What are Chemosemants?

or chemistry of biotic interactions

Part I - Communication

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What is chemistry of biotic interactions?

One from definitions says:

" …chemistry of biotic interactions (or chemical ecology) is multidisciplinary science dealing with origin, function and significance of natural compounds mediating interactions among organisms (chemosemants)…"

- cocktail of chemistry, biology, biochemistry, etiology, ecology, biostatistics…
- rapid development in the last 30 years (hi-tech analytical techniques as are GC, GC-MS, EAG, GC-EAG, with progress in behavioral biology and ecology)

Chemosemants – mediators of chemical interaction

communication - infochemicals

defense
- secondary metabolites in plants (alkaloids)
- toxins in fungi and animals
- defensive secretions
- complex chemical defensive strategies

- both groups penetrate and complement together
- using of chemosemants is often linked with non-chemical type of defense and communication (mimesis, optical or acoustic communication)

Chemical communication

- according to present knowledge about nature, behavior of living organisms is in majority influenced or directly controlled by trace amounts of specific low-molecular organic compounds
- chemical communication has a key importance in lower organisms (plants and invertebrates – insects, spiders etc.)
- compounds employed in transmission of chemical information are called infochemicals

Pheromones
intraspecific communication

Infochemicals
compounds used for
communication among organisms

Allelochemicals
interspecific communication

Releasers
affect sensory receptors,
immediate behavioral changes

- sexual
- aggregation, trail,
- dispersion
- marking & identification

Primers
cause physiological changes,
delayed effect (exohormones)

Allomones
favorable to the emitter

Kairomones
favorable to the receiver

Synomones
favorable to both

Pheromones – intraspecific communication tools

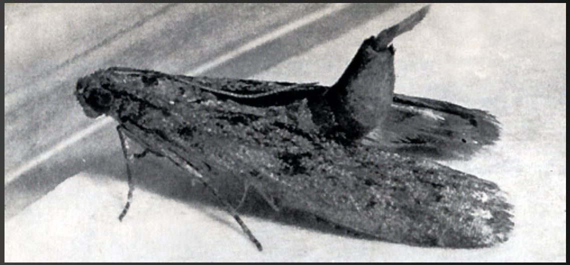
- The broadest pheromone repertoire - insects
- History: moth sexual attractants known for more than 200 years (von Siebold, Henri Fabre)
- First application: gypsy moth (USA), nun moth (Europe)
- First structure: *bombykol*, silk moth female sexual pheromone (Adolf Butenandt, 1959, 500 000 females - 12 mg of compound; Nobel prize)

(*E*,*Z*)-10,12-hexadecadien-1-ol, bombykol

- Today we need only one pheromone gland (5 pg - 100 ng)
- Production - exocrine glands (with external orifice)
- Perception - olfactory or taste receptors, vomeronasal organ in vertebrates (VNO, Jacobson organ)

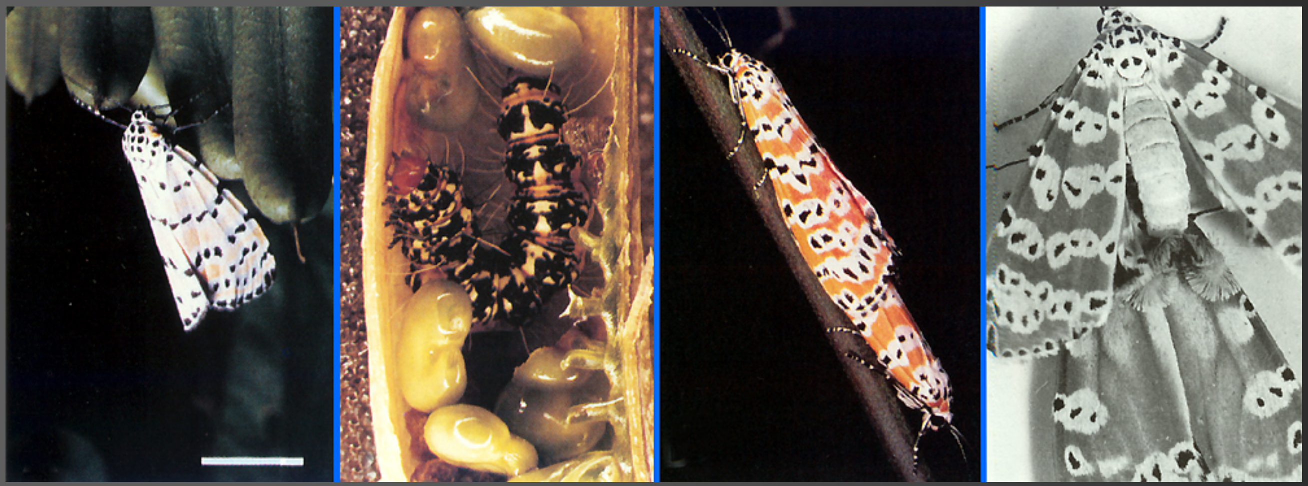
Insect sexual pheromones

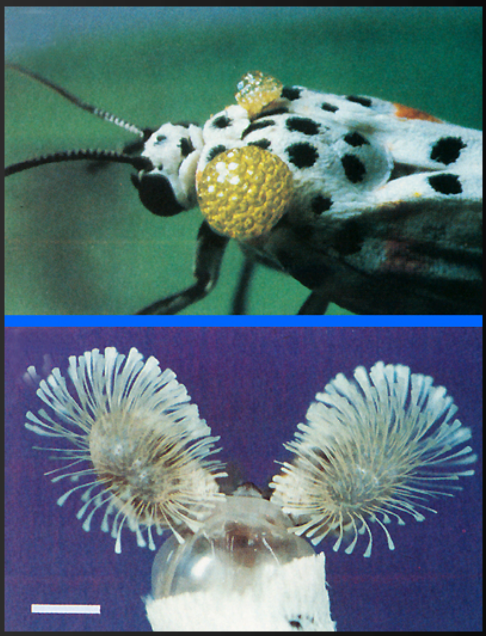
- Female pheromones (sexual attractants), specific for the species:
  - molecular composition (including stereochemistry)
  - specific ratio of compounds in blend (multi-component pheromones)
  - excretion conditions (daytime, habitat, geographical position)
- Male pheromones (aphrodisiacs): short-path effect, in contact, ease copulation - prepares receptive female (excitation, proper position), glands on wings or abdomen, deterrents for another males
- Production – abdominal glands = "calling", intestine or mandibular glands etc.



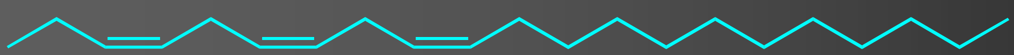
- Application: traps (monitoring, catching), trap-and-kill, mating disruption
- Origin: - products of own biosynthesis
  - conversion of exogenous compounds (sequestration from food sources, e.g. bark beetles ► terpenes from coniferous trees)

Complicated case of Ornate Moth (Utethesia ornatrix)

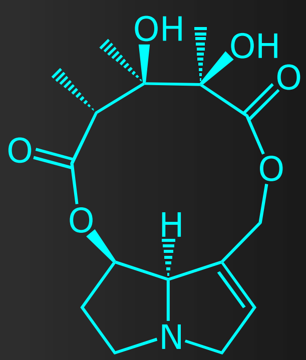




- caterpillar feeds on toxic shrub *Crotalaria spectabilis* (Fabaceae), sequestering alkaloid monocrotaline (MD), used then as a defensive secretion major component
- female attracts male by a classical pheromone



- male proves his “quality” by male pheromone hydroxydanaidal (HD; metabolite of MD) emitted by inflatable coremata
- female chooses the best male and takes over dose of MD in spermatophore of eggs protection



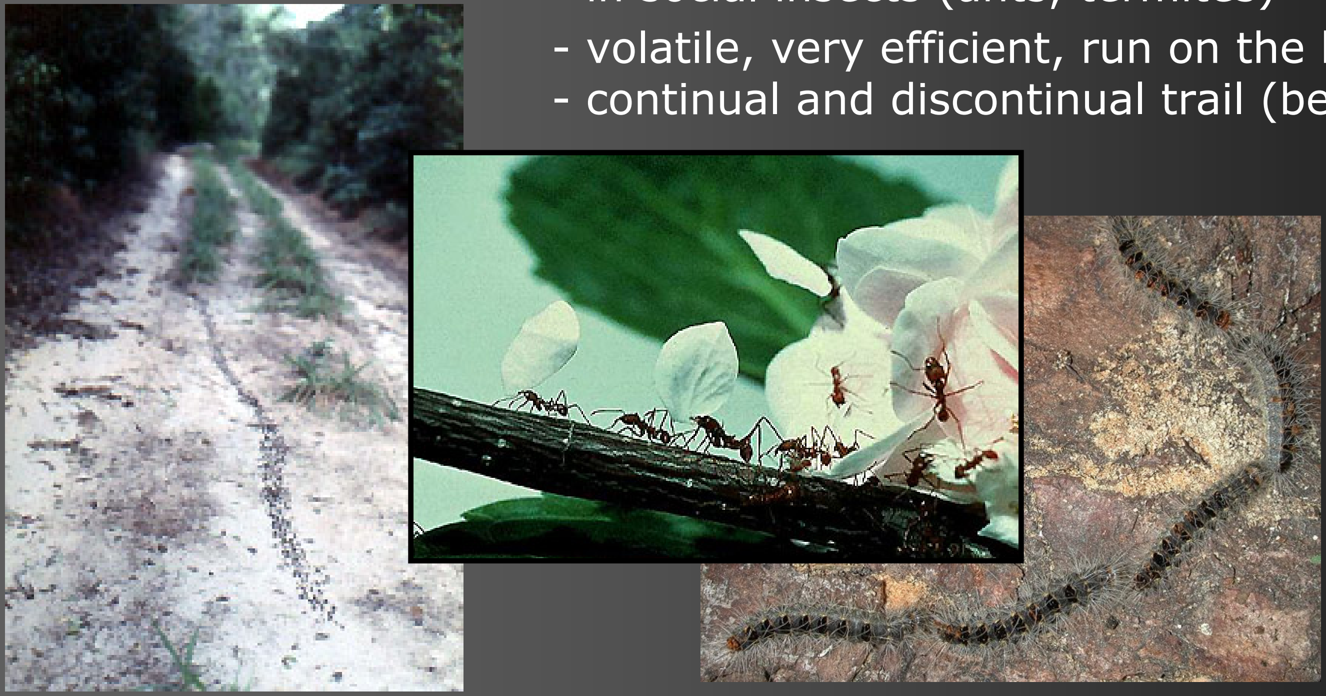
MD

HD

Aggregation & trail insect pheromones

Aggregation of individuals for joint activities (feeding, mating, overwintering, aposematic defense etc.) on the basis of signals, which are not related to these activities…

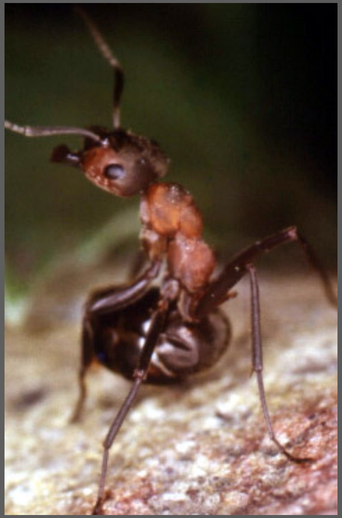
- Aggregation pheromones
  - source is rectal or proctodeal gland
  - common in bark beetles, ladybugs
- Trail pheromones
  - in non-social insects (*Thaumetopoea* caterpillars)
  - in social insects (ants, termites)
  - volatile, very efficient, run on the heels
  - continual and discontinual trail (beacons –bees)



methyl 4-methylpyrrol
-2-carboxylate
["trail" of ants *Atta*]

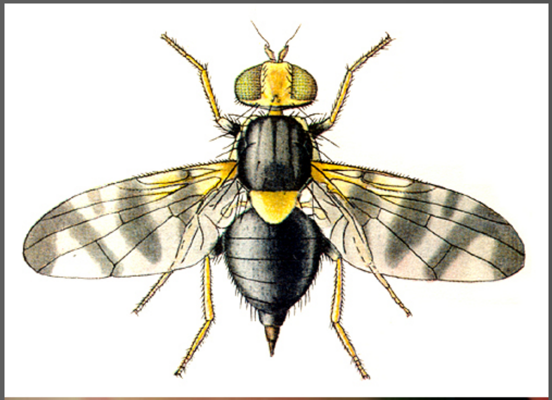
Alarm (dispersion) insect pheromones

- Non-social: - aphids (β-farnesene), also “shepherd” ants react for signal
  - treehoppers (thorn bug *Umbonia* fights back enemies) etc.
- Social insects: in all except *Polistes* wasps and bumble bees.
  - in low concentrations = attractant
  - in high concentrations = dispersant, so concentration control different mode of action: defense, dispersion, excitation, aggregation, call for reinforcement…)
  - defensive compounds are sometimes also alarm pheromones
  - bees & wasps: emission of alarm pheromones with use of sting
  - in kleptoparasites chemical propaganda (citral in cleptobiotic robber bee *Lestrimelitta limao* × attacked bees)



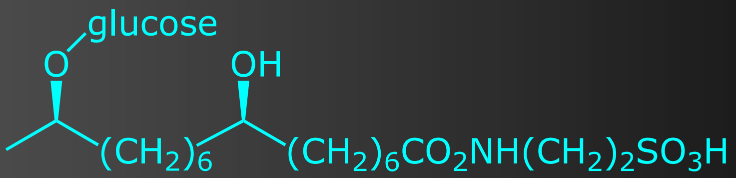
"Marking" insect pheromones

- Marking pheromones: regulate the population density.
  - eggs-laying inchneumonid wasp marks checked terrain
  - flour moth: larval pheromone stimulates dispersion and development
- Identification pheromones: colony "seal" in soc. insects (cuticular hydrocarbons)
- Cadaveric pheromones: products of decay (e.g. fatty acids in social insects)



Cherry fruit fly (Rhagoletis cerasi)

Why is in cherry only one "worm"? Female uses marking oviposition pheromone and thanks to this mark can recognize "occupied" cherry…



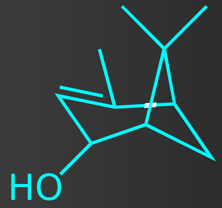
Allelochemicals – interspecific communication tools [allomones, kairomones and synomones]

- Defense
- Symbiotic coexistence
- Search for host or prey
- Misuse of chemical signals
  - chemical propaganda
  - chemical tricks
  - chemical mimicry & masking
  - social parasitism and slavery

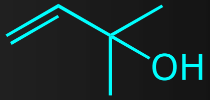
Kairomones, Example I: Bark beetle × Ant beetle

Spruce bark beetle (Ips typographus)

- the most important spruce pest
- terpenes are primary attractants
- powerful aggregation pheromone



cis-verbenol

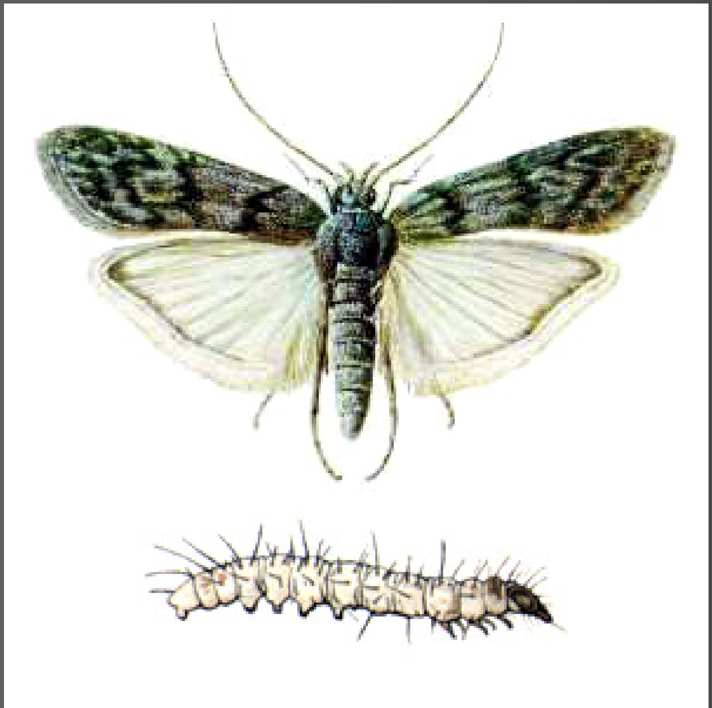


2-methyl-3-buten-2-ol

Common ant beetle (Thanasimus formicarius)

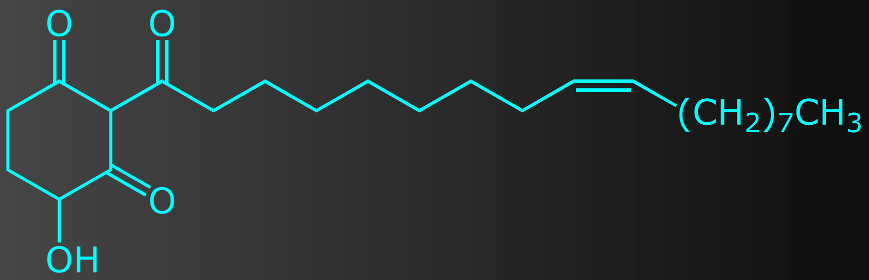
- natural enemy of *Ips typographus*
- seeks Ips pheromone emission
- …so, it is kairomone (for *Thanasimus*)

Kairomones, example II: Flour moth × Ichneumonid



Flour moth (Ephestia kuehniella)

- synantropic storage pest (flour)
- caterpillars use autoregulation pheromone
- *function:* stimulates larvae dispersion, regulates their development and also suppresses female's fertility



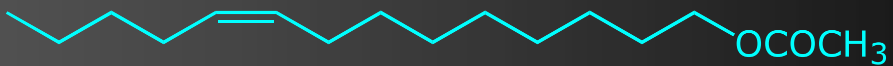
Ichneumonid parasitic wasp (Nemeritis canescens)

- first orientation by flour smell
- final larvae seek – larvae pheromone
- …again, it is kairomone (for wasp)

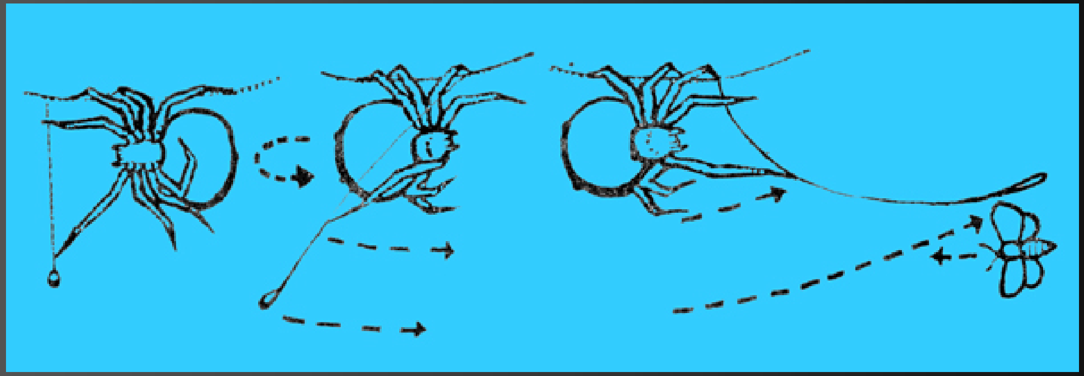
Chemical tricks I

Bola spider (*Mastophora cornigera*)

- bola spider lures males of certain moth species by using major components of their sexual pheromones
- in emissions of 8 females during 2 months were found: *Z*9-14:Ac, *Z*9-14:Al, *Z*11-16:Al, *Z*11-16:Ac
- Attracted males catches using sticky ball (bola)
- in prey found 15 moth species using these compounds
- in that case are these compounds allomones



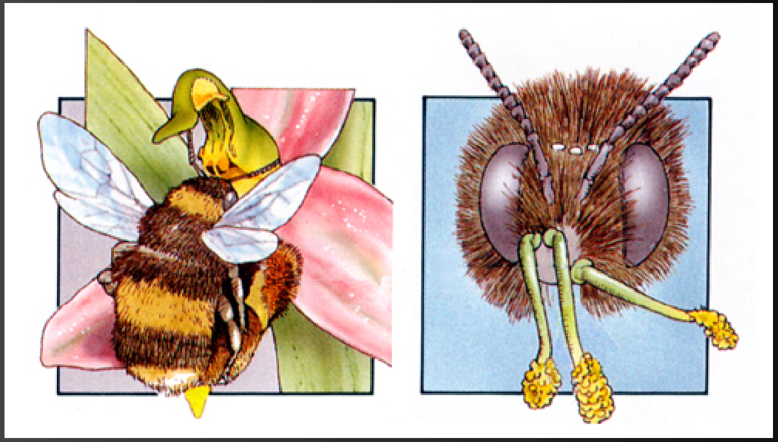
*Z*9-tetradec-9-enyl acetate (*Z*9-14:Ac)



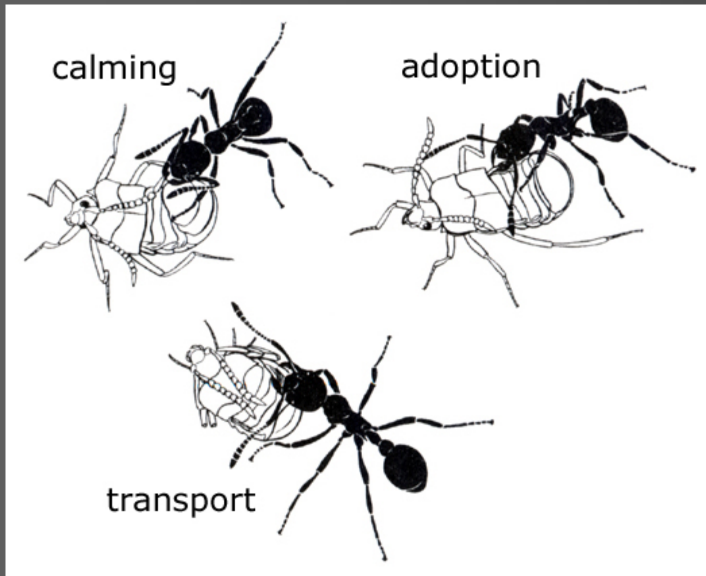
Chemical tricks II

Orchids of Ophrys genus

- orchid lures males of *Eucera* genus bee by flower shape and by smell, which contains compounds identical with components of bee female sexual pheromone
- during contact are on male’s forehead glued sticks with pollen for perfect pollination
- pollinated flowers emit the same infochemicals as are calm pheromones of inseminated bee females

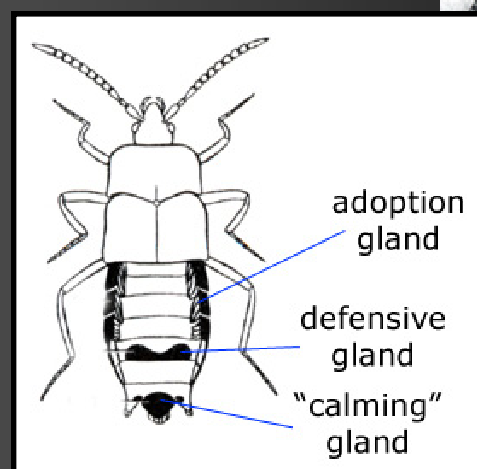


Chemical tricks III



Myrmecophilic rove beetles *Atemeles*

- rove beetle *Atemeles pubicornis is a social parasite in ants of Formica* and *Myrmica*
- during ants deceiving beetle uses two glands: calming and adopting (with ant's fetal pheromone)
- after transfer to the nest and imprinting by colony smell (cuticular hydrocarbons) beetle (and its progeny…) is feeding ant's larvae and pupae



Chemical tricks IV – What is the "bouquet of death" ?

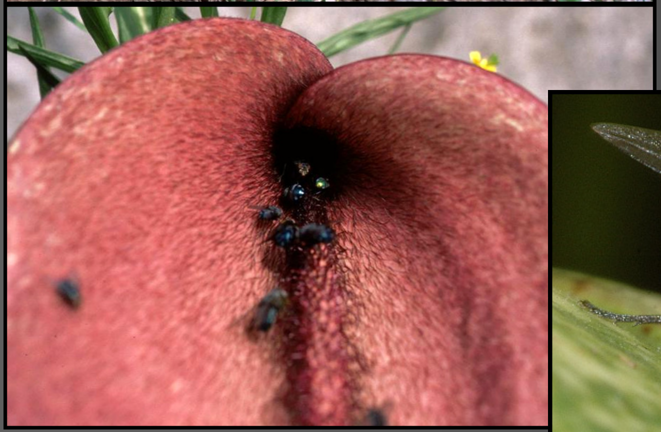
- dead bodies of vertebrates are emitting soon *post mortem* volatiles low-molecular organosulfur compounds (SVOCs)
- these extremely strongly malodorous compounds are perceived by humans as typically sweetish cadaverous stench

CH_3SH	methanethiol
CH_3SCH_3	dimethyl sulfide
CH_3SSCH_3	dimethyl disulfide
CH_3SSSCH_3	dimethyl trisulfide
$CH_3SSSSCH_3$	dimethyl tetrasulfide
CH_3SCOCH_3	methyl thiolacetate

- SVOC-compounds are strong attractants for necrophilous insects (carrion beetles, some dung beetles, flies etc.)
- for above mentioned insect groups are vertebrates carrions the main food source for their offspring (very strong competition)

Chemical tricks IV – False bouquet of death

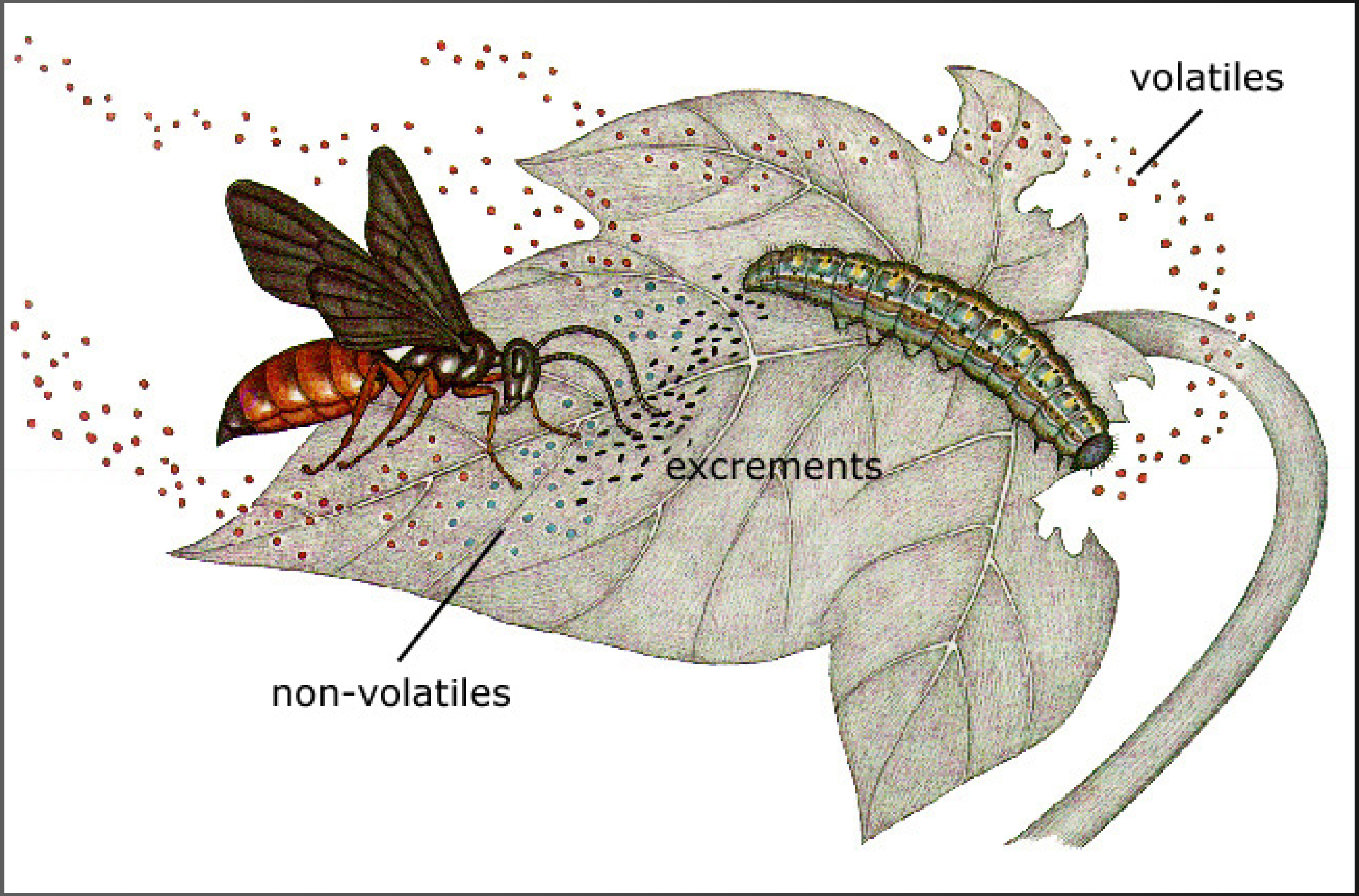
- arum family plants (Araceae) emit the same SVOCs as vertebrate carrions and attract by them insects – especially flies (blow flies *Lucilia* sp. and flesh flies *Sarcophaga*)
- stinkhorn fungi (Phallaceae) use the same "false" cadaverous odor for attraction of insects (flies, but also carrion beetles and dung beetles)
- attracted insects serve after contact with plant (fungi) as pollinator or spore-vector



Helicodiceros muscivorus
vs. Blow flies *of genus Lucilia*

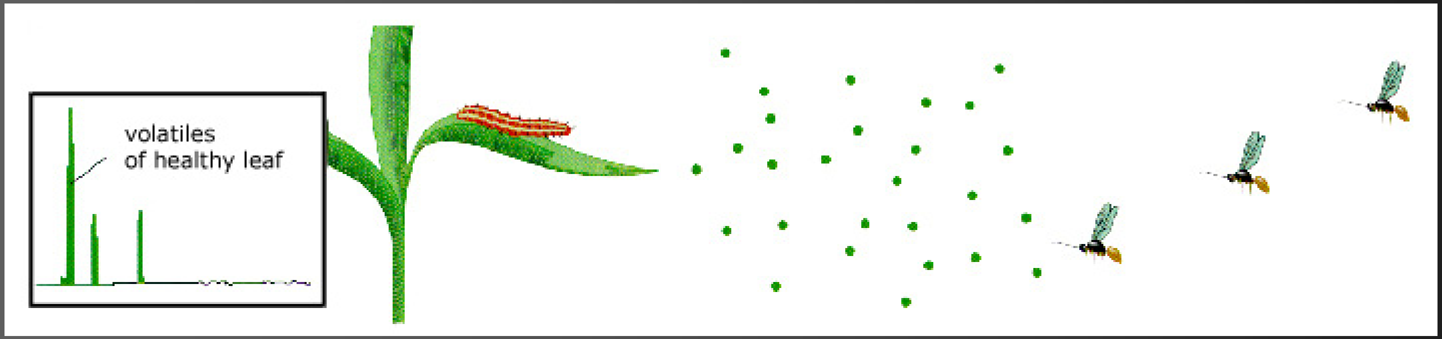
Common stinkhorn *(Phallus impudicus)*
vs. flesh flies of genus *Sarcophaga*

Ditrophic interaction:
Ichneumonid wasp (parasitoid) × moth's caterpillar

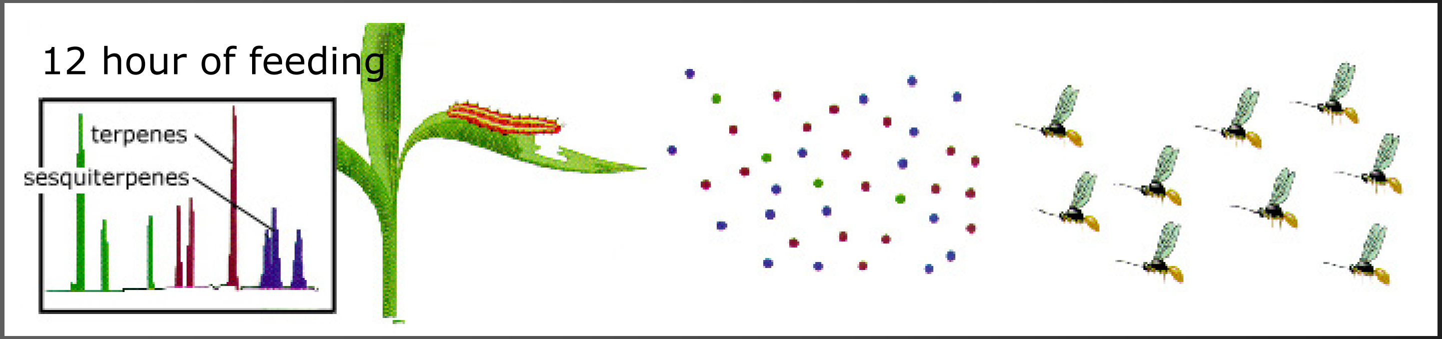


First look: parasitoid detects caterpillar using volatile and non-volatile compounds emitted by caterpillar during its feeding

Tritrophic interaction:
wasp Cotesia × Spodoptera moth's caterpillar × corn Zea mays

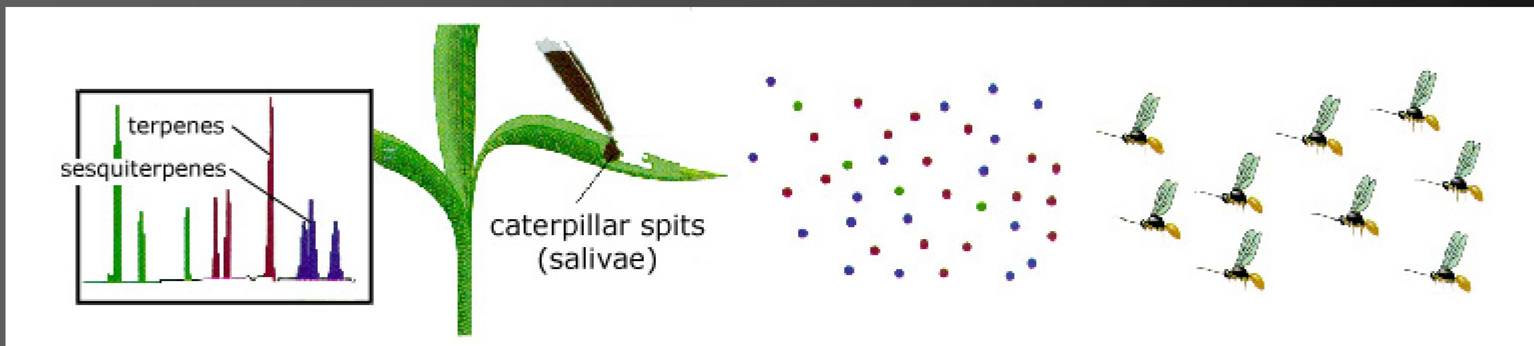


Second look: parasitoid uses for orientation common volatiles emitted by healthy corn leafs



Third look: much more wasps are navigated by sesquiterpenes emitted by damaged corn leafs; attacked plant emits chemical signals even after end of caterpillar feeding; induced volatiles attract another parasitoids; only mechanically damaged plants are not attractive for wasps (why ??)

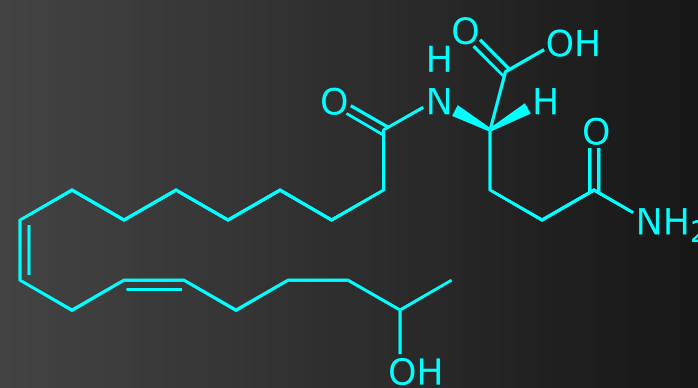
Tritrophic interaction:
wasp *Cotesia* × *Spodoptera* moth's caterpillar × corn *Zea mays*



Fourth look: caterpillars saliva induces the same volatiles as feeding; from saliva was isolated compound, which induces the signal terpenes biosynthesis in plant = volicitine

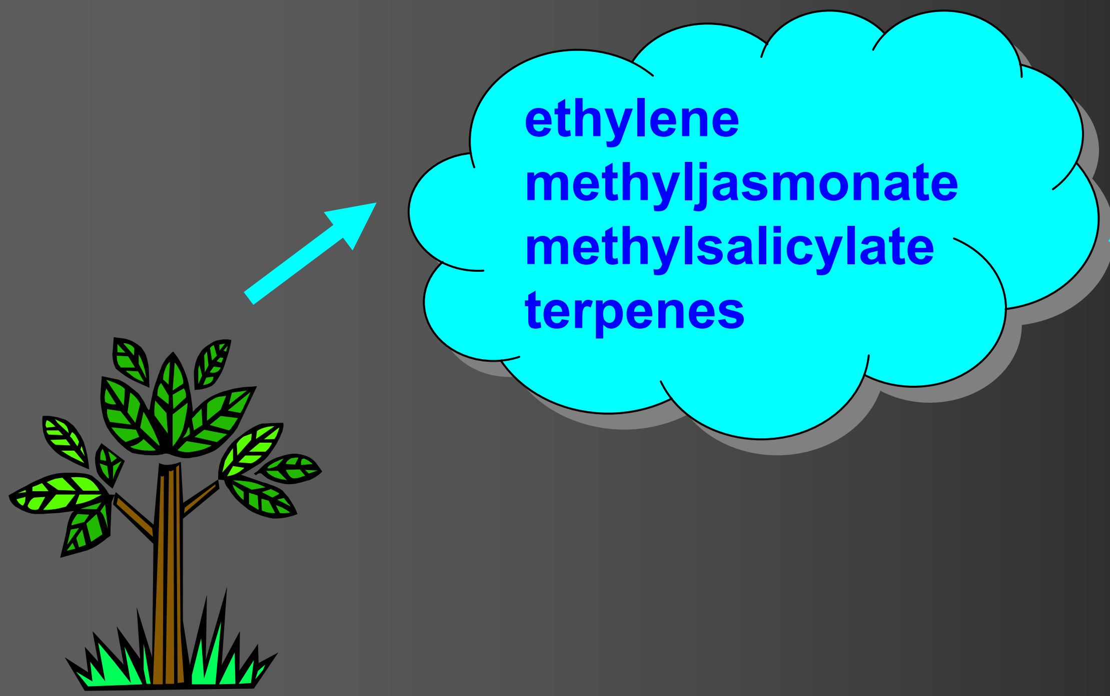
Isolated and synthesized compound:

N-(17-linolenoyl)-L-glutamine



[Tumlinson *et al.* Science 1997]

Plants react complexly with environment



Plant after is attacked by pathogen (insect, fungi etc.) emits:

- volatile infochemicals (viz. ⇧)
- defensive compounds (secondary metabolites: phenylpropanoids, terpenes, alkaloids).

In surrounding plants of the same species is starting synthesis of secondary metabolites without their damage (acquired systemic resistance).

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