valeric acid[26] and, apart from its unusually short chain length, its great abundance in the female (greater than 100 μg) is remarkable.

The sex pheromone attractant of the grass grub beetle *Costelytria zealandica* is phenol,[27] which is believed to be produced by the action of symbiotic bacteria, possibly upon tyrosine, within the collaterial glands of the female.[28] Interestingly, 2,6-dichlorophenol (5) has been isolated from females of the lone star tick *Amblyomma americanum* (an Arachnid) and is suspected as being its sex pheromone attractant.[29] The allene (6) or a closely related structure is suggested as a component of the sex attractant secreted by the male dried bean beetle *Acanthoscelides obtectus*.[30]

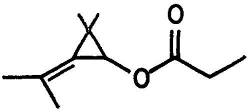
The structure (7) proposed by Jacobson *et al.*[31] for the sex attractant of the female American cockroach *Periplanata americana* (Dictyoptera) has been



(5)



(6)



(7)

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[24] S. Sannasi and C. J. George, *Nature*, 1972, **237**, 457.
[25] See Table 2, ref. *d*.
[26] See Table 2, ref. *e*.
[27] See Table 2, ref. *f*.
[28] C. Hoyt, G. O. Osborne, and A. P. Mulcock, *Nature*, 1971, **230**, 472.
[29] R. S. Berger, *Science*, 1972, **177**, 704.
[30] D. F. Horler, *J. Chem. Soc.* (*C*), 1970, 859.
[31] M. Jacobson, M. Beroza, and R. T. Yamamoto, *Science*, 1963, **139**, 48.

firmly disproved by Whiting's rational synthesis of (7) in conjunction with bioassay testing.[32] Much of the reported chemistry remains inexplicable and clarification of the whole situation is awaited.

D. Sex Attractant Specificity.—The most extensive studies in this area have been with the Lepidoptera, but the conclusions are probably widely applicable. Two aspects must be considered separately in relation to pheromone sex attractants:

Structural Specificity. Studies of the effects of structural modification of the sex attractants of several species demonstrate that simple changes result in dramatic reduction or even complete loss of activity. The cabbage looper moth,[33] the gypsy moth,[34] and the red-banded leaf roller moth[35] have been carefully studied in this respect and the results for the last are summarized in Table 3. Such structure–activity relationships have been used to probe olfaction mechanisms (Section 7).

Species Specificity. The avoidance of cross-mating (*i.e.* the maintenance of reproductive isolation) of species is dependent on factors such as differences in seasonal or geographic distributions and by genetic or physiological incompatibility. However, when similarity occurs in these biological factors, the evolution of species-specific sex pheromone attractants has provided an additional mechanism for reproductive isolation.

Tables 1(a—c) reveal that many species, and especially those which are closely related, utilize the same compound. However, it has been demonstrated that in some such cases, differences in attraction behaviour can be observed in close proximity to the attractant source. Some species are believed to have evolved secondary pheromones which, although inactive alone, augment the potency of the natural pheromone and modify short-range attraction when concentrations are relatively high. Conclusive identification of secondary pheromones has not yet been reported. Both the red- and oblique-banded leaf roller moths employ tetradec-*cis*-11-enyl acetate as a natural sex pheromone, but the addition of dodecyl acetate as a synergist dramatically enhances attraction of the former, but reduces trapping of the latter.[36] The natural occurrence of secondary pheromones is probably more frequent than has been revealed by laboratory bioassays, particularly where simple fatty alcohol or acetate attractant pheromones are involved.

In contrast to species where only one compound is required to achieve attraction, several cases are known where a dual pheromone system is utilized and both components are essential to achieve attraction. This phenomenon has been found with two species of tortricid moths [*Adoxophyes orana* and *A.*

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[32] A. C. Day and M. C. Whiting, *Proc. Chem. Soc.*, 1964, 368; A. C. Day and M. C. Whiting, *J. Chem. Soc.* (*C*), 1966, 464 and references cited therein.

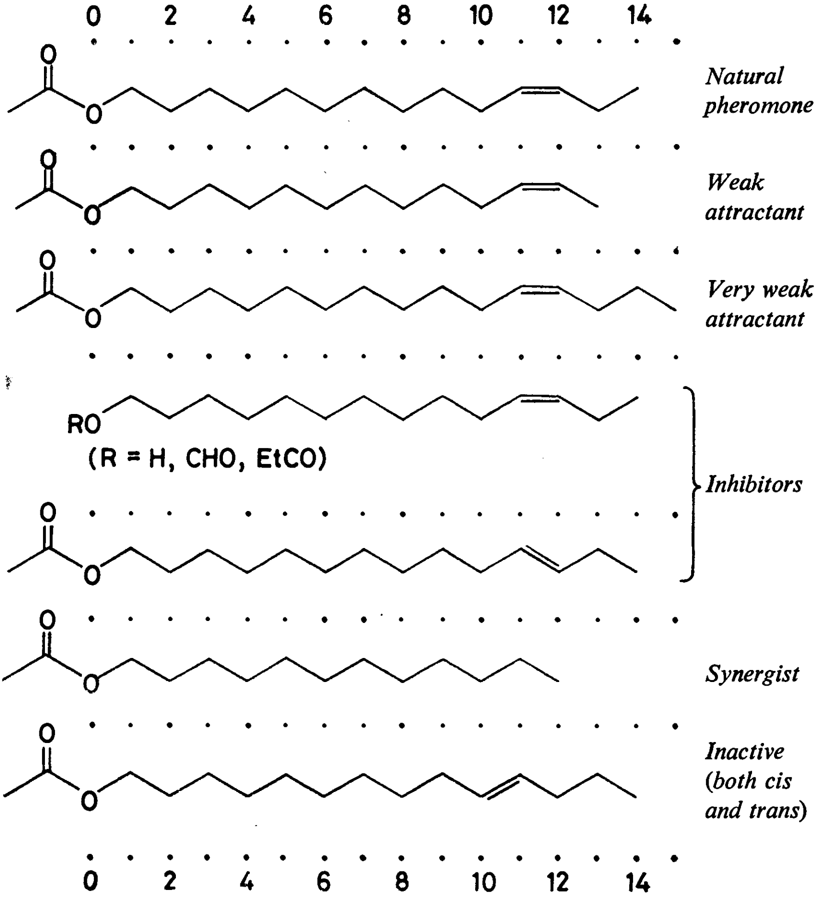
[33] R. S. Berger and T. D. Canerday, *J. Econ. Entomol.*, 1968, **61**, 452; M. Jacobson, H. H. Toba, J. Deboult, and A. N. Kishaba, *ibid.*, 1968, **61**, 84.

[34] V. E. Adler, M. Beroza, B. A. Bierl, and R. Sarmiento, *J. Econ. Entomol.*, 1972, **65**, 665, 679.

[35] W. L. Roelofs and A. Comeau, *J. Insect Physiol.*, 1971, **17**, 435, 1969.

[36] W. L. Roelofs and A. Comeau, *Science*, 1969, **165**, 398.

Table 3 *Effects of structural modification on attraction of the male red-banded leaf roller* (Argyrotaenia velutinana)[a]



[a] W. L. Roelofs and A. Comeau, *J. Insect Physiol.*, 1971, **17**, 435.

fasciata, Table 1(a)].[10] Field screening experiments have also revealed cases where a mixture of both an unsaturated fatty alcohol and the corresponding acetate derivative is required to achieve attraction, *e.g. Clepsis melaleucana.*[8] In contrast, in single component systems where the natural pheromone is an acetate, it has been observed that the corresponding alcohol causes inhibition in the field.[35]

Significantly, there are several reported instances involving morphologically similar species, previously classified as being identical, where one species responds to a *cis*-isomer of a sex attractant whereas its 'twin' is attracted to the *trans*-

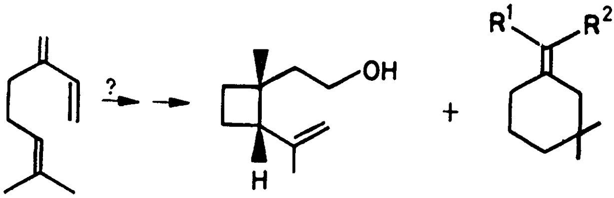
isomer.[8,36] For example, the European corn-borer *Ostrinia nubilalis* in Iowa is attracted to tetradec-*cis*-11-enyl acetate,[37] whereas in New York it is attracted to the *trans*-isomer.[8]

3 Population Attractants

A. Function.—Population attractants assemble large numbers of both sexes of a species at a particular site for mating and subsequent egg-laying. In general, the behavioural sequence is initiated by one sex being attracted by the volatile constituents of a suitable host-plant. The pioneer insects secrete pheromones, usually after feeding, which attract large numbers of both sexes of the species. Such pheromones are found to be sex-selective in that they attract predominantly, but not exclusively, members of the opposite sex to that of the pioneer insects. Such a system of colonization is most widely employed by the beetles, and to date the Scolytid genera have been studied most closely.

B. Chemistry and Specificity.—The aggregation pheromone of the stored-product beetle *Trogoderma granarium* consists largely of a mixture of the ethyl esters of palmitic, linoleic, oleic, and stearic acids together with methyl oleatc.[38] The majority of aggregation pheromones identified, however, are terpenoids.

The male boll weevil *Anthonomus grandis* is attracted by the volatile terpenoid constituents of the cotton bud of which (−)-α-pinene, (−)-limonene, (−)-β-caryophyllene, (+)-β-bisabolol, and caryophyllene oxide have so far been recognized.[39] After feeding, the males secrete an aggregation attractant which has been identified as a synergistic mixture of four novel terpenoids (9)—(12).[40]



(8) (9)

(10) $R^1 = H$; $R^2 = CH_2OH$
(11) $R^1 = H$; $R^2 = CHO$
(12) $R^1 = CHO$; $R^2 = H$

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[37] J. A. Klun and T. A. Brindley, *J. Econ. Entomol.*, 1970, **63**, 779; J. A. Klun and J. F. Robinson, *ibid.*, 1970, **63**, 1281.

[38] U. Yinon, A. Shulov, and R. Ikan, *J. Insect Physiol.*, 1971, **17**, 1037.

[39] J. P. Minyard, D. D. Hardee, R. C. Gueldner, A. C. Thompson, G. Wiygul, and P. A. Hedin, *J. Agric. Food Chem.*, 1969, **17**, 1093.

[40] J. H. Tumlinson, D. D. Hardee, R. C. Gueldner, A. C. Thompson, P. A. Hedin, and J. P. Minyard, *Science*, 1969, **166**, 1010.

The probable biosynthetic route to these pheromones is metabolic transformation of ingested cotton terpenes (8)→(9)—(12).[41a] Field trapping with the synthetic pheromone mixture ('grandlure') produced catches of only 50—80 % of those of live males. Although this may merely be a formulation problem, the possibility exists that unidentified secondary pheromones are secreted by the males.[42]

The bark beetles (Scolytidae) are major forestry pests and achieve aggregation by a complex interplay of pheromonal secretions and volatile terpenoids of the host tree.[41b,43a] In the monogamous *Dendroctonus* species, females initiate the attack on a suitable host, whereas males perform the task in the polygamous *Ips* species. The pioneer beetles release pheromones which act in combination with the volatile terpenes of tree resin exudate to signal the suitability for mass attack. Table 4 lists the combinations of the several compounds involved.

It appears that the *Ips* species utilize solely male pheromones, in contrast to *Dendroctonus* species where secretions from both sexes effectively balance the sex-ratios of attacking beetles. The release of *exo*-brevicomin (14) by *D. brevicomis* females attracts a predominance of males, whereas secretion of frontalin (13) produces a counterbalancing effect by selectively attracting females of this species. In contrast, the related *D. frontalis* females attract predominantly the males of their species with frontalin, and the males compensate by release of a male inhibitor, verbenone (19), after alighting and feeding. The review of Renwick and Vité is recommended for a more detailed discussion of this complex system.[41c]

Frontalin is present prior to feeding in emergent adult females of *D. frontalis* and is presumed to be a product of lipid catabolism,[41c] and *exo*-brevicomin probably has an analogous biosynthetic origin. The pheromones *trans*-verbenol (18) and verbenone (19), although recognized as constituents of certain trees, could plausibly arise by metabolic oxidation of ingested α-pinene [(17)→(18)→(19)].[41d]

In contrast to *Dendroctonus* species, the *Ips* pheromones are not secreted until after several hours feeding by males. Their origin is probably by metabolic transformation of ingested terpenes, but this hypothesis is in dispute.[44]

A high degree of structural specificity is exhibited by the bark beetle pheromones.[41d] Individual pheromones and host-tree terpenes[41e,45] possess both

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[41] 'Symposium on Population Attractants', *Contributions from the Boyce Thompson Institute*, 1970, **24**, No. 13.
(*a*) D. D. Hardee, p. 315; (*b*) G. L. McNew, p. 251; (*c*) J. A. A. Renwick and J. P. Vité, p. 283; (*d*) J. A. A. Renwick, p. 337; (*e*) H. Oksanen, V. Perttunen, and E. Kangas, p. 299; (*f*) T. L. Payne, p. 275; (*g*) J. P. Vité, p. 343.

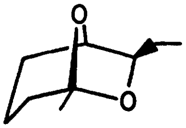
[42] D. D. Hardee, G. H. McKibben, R. C. Gueldner, E. B. Mitchell, J. H. Tumlinson, and W. H. Cross, *J. Econ. Entomol.*, 1972, **65**, 97.

[43] 'Control of Insect Behaviour by Natural Products', ed. D. L. Wood, R. M. Silverstein, and M. Nakajima, Academic Press, New York, 1970.
(*a*) D. L. Wood, p. 301; (*b*) J. C. Moser, p. 161; (*c*) V. G. Dethier, p. 21; (*d*) T. Sakan, S. Isoe, and S. B. Hyon, p. 244; (*e*) T. Muto and R. Sugawara, p. 189; (*f*) M. Jacobson, p. 111; (*g*) R. M. Silverstein, p. 285.

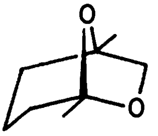
[44] J. H. Borden, K. K. Nair, and C. E. Slater, *Science*, 1969, **166**, 1626.

[45] H. J. Heikkenen and B. F. Hrutfiord, *Science*, 1965, **150**, 1457.

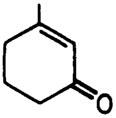
Table 4 *Bark beetle population attractants*



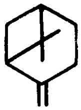
(13)



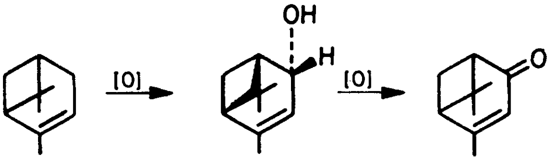
(14)



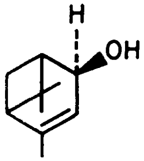
(15)



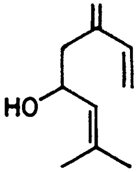
(16)



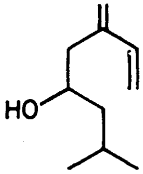
(17) (18) (19).



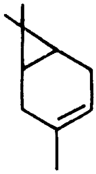
(20)



(21)



(22)



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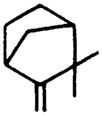


(24)

Species	*Pheromones*		*Host-tree attractants*	*Ref.*
	Female	*Male*		
Dendroctonus species:				
D. frontalis	(13)+(18)	(19)	(17)	*a*
D. brevicomis	(13)+(14)+(18)	(13)+(19)	(8)+(16)+(23)	*a, b*
D. ponderosae	(18)	(14)	(17)	*a*
D. pseudotsugae	(13)+(15)	—	(17)	*c*
Ips species:				
I. confusus	—	(20)+(21)+(22)	?	*d*
I. grandicollis	—	(22)	(8)+(18)+(24)	*e*
I. calligraphis	—	(20)+(21)	?	*f*

(*a*) J. A. A. Renwick and J. P. Vité, *Contributions from the Boyce Thompson Institute*, 1970, **24,** 283; (*b*) W. D. Bedard, P. E. Tilden, D. L. Wood, R. M. Silverstein, R. G. Brownlee, and J. O. Rodin, *Science*, 1969, **164,** 1284, and references cited therein; W. D. Bedard, R. M. Silverstein, and D. L. Wood, *ibid.*, 1970, **167,** 1638; (*c*) G. W. Kinzer, A. F. Fentiman, jun., R. L. Foltz, and J. A. Rudinsky, *J. Econ. Entomol.*, 1971, **64,** 970; J. Rudinsky, *Science*, 1969, **166,** 884; (*d*) R. M. Silverstein, J. O. Rodin, and D. L. Wood, *Science*, 1966, **154,** 509; D. L. Wood, R. W. Stark, R. M. Silverstein, and J. O. Rodin, *Nature*, 1967, **215,** 206; (*e*) J. P. Vité and J. A. A. Renwick, *J. Insect Physiol.*, 1971, **17,** 1699; R. A. Werner, *ibid.*, 1972, **18,** 423, 1403; (*f*) J. A. A. Renwick, and J. P. Vité, *J. Insect Physiol.*, 1972, **18,** 1215.

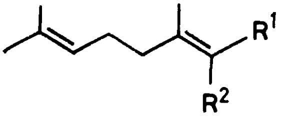
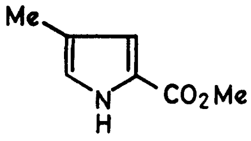
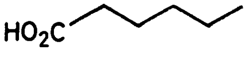
sex- and species-selectivity, and reproductive isolation of species is achieved by the specific action of a combination of the pheromones and host-tree terpenes.

4 Trail Pheromones

A. Function.—Among the complex chemosensory communication systems evolved by social insects, trail following is one of the most highly developed responses triggered by pheromones.[2,43b] Trail marking is usually performed only by successful foragers on returning to the nest in order to recruit and guide other members to the food source. Trail pheromones are also believed to be involved in controlling colony migration, *e.g.* in the swarming of honeybees.

B. Chemistry and Specificity.—The trail pheromones of most social insects appear to consist of complex multicomponent systems, and there exists at present

Table 5 *Trail pheromones*

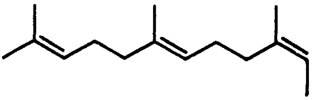
Structure	*Insect Species*	*Ref.*
 (25) geraniol, $R^1 = CH_2OH; R^2 = H$ (26) geranial, $R^1 = CHO; R^2 = H$ (27) neral, $R^1 = H; R^2 = CHO$ (28) geranic acid, $R^1 = CO_2H; R^2 = H$ (29) nerolic acid, $R^1 = H; R^2 = CO_2H$	Honey bee (*Apis mellifera*)	*a*
Citral, *i.e.* (26) + (27)	Stingless bee (*Trigona subterranea*)	*b*
	Leaf-cutting ant (*Atta texana*)	*c*
	*Zootermopsis nevadensis* (termite)	*d*
	Southern subterranean termite (*Reticulitermes virginicus*)	*e*

(*a*) C. G. Butler and D. H. Calam, *J. Insect Physiol.*, 1969, **15**, 237, and references cited therein; (*b*) M. S. Blum, R. M. Crewe, W. E. Kerr, L. H. Kieth, A. W. Garrison, and M. M. Walker, *J. Insect Physiol.*, 1970, **16**, 1637; (*c*) J. H. Tumlinson, J. C. Moser, R. M. Silverstein, R. G. Brownlee, and J. M. Ruth, *J. Insect Physiol.*, 1972, **18**, 809; (*d*) H. Hummel and P. Karlson, *Z. physiol. Chem.*, 1968, **349**, 725; (*e*) F. Matsumura, H. C. Coppel, and A. Tai, *Nature*, 1968, **219**, 963; A. Tai, F. Matsumura, and H. C. Coppel, *J. Org. Chem.*, 1969, **34**, 2180.

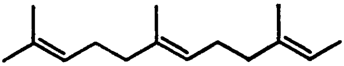
little chemical information in this area. Table 5 summarizes current knowledge and the compounds listed are best regarded as being the principal active components of pheromones. Whereas most of the trail markers listed refer to compounds used to lay ground trails, the bee pheromones discussed here are airborne markers, effective only over a very short range.

The origin of some trail pheromones appears to be direct utilization of plant constituents rather than by biosynthesis in specialist organs. For example, citral which is employed by honeybees is almost certainly of phytochemical origin;[46] and the fatty alcohol trail pheromone of the southern subterranean termite (Table 5) is present in the fungus-infected wood of its diet.[47]

The isoprenoids (30) and (31), extracted from *Santalum spicatum* wood oil, have been shown to possess trail-marking activity for several *Nasutitermes* species of termites.[48] However, the natural trail pheromone is considerably more potent, and structural studies indicate that it is a monocyclic diterpene.



(30)



(31)

The few trail pheromones studied exert some degree of inter-species response and structural analogues of the natural pheromones possess some degree of activity.

5 Host Attractants

A. Function.—Olfaction is an important means by which many insects locate sources of food plants and other animals on which they prey. However, the potency of such host attractants is often of a lower order than that of pheromone attractants.

A very close relationship frequently exists between host-food attraction and insect reproduction behaviour, particularly in relation to egg-laying.[43c] Mention has already been made of some aspects of these relationships with respect to population assembly of bark beetles (Section 3). Additionally it is of interest that many species of moths do not feed as adults, but nevertheless females are attracted to suitable oviposition sites by the volatile constituents of a host plant, the latter being suitable for the feeding of the larvae. Frequently, the same host attractants are used by the larvae to seek food.

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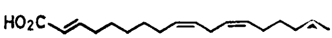
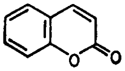
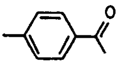
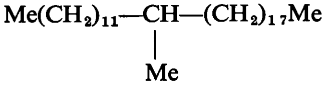
[46] M. S. Blum and G. E. Bohart, *Ann. Entomol. Soc. Amer.*, 1972, **65**, 274.

[47] See Table 5, ref. *e*. See also F. L. Carter, L. A. Dinus, and R. V. Smythe, *J. Insect Physiol.*, 1972, **18**, 1387, and references cited therein.

[48] A. J. Birch, K. B. Chamberlain, B. P. Moore, and V. H. Powell, *Austral. J. Chem.*, 1970, **23**, 2337.

B. Chemistry.—Table 6 reveals that great structural diversity is encountered in animal- and plant-host attractants. Again, it is certain that complex mixtures are involved, and the attractants listed are best regarded as a principal component in host attractant complexes.

Table 6 *Some examples of host-food and host-prey attractants*

Attractant	*Insect*	*Host*	*Ref.*
Food Attractants			
	Honey bee (*Apis mellifera*)	Clovers of various types (isolated from pollen)	*a*
R—N=C=S (*e.g.* R = CH_2=CH—CH_2—; $C_6H_5CH_2$—; $C_6H_5CH_2CH_2$—)	Vegetable weevil (*Listoderes obliquus*)	Plants of the Cruciferae	*b*
	Sweet clover weevil (*Sitona cylindricollis*)	Sweet clover (*Melitotus officinalis*)	*c*
Oviposition Attractants			
	Rice stem borer moth (*Chilo suppressalis*)	Rice	*d*
	Onion maggot (*Hylemya antiqua*)	Onions	*b*
Prey Attractants			
 $\underset{\displaystyle Me}{Me(CH_2)_{11}—\overset{}{CH}—(CH_2)_{17}Me}$	*Microplitis croceipes* (parasite)	Larvae of the corn earworm moth (*Heliothis zea*)	*e*

(*a*) C. Y. Hopkins, A. W. Jevans, and R. Boch, *Canad. J. Biochem.*, 1969, **47**, 433; (*b*) Y. Matsumoto, in 'Control of Insect Behaviour by Natural Products', ed. D. L. Wood, R. M. Silverstein, and M. Nakajima, Academic Press, New York, 1970, p. 133; (*c*) H. Hans and A. J. Thorsteinson, *Ent. Exp. and Appl.*, 1961, **4**, 165; (*d*) T. Saito and K. Munakata, ref. (*b*), p. 225; (*e*) R. L. Jones, W. J. Lewis, M. C. Bowman, M. Beroza, and B. A. Bierl, *Science*, 1971, **173**, 843.

Insects which prey upon or parasitize others are attracted to the odour of their host victims. The female yellow fever mosquito *Aedes aegypti* is attracted to carbon dioxide and L-lactic acid when simultaneously present,[49] the latter being *inter alia* a component of human perspiration. Several insects that prey

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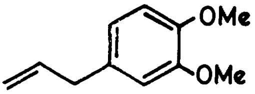
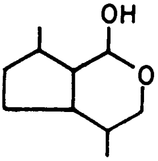
[49] F. Acree, R. B. Turner, H. K. Gouck, M. Beroza, and N. Smith, *Science*, 1968, **161**, 1346.

upon the larvae of bark beetles are known to be attracted by the aggregation pheromones of the beetle adults.[50]

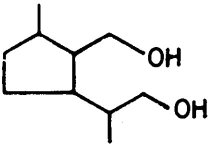
Some plants exert sex-specific attraction, which suggests that the volatile phyto-attractant resembles a pheromone of the insect.[51] Eugenol dimethyl ether (32) from the golden shower blossom *Cassia fistula* attracts the males of the oriental fruitfly *Dacus dorsalis*.[52] Male lacewings (*Chrysopa* species) are attracted to and feed upon the Japanese plant *Actinidia polygama*, and among its most potent attractant constituents are neomatatabiol (33) and iridodiol (34).[43d] In this context, it is noteworthy that the *Iridomyrmex* ants employ such compounds at a higher oxidation state [*e.g.* iridodial (35)] as defence-secretions.[53]



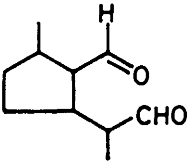
(32)



(33)



(34)



(35)

Many attractants of fungal origin have been observed, but little chemical information is available. However, the fly-agaric mushroom *Amanita muscaria* which attracts houseflies has been extensively studied and the attractant has been shown to be 1,3-diolein (36).[43e,54] The flies die as a result of consumption of the mushroom fruiting body and it is possible that (36) is closely related to another housefly attractant.

An interesting relationship has been observed between the mating behaviour of the polyphemus moths *Antheraea polyphemus* and the red oak, *Quercus rubra*.[55] The volatile leaf constituent hex-*trans*-2-enal is suspected to trigger the release of sex pheromone by the female.

[50] F. B. Camors and T. L. Payne, *Ann. Entomol. Soc. Amer.*, 1972, **65**, 31; W. D. Bedard, P. E. Tilden, D. L. Wood, R. M. Silverstein, R. G. Brownlee, and J. O. Rodin, *Science*, 1969, **164**, 1284.

[51] B. S. Fletcher, *Nature*, 1968, **219**, 631.

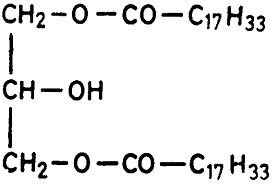
[52] Y. Kawano, W. C. Mitchell, and H. Matsumoto, *J. Econ. Entomol.*, 1968, **61**, 986, and references cited therein.

[53] G. W. K. Cavill in 'Cyclopentanoid Terpene Derivatives', ed. W. I. Taylor and A. R. Battersby, Marcel Dekker, New York, 1969, p. 203.

[54] T. Muto and R. Sugawara, *Agric. and Biol. Chem.* (*Japan*), 1965, **29**, 949.

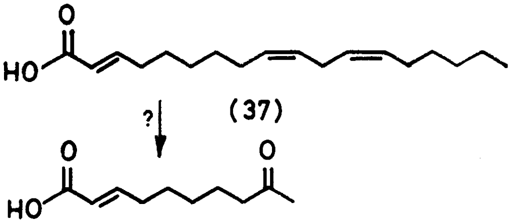
[55] L. Riddiford, *Science*, 1967, **158**, 139.

The possible biogenetic relationship between plant-food constituents and insect pheromones has been remarked upon in earlier sections of this review. Boch[56] has pointed out the similarity of the honeybee attractant in clover pollen [(37) and Table 6] to the queen bee substance [(38) and Table 2] and has suggested a metabolic inter-relationship.



$$\begin{array}{l}\mathrm{CH_2{-}O{-}CO{-}C_{17}H_{33}}\\ |\\ \mathrm{CH{-}OH}\\ |\\ \mathrm{CH_2{-}O{-}CO{-}C_{17}H_{33}}\end{array}$$

(36)



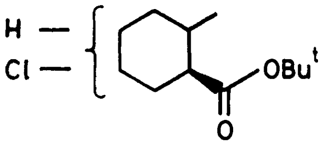
(37)

(38)

6 Artificial Lures

Considerable effort has been devoted to the screening of synthetic compounds for attractant activity in pursuit of methods of insect control. Recent reviews provide a fuller coverage of the extensive research in this area.[57]

Artificial lures are structurally diverse but can be conveniently subdivided into two types. Some possess structures analogous to those of natural attractants, *e.g.* eugenol used for the attraction of the Japanese beetle *Popillia japonica*.[58] The other category comprises compounds which are totally unrelated to natural products, *e.g.* trimedlure (39), which attracts male Mediterranean fruitflies, (*Ceratitis capitata*).[57,59]



(39) mixture of four isomers

7 Insect Olfaction Mechanisms

The current understanding of insect olfaction is limited and only the salient

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[56] See Table 6, ref. *a*.

[57] M. Beroza and N. Green, *Adv. Chem. Ser.*, 1963, no. 41, p. 11; M. Beroza, in 'Chemicals Controlling Insect Behaviour', ed. M. Beroza, Academic Press, New York, 1970, p. 145.

[58] H. F. Goonwardene, J. H. White, A. E. Grosvenor, and D. B. Zepp, *J. Econ. Entomol.*, 1970, **63**, 1289.

[59] M. Beroza, N. Green, S. I. Gertler, L. F. Steiner, and D. H. Miyashita, *J. Agric. Food Chem.*, 1961, **9**, 361; T. P. McGovern and M. Beroza, *J. Org. Chem.*, 1966, **31**, 1472.

features are discussed in this review. Interested readers are referred to the article of Schneider for a more detailed treatment.[60]

The olfactory receptor cells of insect antennae are categorized either as 'specialist' or 'generalist'. Typical odour specialists are the sex pheromone attractant receptors of male moths which are absent in the females. The generalist receptors respond to a wide variety of stimuli, and the food odour receptors of most insects are of this type.

Where a single compound can elicit attraction, for example with the majority of male moths, triggering of a single type of specialist receptor induces the behavioural response. Where two compounds having disparate structures are necessary for attraction, *e.g.* tortricid moths and the bark beetles,[41f] it is likely that triggering of two different types of specialist receptors is required.

Qualitative and quantitative evaluation of the electrical responses produced by receptor cells on stimulation by different compounds can be measured by insertion of microelectrodes at the base and tip of the antennae, *i.e.* the electroantennogram (EAG) method.[61] Recording the overall slow responses of receptor cells by this technique is widely employed as a bioassay to assist attractant identification.

EAG studies have demonstrated that the impact of a single pheromone molecule upon specialist antennal receptors of some male moths is sufficient to trigger a response. Communication distances for moth sex attractants have been calculated by this method to be in excess of 100 metres,[62] and this figure is in good agreement with that suggested by field studies.[63]

Several theories have been proposed to rationalize the structure–activity relationship of attractants. The Dyson–Wright theory[64] suggests an interrelationship between olfactory response and molecular vibrations in the 50—500 cm^{-1} region of the far infrared spectrum of the pheromone molecule, but experimental testing has failed to support this hypothesis.[65] An alternative theory proposed by Amoore relates elements of molecular structure and stereochemistry to activity,[66] and in this context Roelofs and Comeau have proposed an 'induced fit' theory bearing analogy to enzyme–substrate binding, where the pheromone molecule binds to a receptor protein.[35]

8 Attractant Identification and Bioassay

A. Materials and Methods.—Two major problems confront a natural product chemist working in this field: locating the attractant and any synergists among the numerous components present in a plant or animal extract, and structure

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[60] D. Schneider, *Science*, 1969, **163**, 1031.

[61] D. Schneider, *Z. vergl. Physiol.*, 1957, **40**, 8.

[62] L. L. Sower, L. K. Gaston, and H. H. Shorey, *Ann. Entomol. Soc. Amer.*, 1971, **64**, 1448.

[63] A. N. Kishaba, H. H. Toba, W. W. Wolf, and P. A. Vail, *J. Econ. Entomol.*, 1970, **63**, 178.

[64] R. H. Wright, *Nature*, 1963, **198**, 455; 1972, **239**, 226; *Canad. Entomol.*, 1966, **98**, 1083.

[65] R. E. Doolittle, M. Beroza, I. Keiser, and E. L. Schneider, *J. Insect Physiol.*, 1968, **14**, 1697.

[66] J. F. Amoore, J. W. Johnston, and M. Rubin, *Scientific American*, 1964, **210**, 42.

elucidation on minute quantities of material. The yields of pheromone sex attractants can range from as little as five nanograms per virgin female in moths to the order of micrograms in beetles.

Excision of insect glands responsible for pheromone production is rarely practicable, and instead larger clippings of the appropriate body portions are generally used. In beetles, pheromones are found in the hindgut, and excreta can profitably be used as a pheromone source. Cuticular washings have also provided active samples. Air entrainment over living insects rarely provides sufficient material for chemical study.

The classical procedure for the rigorous chemical characterization of an attractant may require up to 500 000 insects, but this requirement is being continually reduced by progress in instrumentation techniques. In a typical case, the active components are located by chromatography monitored by bioassays. Since attractants possess *per se* a degree of volatility, both gas chromatography and mass spectrometry are ideally suited to this type of structural identification, particularly when interfaced as a combined system. Microscale chemical degradations (*e.g.* location of olefinic bonds by microozonolysis) monitored by gas chromatography are employed to confirm structures, and ancillary spectroscopic techniques are used where sufficient material is available. The methodology of identification of insect attractants has been the subject of recent review articles.[41g,43f,43g,67]

B. Bioassays.—The bioassay is the lynch-pin of all chemical investigations. Ideally, the bioassay should be based on a knowledge of the behaviour under natural conditions. A full behavioural bioassay of orientation and attraction over a distance is desirable, but this is frequently impossible under laboratory conditions. Many investigators employ simple bioassays based upon observation of excitory behaviour in an insect on exposure to a candidate sample ('flutter test'). This method is of dubious reliability in that it fails to differentiate between true attractants and other compounds to which the antennal receptors respond (*e.g.* inhibitors and aphrodisiacs). Also, synergists can be overlooked since in isolation they fail to produce responses. The inadequacy of this type of laboratory bioassay partly explains a number of incorrect structures for sex pheromones reported in the literature.

The development of the EAG technique (Section 7) has greatly facilitated attractant identification, and its advantages and limitations have been reviewed.[8] EAG screening of gas chromatographic fractions of crude extracts aids rapid location of both attractants and synergists. The development of a simultaneously recording gas chromatography–EAG instrument is especially useful, particularly for the location of synergists which may be overlooked by other laboratory bioassay techniques.[68]

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[67] M. Beroza, *Toxicol. Environ. Chem. Rev.*, 1972, **1**, 1.

[68] J. E. Moorehouse, R. Yeadon, P. S. Beevor, and B. F. Nesbitt, *Nature*, 1969, **223**, 1174.

C. EAG Techniques in Structural Studies.—The most powerful application of the EAG technique is in the *prediction* of sex attractant structure.[8,69] This is only possible in cases where there exists a uniformity of attractant structure, *e.g.* within related species of the Lepidoptera. The first stage of this process involves location of an active component of the natural extract by EAG–gas chromatography. For lepidopterous attractants, retention time data with respect to known standards provide a clue to approximate chain-length, functionality, and unsaturation. EAG screening of a 'library' of appropriate synthetic compounds leads to prediction of exact chain-length and position and configuration of double bonds by observation of maximum response for variation along a particular series.

The Figure shows the antennal responses of the male grape berry moth *Paralobesia viteana* to various *cis*- and *trans*-mono-unsaturated dodecenyl acetates, from which it is evident that dodec-*cis*-9-enyl acetate is a potent stimulant. Proof of identity with a natural pheromone requires confirmation of the actual presence of the attractant in the insect by 'classical' methods. However, under these circumstances, this process is greatly facilitated and Roelofs *et al.* have succeeded in comparative identification using only 50—200 insects.[8,69]

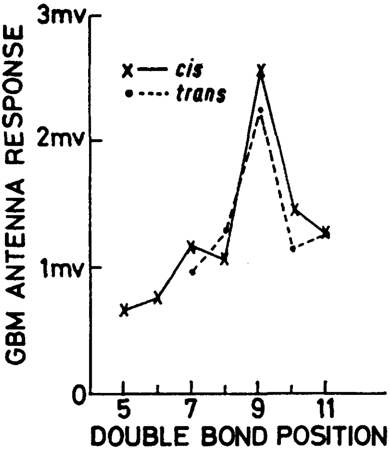

Figure *Antennal responses of the male grape berry moth (GBM)* (Paralobesia viteana) *to various* cis- *and* trans-*mono-unsaturated dodecenyl acetates. The naturally occuring sex pheromone is dodec*-cis-9-*enyl acetate.* (Reproduced by permission from *J. Insect Physiol.*, 1971, **17**, 2235.)

The ultimate proof of a proposed attractant requires field-testing using a synthetic sample which should achieve attraction to a degree comparable to the

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[69] See Table 1, refs. *u* and *v*.

natural source. Several workers have emphasized the importance of the purity of synthetic attractants in field-testing or bioassays.[70] As little as five per cent of the 'wrong' geometrical isomer can lead to masking of response.

9 Economic Uses of Attractants

The potential economic and environmental importance of biological pest control is currently undergoing experimental evaluation,[71] and the successful use of natural insect attractants has been reported by several groups.[72] Insect attractants have been used to reduce pest populations by employing attractant-baited traps. Sex pheromone attractants have also been used in the 'confusion technique' whereby normal mating behaviour is disrupted by permeating the atmosphere with synthetic sex attractants.

These methods of pest control have considerable advantages over the use of conventional insecticides. The relatively small amounts of synthetic attractant required minimizes the possibility of environmental pollution, and the species-specificity of many natural attractants reduces the risk of destroying beneficial insects such as predators, parasites, and pollenators. Furthermore, the evolution of strains of pest populations resistant to natural attractants is very unlikely.

The most general application of insect attractants probably lies in integrated control measures as population survey tools to probe the degree of infestation. Limited application of chemical pesticides would then suffice in areas of intolerable infestation, and the need for blanket spraying programmes throughout the season, with its attendant hazards, would be obviated.

In conclusion, it should be emphasized that this Review has attempted to survey only a minute area of the field of chemosensory communication in animals. At present, more rapid progress is being made in the chemical aspects than in the understanding of the biological aspects. The efficient exploitation of these substances, such as in insect control programmes, can only be achieved when a full understanding of their role in animal behaviour is achieved.

The authors wish to thank their colleagues at the University of Southampton, the Tropical Products Institute and the Centre for Overseas Pest Research for their valuable comments, and also many workers in this field who have provided information.

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[70] W. L. Roelofs and A. Comeau, *Nature*, 1969, **220**, 600.

[71] M. Beroza, in 'Pest Control: Strategies for the Future', Nat. Acad. Sci. Publication No. 1945, 1972, p. 226, and references cited therein.

[72] D. Hamilton, *J. Econ. Entomol.*, 1971, **64**, 150; D. Hardee, *ibid.*, p. 928; H. H. Shorey, L. K. Gaston, and L. L. Sower, *California Agriculture*, 1971, **25**, 11; M. Beroza and E. F. Knipling, *Science*, 1972, **177**, 19.