## The Language of Chemical Ecology Chemical Ecology Memories



### 25<sup>th</sup> Annual Meeting of The International Society of Chemical Ecology

David L. Wood Department of Environmental Science, Policy and Management University of California Berkeley, CA 94720 Chemical communication systems play a major role in the survival of all organisms, from bacteria to primates. They have been described from the following phyla:

bacteria	blue-green algae		slime molds	true fungi
nematodes &	rotifers	annelids	mollusks	arthropods
	chordates		protozoans	

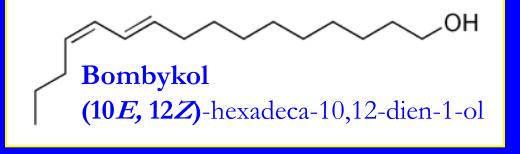
## +



Wilson, E. O. 1970. Chemical communication within animal species, pp. 133-135,*in* E. Sondheimer and J. B. Simeone (eds.).Chemical Ecology. Academic Press, New York.



The identification of the silkworm moth sex attractant by Adolf Butenandt & colleagues in 1959 is often cited as the founding study in Chemical Ecology.





Butenandt, A., Beckmann, R., Stamm, D., & Hecker, E. 1959. Uber den Sexuallockstoff des Seidenspinners *Bombyx mori* Reindarstellung und Konstitution. *Z. Naturforsch* 14b:283–284.

### The Language of Chemical Ecology:

Highlights of discoveries made from these organisms during this "early period" of chemical ecology leading up to the founding of *The Journal of Chemical Ecology* in 1975.

#### **PHEROMONES**

Karlson, P., & Lüscher, M. 1959. Pheromones: A new term for a class of biologically active substances. *Nature* 183:55–56.

#### **RELEASERS & PRIMERS**

Wilson, E. O., & Bossert, W. H. 1963. Chemical communication among animals. *Recent Progr. Hormone Res.* 19:673–716.

#### KAIROMONES & ALLOMONES

Brown, W., Jr., Eisner, T., & Whittaker, R. 1970. Allomones and kairomones: *trans*-specific chemical messengers. *Bioscience* 20:21–22.

The Language of Chemical Ecology:

Highlights of discoveries made from these organisms during this "early period" of chemical ecology leading up to the founding of *The Journal of Chemical Ecology* in 1975.

#### ALLELOCHEMICAL INTERACTIONS & SEMIOCHEMICALS

Whittaker, R. H., & Feeny, P. P. 1971. Allelochemics: Chemical interactions between species. *Science* 171:557–770.

Law, J. H., & Regnier, F. E. 1971. Pheromones. Ann. Rev. Biochem. 40:533–548.



The Journal of Chemical Ecology was first published in 1975 and is devoted to promoting an ecological understanding of the origin, function, and significance of natural chemicals that mediate interactions within and between organisms. In the period leading up to the first issue of the Journal of Chemical Ecology,



biologically active compounds were identified from many organisms in diverse taxa such as:

water mold slime mold honeybee bark and ambrosia beetles carpet beetle boll weevil ground beetle cabbage looper moth red-banded leaf roller moth Indian meal moth pink bollworm moth European corn borer monarch butterfly leaf-cutting ant housefly millipede whip scorpion minnow boar black-tailed deer pronghorn antelope rhesus monkey and many more Also during this period many new behavioral chemical or "semiochemical" phenomena were discovered, e.g.:

> multi-component chemical stimuli synergism among components interruption/disruption structural and enantiomeric specificity interspecific interactions releaser and primer effects and many others

At the same time an amazing diversity of new biologically active chemicals was discovered.

These studies on semiochemical phenomena and biologically active compounds were summarized in more than ten books during this period:

Hall, S. A. (ed.). 1963. *New Approaches to Pest Control and Eradication*, Advances in Chemistry: Series 41. American Chemical Society, Washington, D. C., 74 pp.

Jacobson, M. (ed.). 1965. Insect Sex Attractants. John Wiley and Sons, Inc., New York, 154 pp.

Crosby, D. G. (ed.). 1966. *Natural Pest Control Agents*, Advances in Chemistry: Series 53. American Chemical Society, Washington, D. C., 24 pp.

Pfaffmann, C. (ed.). 1969. Olfaction and Taste. Proceedings of the Third International Symposium. Rockefeller Univ. Press, New York, 648 pp.

Wood, D. L., Silverstein, R. M. & Nakajima, M. (eds.). 1970. Control of Insect Behavior by Natural Products. Academic Press, New York, 345 pp.

Sondheimer, E., & Simeone, J. B. (eds.). 1970. *Chemical Ecology*. Academic Press, New York, 336 pp.

Johnston, J. W., Jr., Moulton, D. G., & Turk, A. (eds.). 1970. *Communication by Chemical Signals*. Appleton-Century-Crofts, New York, 412 pp.

M. Beroza (ed.). 1970. *Chemicals Controlling Insect Behavior*. Academic Press, New York, 170 pp.

Tahori, A. (ed.). 1971. Chemical Releasers in Insects. Gordon and Breach, New York. 227 pp.

Jacobson, M. 1972. Insect sex pheromones. Academic Press, New York, 382 pp.

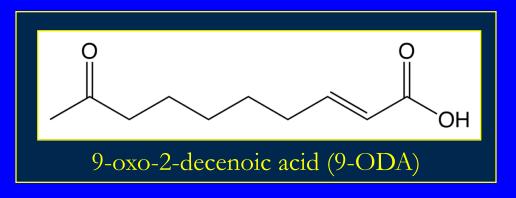
H. F. van Emden (ed.). 1972. *Insect/Plant Relationships*. Blackwell Scientific Publications, Oxford, England. 215 pp.

M. C. Birch (ed.). 1974. *Pheromones*. North-Holland Publishing Co., Amsterdam, Holland. 495 pp.



Following identification of the silkworm moth sex pheromone, Callow and Johnston (1960) & Barbier and Lederer (1960) identified the "queen substance" in the mandibular gland secretion of the queen honeybee, which inhibits queen cell construction.





Callow, R. K., & Johnston, N. C. 1960. The chemical constitution and synthesis of queen substance of honeybees, *Apis mellifera*. *Bee World* 41:152–153.

Barbier, J., & Lederer, J. 1960. Structure chimique de la substance royale de la reine d'abeille *Apis mellifera* L. *C. R. Acad. Sci. Paris* 250:4467–4469.

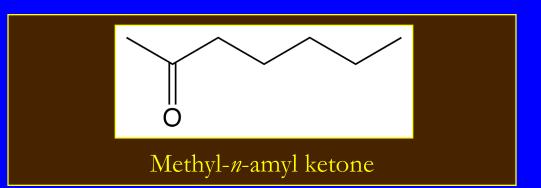
### <u>RELEASER</u>

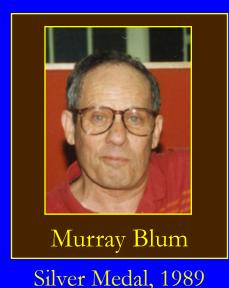
Gary, N. E. 1962. Chemical mating attractants in the queen honey bee. Science 136:773-774.

The following year, Blum and colleagues (1963) identified methyl-*n*-amyl ketone as the alarm pheromone of the ant, *Iridomyrmex pruinosus*.



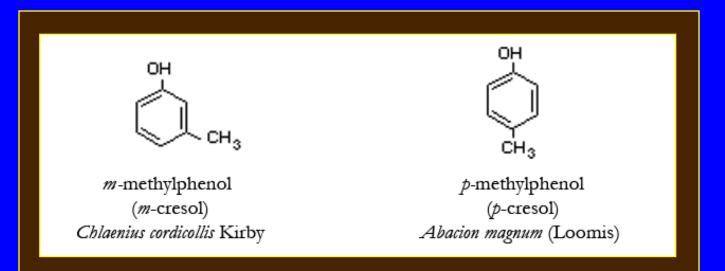
Iridomyrmex pruinosus (Roger)





Blum, M. S., Warter, S. L., Monroe, R. S., & Chidester, J. C. 1963. Chemical releasers of social behavior. I. Methyl *n*-amyl ketone in *Iridomyrmex pruinosus* (Roger) (Formicidae: Dolichoderinae). *J. Insect Physiol.* 9:881–885.

Eisner, Hurst, & Meinwald (1963) identified phenolic glandular defense secretions of a carabid beetle, *Chlaenius cordicollis* Kirby, and the chordeumoid millipede, *Abacion magnum* (Loomis).



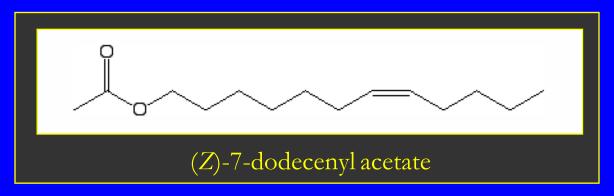


Jerrold Meinwald Thomas Eisner

Co-Silver Medal, 1991

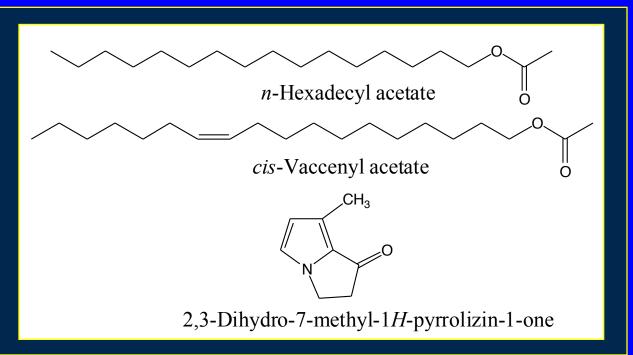
Eisner, T., Hurst, J. J., & Meinwald, J. 1963. Defense mechanisms of arthropods XI. The structure, function and phenolic secretions of the glands of a chordeumoid millipede and a carabid beetle. *Psyche* 70:94–116. Berger identified the sex pheromone of the cabbage looper, *Trichoplusia ni*, in 1966.





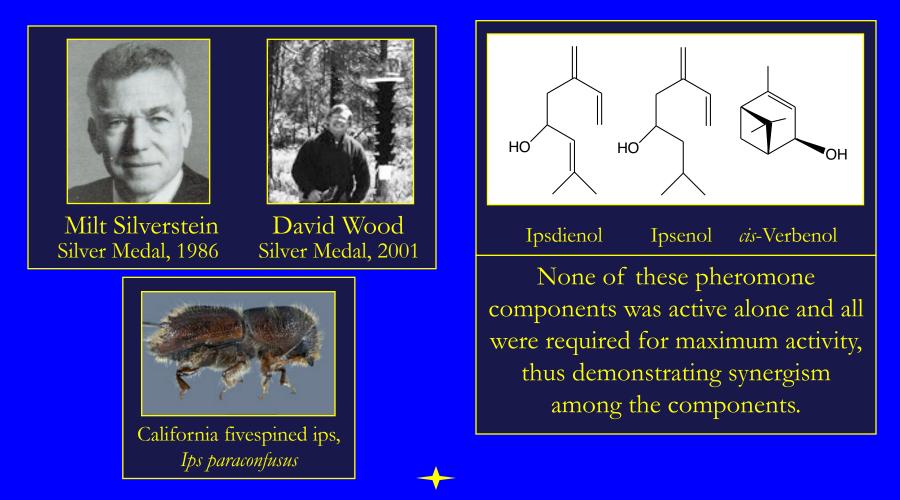
Berger, R. S. 1966. Isolation, identification, and synthesis of the sex attractant of the cabbage looper, *Trichoplusia ni. Ann. Entomol. Soc. Amer.* 59:767–771.

Meinwald & colleagues (1966) identified 3 major components of the "hair-pencilling" secretion of the male danaid butterfly, *Lycorea ceres ceres*. These compounds, termed aphrodisiacs, are essential for successful courtship resulting in mating.





Meinwald, J., Meinwald, Y. C., Wheeler, J. W., Eisner, T., & Brower, L. P. 1966. Major components in the exocrine secretion of a male butterfly (*Lycorea*). *Science* 151:583–585. In 1966, Silverstein and colleagues identified three monoterpene alcohols that elicit mass aggregation of male and female engraver beetles (*Ips paraconfusus*) during host colonization.



Silverstein, R. M., Rodin, J. O., & Wood, D. L. 1966. Sex attractants in frass produced by male *Ips confusus* in ponderosa pine. *Science* 154:509–510.

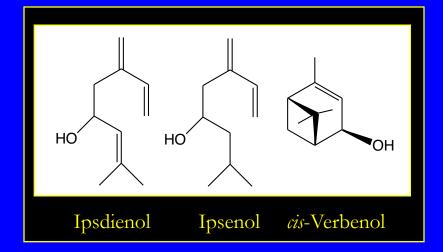
# Bark beetle aggregation behavior can result in the death of living trees, often over vast forested areas.



Tree damage caused by mountain pine beetle in B.C. (The largest recorded North American outbreak, 1995-the present) Interactions between two co-colonizing species were also discovered: Ipsenol + *cis*-Verbenol attracted *Ips latidens* Ipsenol + *cis*- Verbenol + Ipsdienol attracted *Ips paraconfusus* Ipsdienol is an allomone for *Ips paraconfusus* 



Western pine engraverCalif. fivespined ipsIps latidensIps paraconfusus



This study demonstrated that bark beetle pheromones also function as allomones to reduce competition between species.

Wood, D. L., Stark, R. W., Silverstein, R. M., & Rodin, J. O. 1967. Unique synergistic effects produced by the principal sex attractant compounds of *Ips confusus* (LeConte) (Coleoptera: Scolytidae). *Nature* 215:206.

Shorey & colleagues (1967) and Gaston & colleagues (1967) demonstrated disruption of pheromone communication in the cabbage looper as a method of population control.



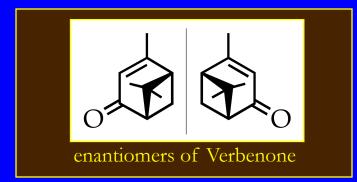
Cabbage looper moth, Trichoplusia ni

Shorey, H. H., Gaston, L. K., & Saario, C. A. 1967. Sex pheromones of noctuid moths. XI. Feasibility of behavioral control by disrupting pheromone communication in cabbage loopers. *J. Econ. Entomol.* 60:1541–1545.

Gaston, L. K., Shorey, H. H., & Saario, C. A. 1967.Insect population control by the use of sex pheromone to inhibit orientation between the sexes. *Nature* 213:1155.



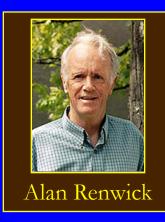
Renwick (1967) identified verbenone from the volatiles of extracted hindguts of male *Dendroctonus* species, but no biological activity was known at that time.





D. brevicomis





Silverstein/Simeone Lecture Award, 1999

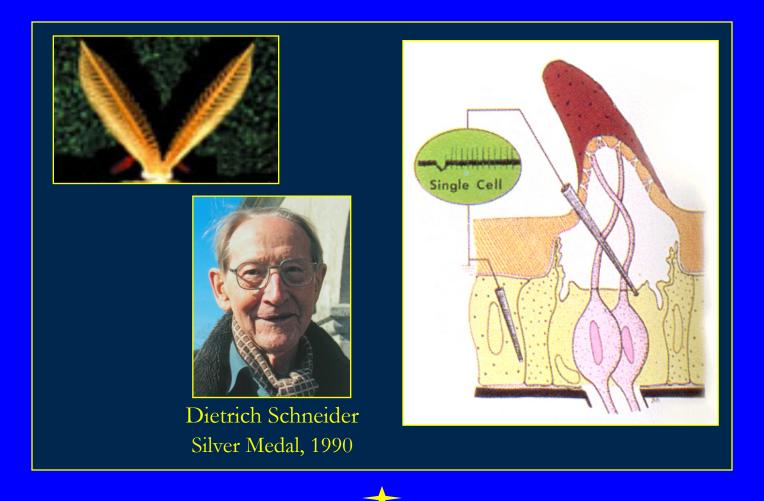
Renwick, J. A. A. 1967. Identification of two oxygenated terpenes from the bark beetles *Dendroctonus frontalis* and *Dendroctonus brevicomis*. *Contrib. Boyce Thompson Instit.* 23:355–360.

1998: Phero Tech verbenone pouches registered by EPA for control of southern pine beetle

2008: Hercon laminated flakes with verbenone registered by EPA for control of mountain pine beetle Flakes on ground following application (Water bottle shown for scale)

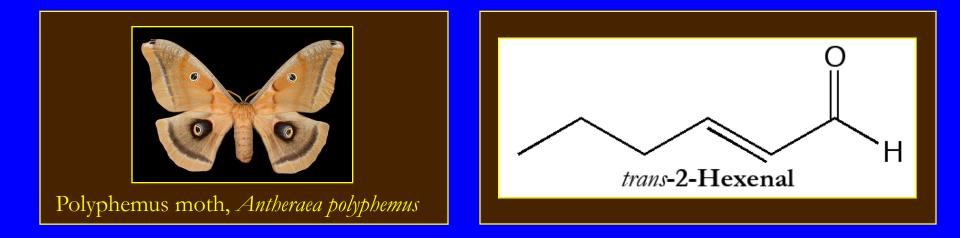


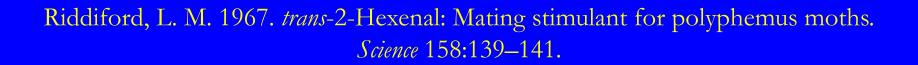
Gillette, N. E., Erbilgin, N., Webster, J. N., Pederson, Mori, S. R., Stein, J. D., Owen, D. R., Bischel, K. M., & Wood, D. L. 2008. Aerially applied verbenonereleasing flakes protect *Pinus contorta* stands from attack by *Dendroctonus ponderosae* in California and Idaho. *For. Ecol. Manage*. In Review. Pheromone identification by using electroantennograms (EAG) and laboratory and field behavioral responses.



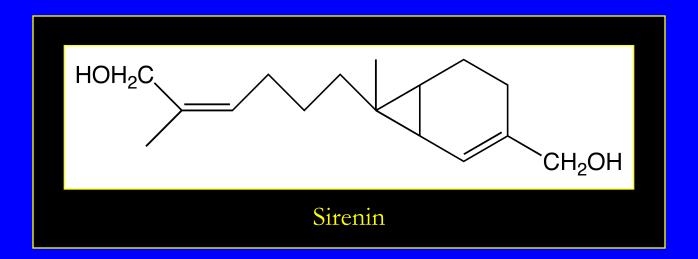
Schneider, D. 1967. Insect olfaction: deciphering system for chemical messages. *Science* 163:1031–1038.

Riddiford (1967) identified the volatile compound *trans*-2-hexenal from oak leaves that stimulates the female polyphemus moth (*Antheraea polyphemus*) to release her sex pheromone.

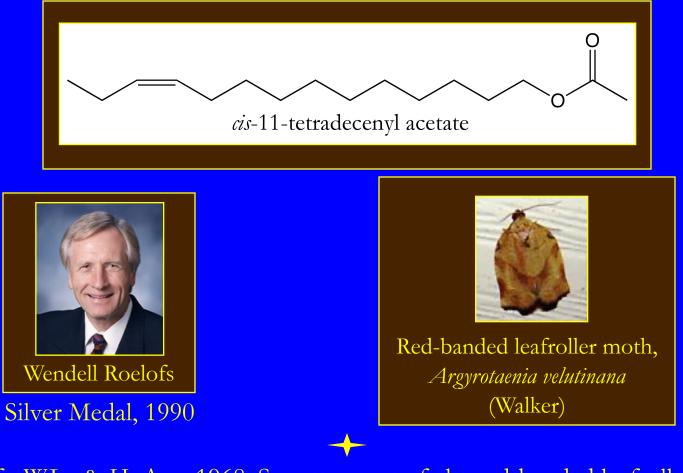




In 1968, Machlis & colleagues published the structure of sirenin, which was isolated from a water mold, *Allomyces* sp.
 This compound functions as a female plant "sex hormone," which attracts the highly motile male gametes.



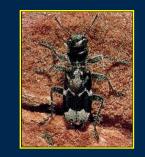
Machlis, L., Nutting, W. H., & Rapoport, H. 1968. The structure of sirenin. J. Am. Chem. Soc. 90:1674–1676. Roelofs & Arn (1968) identified the sex attractant for the redbanded leafroller moth.



Roelofs, W.L., & H. Arn. 1968. Sex attractant of the red-banded leafroller moth. *Nature* 219:513.

Roelofs, W. L. & A. Comeau. 1971. Sex pheromone perception: Electroantennogram responses of the red-banded leafroller moth. J. Insect Physiol. 17:1969–1982.

In field tests, ipsdienol, ipsenol, and *cis*-verbenol also attracted two predaceous beetles that aggregate on the tree under attack.

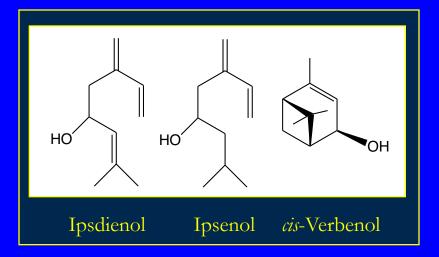




Enoclerus lecontei

Temnochila chlorodia

Wood, D. L., Browne, L. E., Bedard, W. D., Tilden, P. E., Silverstein, R. M., & Rodin, J. O. 1968. Response of *Ips confusus* to synthetic sex pheromones in nature. *Science* 159:1373–1374.



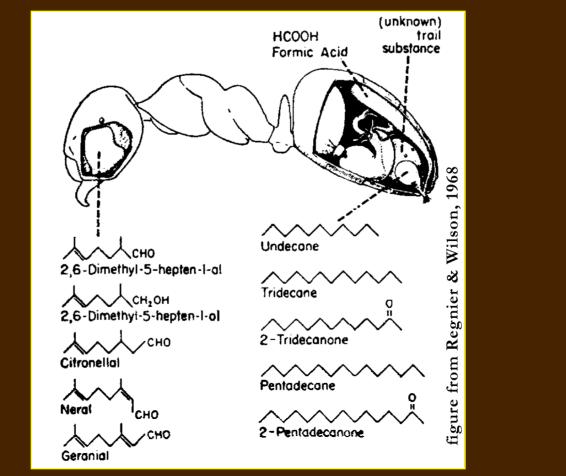
This study demonstrated that bark beetle pheromones also function as kairomones for these predators, directing them to areas with high prey densities

# Regnier and Wilson (1968) identified the volatile substances involved in the alarm-defense system of the ant *Acanthomyops claviger*.



Acanthomyops claviger

Regnier, F. E., & Wilson, E. O. 1968. The alarm-defence system of the ant *Acanthomyops claviger. J. Insect Physiol.* 14:955–970.



Structural formulas of volatile substances found in various exocrine glands of the ant *Acanthomyops claviger* 

Bergström and Löfqvist (1968) identified the volatile compounds from ant gasters in four formicine ants: slave-keepers *Formica sanguinea* Latr. and *Polyergus rufescens* (Latr.), and slaves *F. fusca* L. and *F. rujibarbis* 



Gunnar Bergstrom

Silver Medal, 2008

Bergström, G., & Löfqvist, J. 1968. Odour similarites between the slave-keeping ants *Formica* sanguinea and *Polyergus rufescens* & their slaves *F. fusca* & *F. rufabarbis. J. Ins. Physiol.* 14: 995–1011. Formicine ants: multicomponent & multifunctional pheromone secretions

Formica sanguinea (slave keeper)C10-acC10-olAcetates: C11-acAlcohols: C11-olC12-acC12-olHydrocarbon: Undecane (C11-ane)

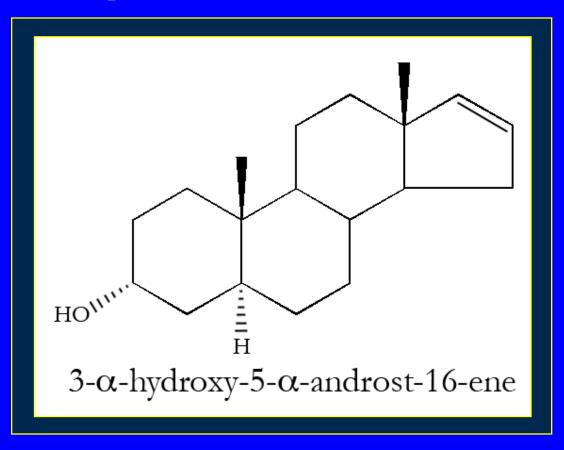
Polyergus rufescens (slave keeper) trans, trans-α-Farnesene

Formica fusca (slave)

Hydrocarbons: Undecane (C11-ane), Tridecane (C13-ane)

Formica rufibarbis (slave)

C10-ac Acetates: C11-ac Hydrocarbons: Undecane (C11-ane) C12-ac Tridecane (C13-ane) Patterson (1968) identified 3-α-hydroxy-5-α-androst-16-ene as the musk odor component of boar submaxillary salivary glands.

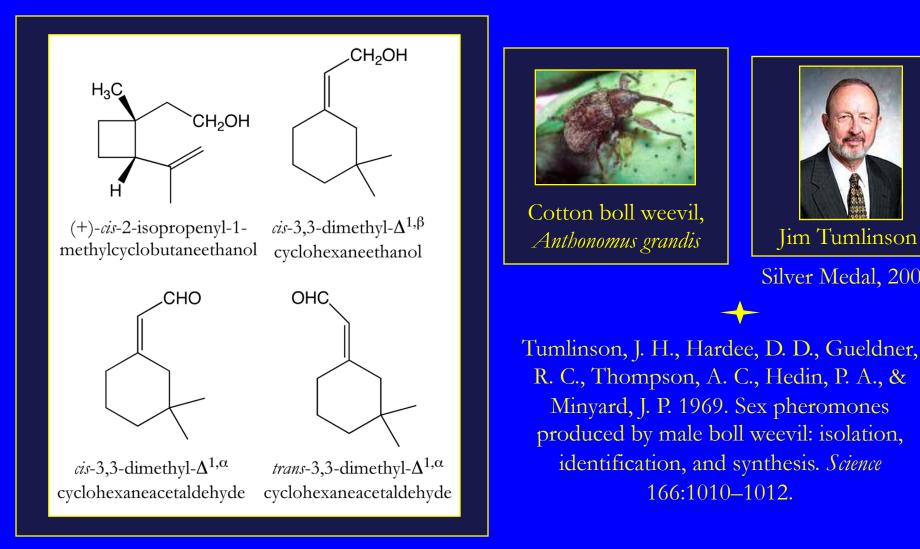


Patterson, R. L. S. 1968. Identification of 3-alpha-hydroxy-5-alpha-androst-16ene as the musk odour component of boar submaxillary salivary glands and its identification to the sex odour taint in pork meat. J. Sci. Fd. Agric. 19:434–438.

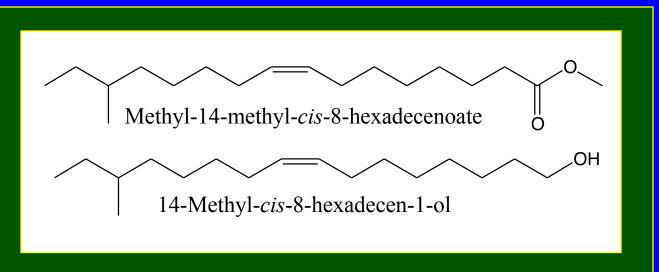
Tumlinson & colleagues (1969) identified four terpenoids as the aggregation pheromone of the boll weevil. As with bark beetles, these compounds also exhibited synergism.

Jim Tumlinson

Silver Medal, 2005

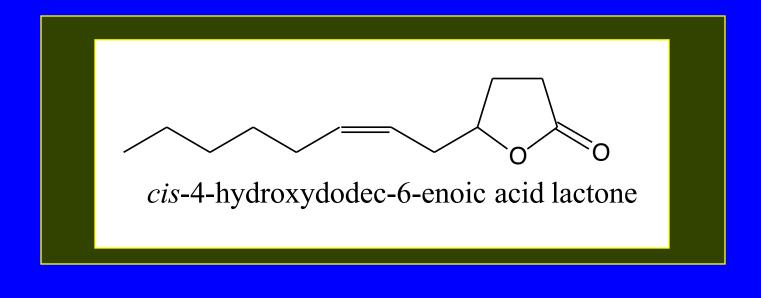


Rodin & colleagues (1969) identified two individually active compounds that account for the attractive response of the male dermestid beetle, *Trogoderma inclusum* Le Conte to females.





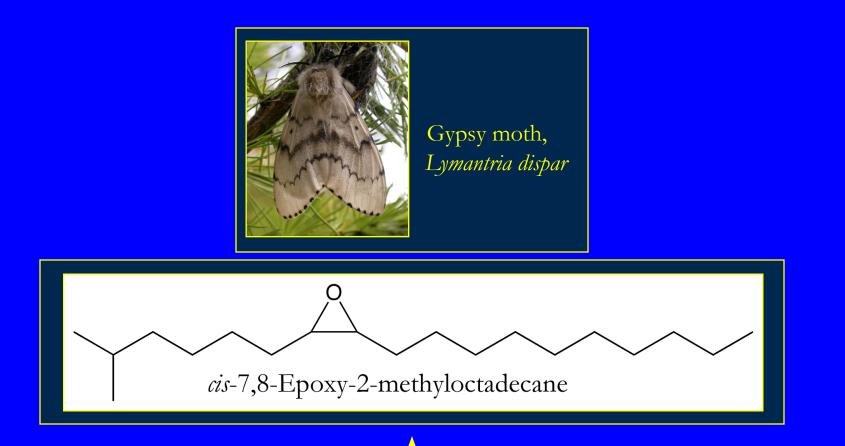
Dermestid beetle, Trogoderma inclusum Rodin, J. O., Silverstein, R. M., Burkholder, W. E., & Gorman, J. E. 1969. Sex attractant of female dermestid beetle, *Trogoderma inclusum* LeConte. *Science* 165:904–906. Brownlee & colleagues (1969) identified the "individual recognition" pheromone found in the tarsal secretion of the black-tailed deer, *Odocoileus hemionus columbianus*.



Brownlee, R. G., Silverstein, R. M., Müller-Schwarze, D., & Singer, A. G. 1969. Isolation, identification and function of the chief component of the male tarsal scent in black-tailed deer. *Nature* 221:284–285.

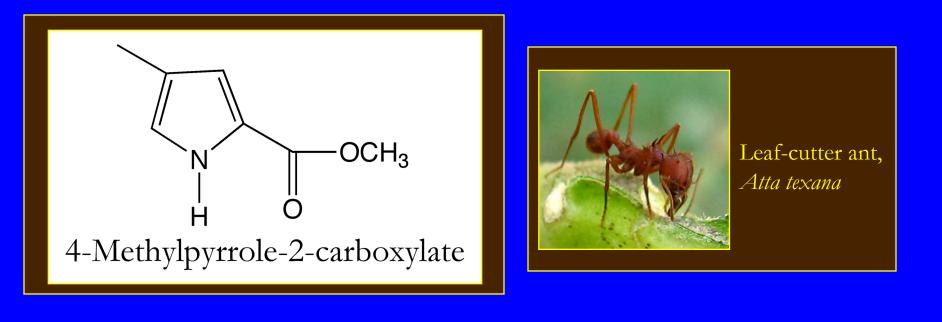
# Bierl & colleagues (1970) identified the sex pheromone for the gypsy moth, a destructive forest defoliator.

The Hercon plastic chip formulated with this sex pheromone disrupts mating and is applied widely to "slow the spread" of this pest in North America.



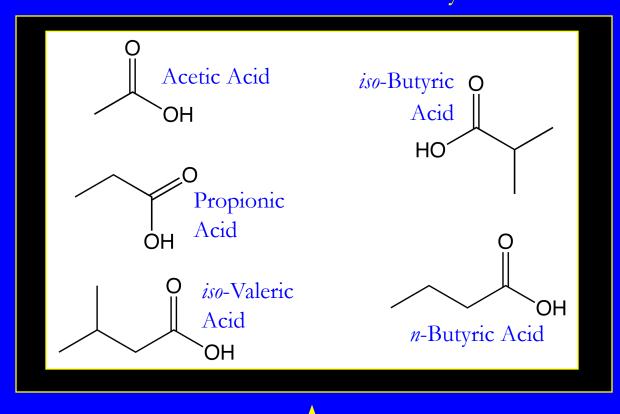
Bierl, B. A., Beroza, M., & Collier, C. W. 1970. Potent sex attactant of the gypsy moth: its isolation, identification and synthesis. *Science* 70:87.

# The trail-following pheromone of the a leaf-cutter ant was identified by Tumlinson and colleagues (1971).



Tumlinson, J. H., Silverstein, R. M., Moser, J. C., Brownlee, R. G., & Ruth, J. M. 1971. Identification of the trail pheromone of a leaf-cutting ant, *Atta texana*. Nature 234:348–349.

Curtis & colleagues (1971) and Michael & colleagues (1971) identified the sex attractants from vaginal secretions of female rhesus monkeys.



Curtis, R. F., Ballantine, J. A., Keverne, E. B., Bonsall, R. W., & Michael, R.P. 1971. Identification of primate sexual pheromones and the properties of synthetic attractants. *Nature* 232:396–398.

Michael, R. P., Keverne, E. B., & Bonsall, R.W. 1971. Pheromones; Isolation of male sex attractants from a female primate. *Science* 172:964–966.

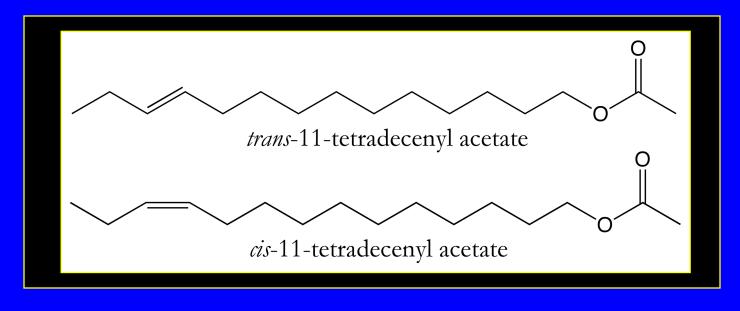
# In 1971, Carlson & colleagues identified the house fly, *Musca domestica*, sex pheromone.





Carlson, D. A., Mayer, M. S., Silhacek, D. L., James, J. D., Beroza, M., & Bierl, B. A. 1971. Sex attractant pheromone of the house fly: Isolation, identification and synthesis. *Science* 174:76–78.

Klun & colleagues (1973) showed that maximum attractiveness depended upon a precise mixture of *cis*- and *trans*-isomers in the European corn borer, Iowa strain *Ostrinia nubilalis* (Hübner) and the redbanded leafroller, *Argyrotaenia velutinana* (Walker).



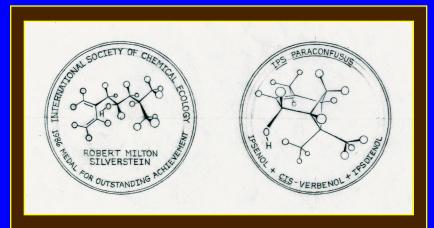
#### $\rightarrow$

Klun, J. A., Chapman, O. L., Mattes, K. C., Wojtkowski, P. W., Beroza, M. & Sonnet, P. E. 1973. Insect sex pheromones: Minor amount of opposite geometrical isomer critical to attraction. *Science* 181:661–663. The International Society of Chemical Ecology (ISCE) was founded in 1983 and the first annual meeting was held in Austin, TX. Lincoln Brower was the first president.

+ The Silver Medal for career achievement in chemical ecology was first awarded in 1986 to Robert M. (Milt) Silverstein in Berkeley, CA.
+ Wilhelm Boland received the first Silverstein/Simeone Lecture Award for significant mid-career scientific achievement in 1995 in Los Andes,

Chile.





Initial illustrations of the Silver Award medal awarded to Milt Silverstein

## The 38 Winners of the *ISCE* Silver Medal and Silverstein-Simeone Awards

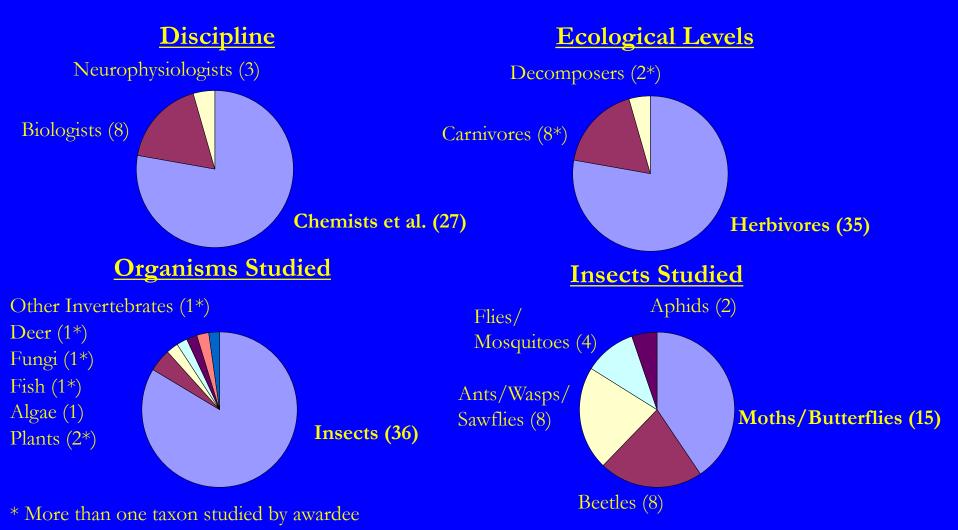
#### Silver Medal Awards:

- 1986 | Robert Silverstein
- 1989 | Murray Blum & Miriam Rothschild
- 1990 | Wendell Roelofs & Dietrich Schneider
- 1991 | Jerrold Meinwald & Thomas Eisner
- 1993 | Jeffrey Harborne
- 1994 | Gerald Rosenthal & Dan Janzen
- 1995 | Wittko Francke
- 1996 | Kenji Mori & Jacques Pasteels
- 1997 | William Fenical
- 1998 | Thomas Hartmann
- 1999 | Elizabeth Bernays & Reginald Chapman
- 2000 | William Bowers
- 2001 | David Wood
- 2002 | John Pickett
- 2004 | Jeremy McNeil
- 2005 | Jim Tumlinson
- 2006 | John Hildebrand & A.C. Oehlschlager
- 2007 | Koji Nakanishi
- 2008 | Gunnar Bergstrom

Silver	stein-Simeone Lecture Award
1995	Wilhelm Boland
1996	Louise Vet
1997	Clarence Ryan
1998	Ian Baldwin
1999	Alan Renwick
2000	May Berenbaum
2001	Glenn Prestwich
2002	Thomas Baker
2004	Richard Vogt
2005	John Carlson
2007	Walter Leal
2008	Leslie Vosshall

### Analysis of the Contributions of ISCE Award Winners

- Chemists/biochemists/molecular biologists were dominant among disciplines (27/38)
- Insects were the most studied organisms (36/38), especially moths/butterflies (15), beetles (8), ants, wasps, & bees (8).



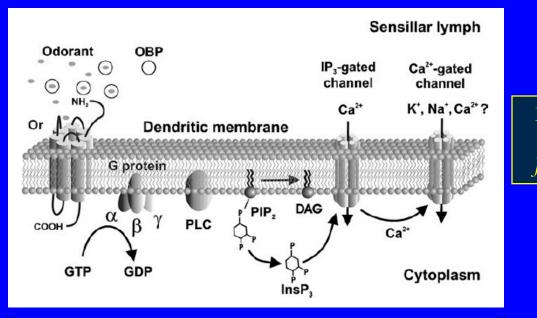
This trend in research may actually be representative of the trend in our society. However, this is a very small and biased sample and there are no statistical analyses to support the obvious conclusions from this sample.We are a society comprised, in large part, of chemists working on insects that are mostly consumers and herbivores.





Jeffrey Harborne Silver Medal, 1993 There has been a notable increase in investigations of the physiology & molecular biology of the transduction of chemical signals among organisms.

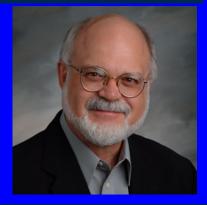
Vogt & colleagues (1981) provided the first biochemical and molecular evidence for pheromone-binding proteins from the antennae of the male silk moth, *Antheraea polyphemus* 



From: Jacquin-Joly and Merlin 2004. JCE 30: 2359-2397



Dick Vogt Silverstein-Simeone Award, 2004

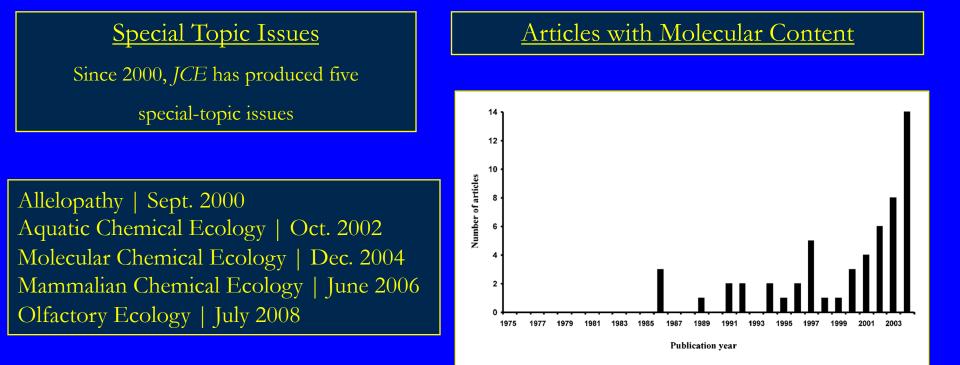


John Hildebrand Silver Medal, 2006

Vogt, R. G., & Riddiford, L. M., 1981. Pheromone binding and inactivation by moth antennae. *Nature* 293:161–163.

Stengl, M. Zufall, F., Hatt, H., & Hildebrand, J. G. 1992. Olfactory receptor neurons from antennae of developing male *Manduca sexta* respond to components of the species-specific sex pheromone *in vitro*. *J. Neurosci.* 12: 2523–2531.

### Trends in Publication in The Journal of Chemical Ecology



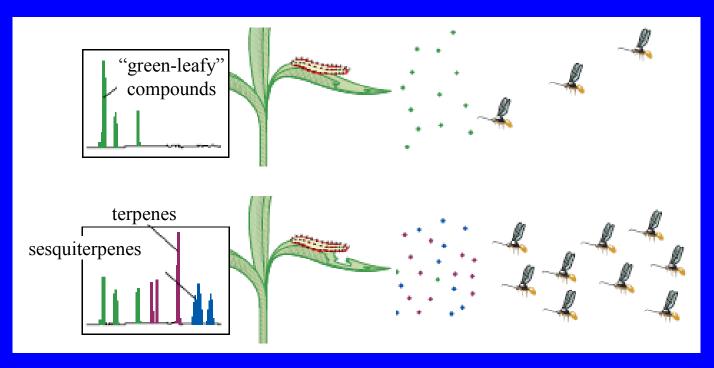
Trends in publication of articles in *The Journal of Chemical Ecology* with molecular content from 1975-2003.

Seybold, S.J. 2004. The eighth day of discovery: Molecular biology comes to chemical ecology.

J. Chem. Ecol. 30: 2327–2333.

+ Many frontiers for the study of interacting species at the guild, community, and ecosystem levels of biological organization.

+ The few investigations of tri-trophic interactions among herbivorous insects, parasitoids, and predators, and plants are important steps toward this frontier.



Tumlinson & Colleagues. 1993. How parasitic wasps find their hosts. Scientific American 268:100–106.

### Looking Forward

+Recent examples of "chemical ecology" have been noted at the biome and global levels (Gore, A. 2006. "An Inconvenient Truth").

- +There are effects of the major "greenhouse" gases (H<sub>2</sub>O, CO<sub>2</sub>, MH<sub>4</sub> O<sub>3</sub><sup>-</sup>) on:
  - 1) increased global temperature;
  - 2) projected decline in polar bear populations; and
  - 3) human behavior.
- +The link between greenhouse gas emissions and distant observations of impacts on species is difficult for regulators to establish.
- +Thus, we see life-threatening ecological impacts of simple compounds produced by respiration and decomposition on our biosphere and ultimately on human survival.

A4 News | The Seattle Times | TUESDAY, AUGUST 12, 2008

## **Nation**Report

## Species protection in flux

BUSH PROPOSES NEW REGULATIONS

Fewer mandatory reviews by scientists

BY DINA CAPPIELLO The Associated Press

WASHINGTON – Parts of the Endangered Species Act may soon be extinct.

The Bush administration wants federal agencies to decide for themselves whether highways, dams, mines and other construction projects might harm endangered animals and plants.

New regulations, which don't require the approval of Congress, would reduce the mandatory, independent reviews government scientists have been performing for 35 years, according to a draft first obtained by The Associated Press.

Interior Secretary Dirk Kempthorne said late Monday the changes were needed to ensure that the Endangered Species Act would not be used as a "back door" to regulate the gases blamed for global warming. In May, the polar bear became



The Seattle Times, Tuesday August 12, 2008

Meanwhile, we applaud our colleagues in chemical ecology who have discovered many new compounds that may serve to benefit human survival.

alkaloids amino acids fatty acid derivatives proteins shikimic acid derivatives terpenes and others This theme was developed with the collaboration of Jim Tumlinson, Steve Seybold, Julie Tillman, & Andrew Graves.