What are Chemosemants?

or chemistry of biotic interactions

Part II - Defense

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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 defense of living organisms

Defensive compounds, used by organisms as a protection against their potential consumers, are in majority products of secondary metabolism.

- *plants*: widespread (alkaloids, food deterrents…)
- *animals*: spread in small or immobile animals with limited opportunities of defensive behavior of another type; practically unknown in animals on the tops of food-pyramids (big predators)

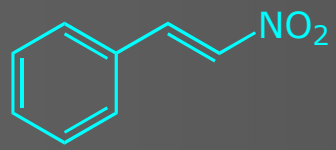
Arachnoids and millipedes

Giant whipscorpion *Mastigoproctus giganteus*

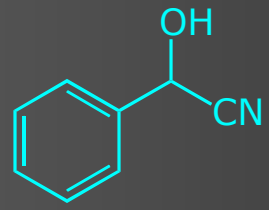
- irritated sprays defensive compounds
- pygidial gland
- nontoxic, but strongly irritating eyes etc.
  composition: lower fatty acids with prevalence of acetic acid (75% !!) and octanoic acid (15%)

Millipedes (Fig. *Narceus* sp.)

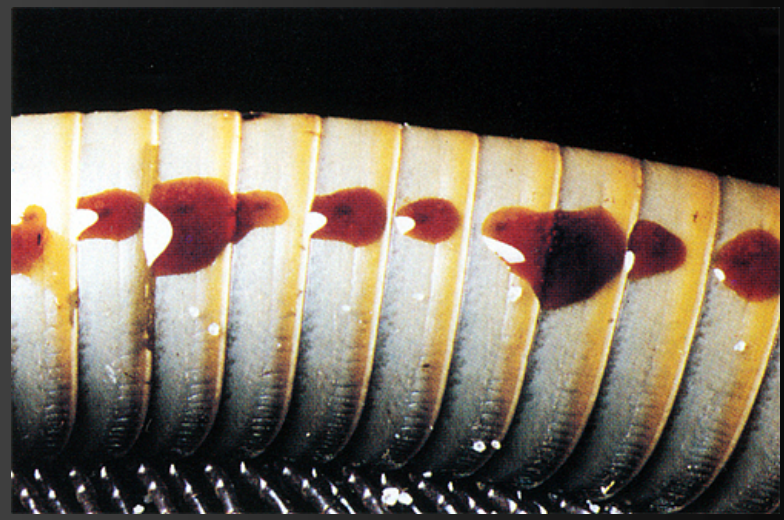
- irritated excretes defensive compounds
- gland orifices on each body segment
- composition: aromatic and nitro compounds



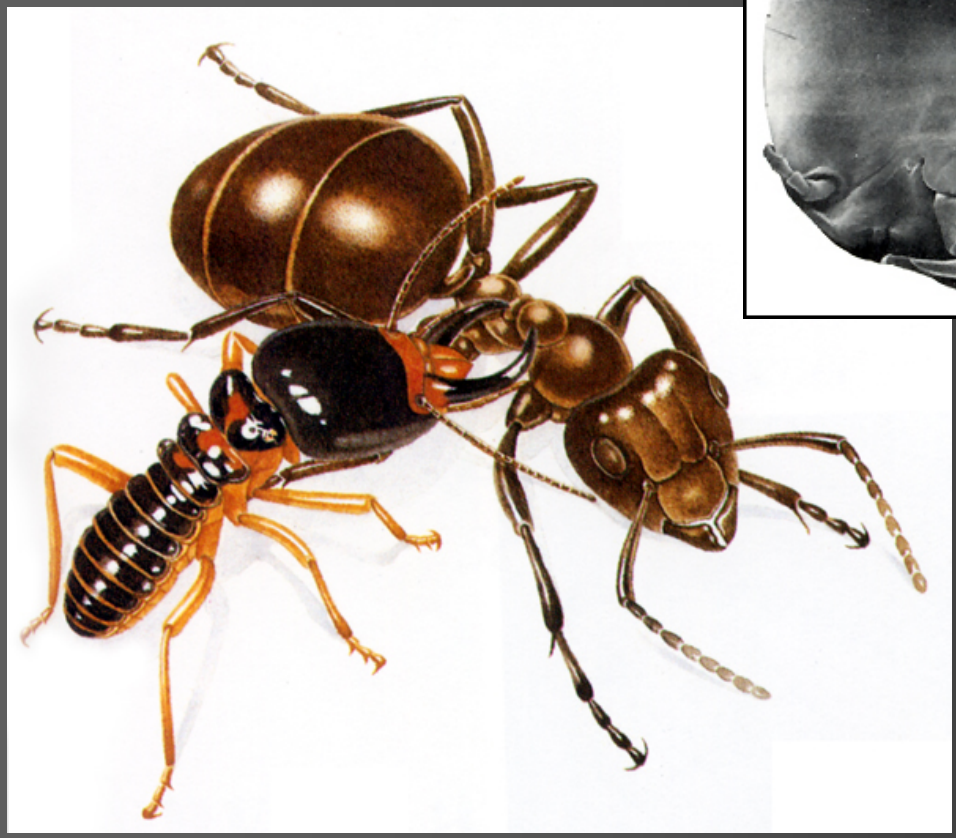
2-nitroethenyl benzene



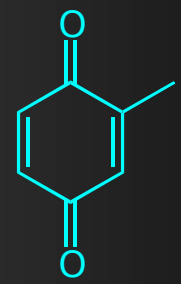
mandelonitrile



Termites I: genus Macrotermes

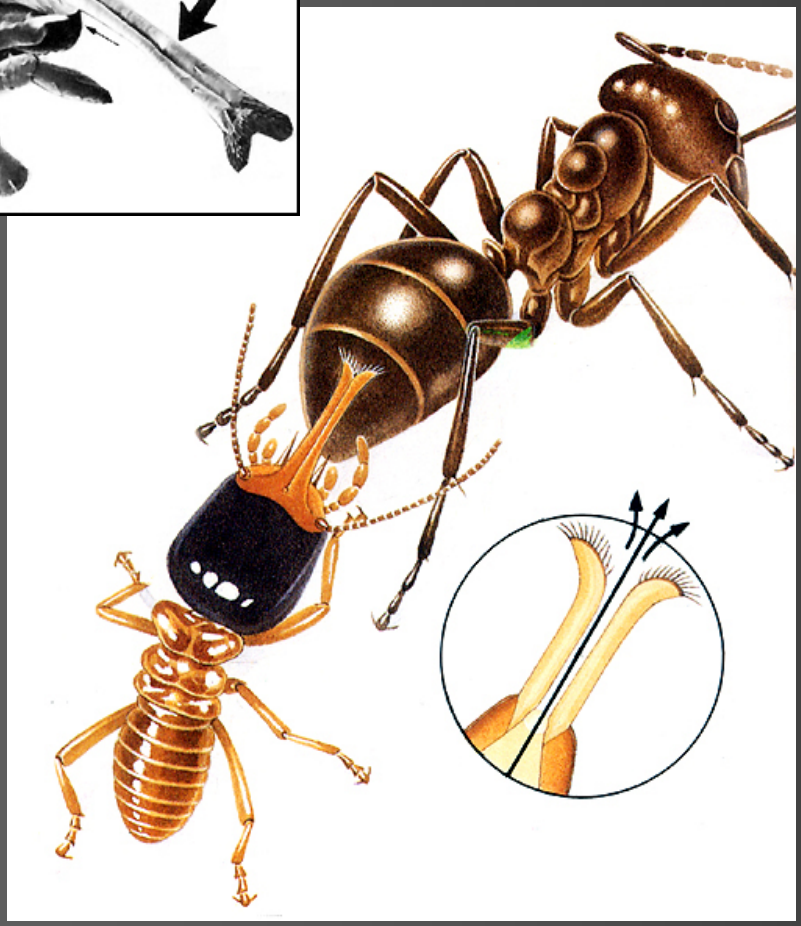


- frontal gland – forehead orifice
- composition: hydrocarbons and chinones

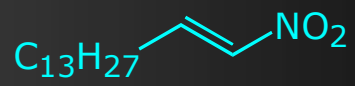


2-methyl-1,4-benzochinone

Termites II: genera Rhinotermes and Prorhinotermes

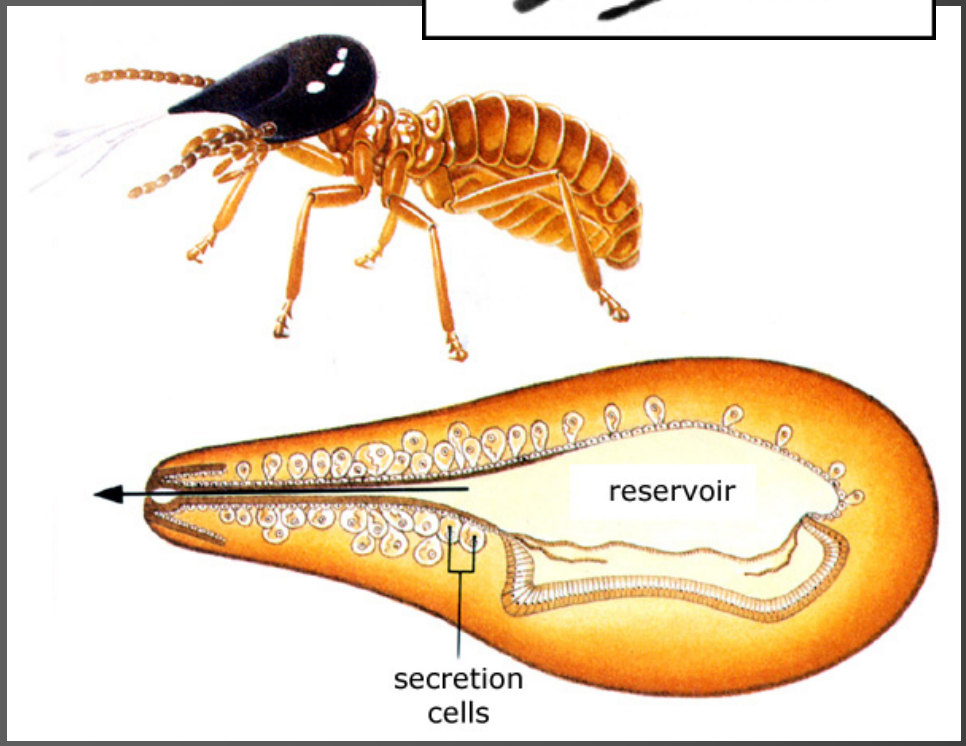


- gland's orifice on transformed clypeolabrum (upper lip)
- composition: hydrocarbons, ketones, aldehydes, keto-aldehydes and unique natural nitro compounds

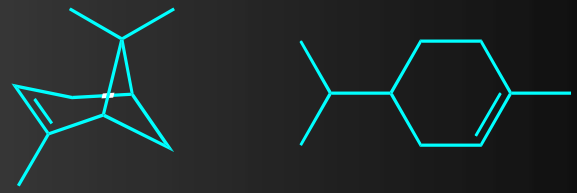


1-nitro-1-pentadecene
[*Prorhinotermes simplex*]

Termites III: genera Trinervitermes and Nasutitermes

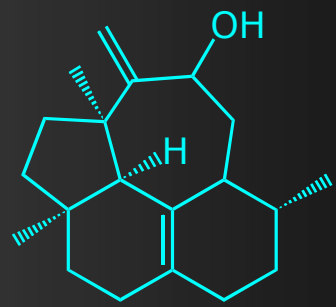


- gland's orifice: distinctly elongated frontal part of head
- composition: mixtures of simple and complex mono- / diterpenes



α-pinene limonene

[*Nasutitermes exitiosus*]



trinervitene

[*Trinervitermes gratiosus*]

True bugs (Heteroptera)

Striped shield bug
(*Graphosoma lineatum*)
hydrocarbons, aldehydes, furanones…

- chemical defense commonly used
- intensively stinking secretions
- composition: broad compounds' spectrum

Fire bug
(*Pyrrhocoris apterus*)
hydrocarbons, aldehydes, alcohols, ketones…

Ground beetles (Carabidae): Carabus genus

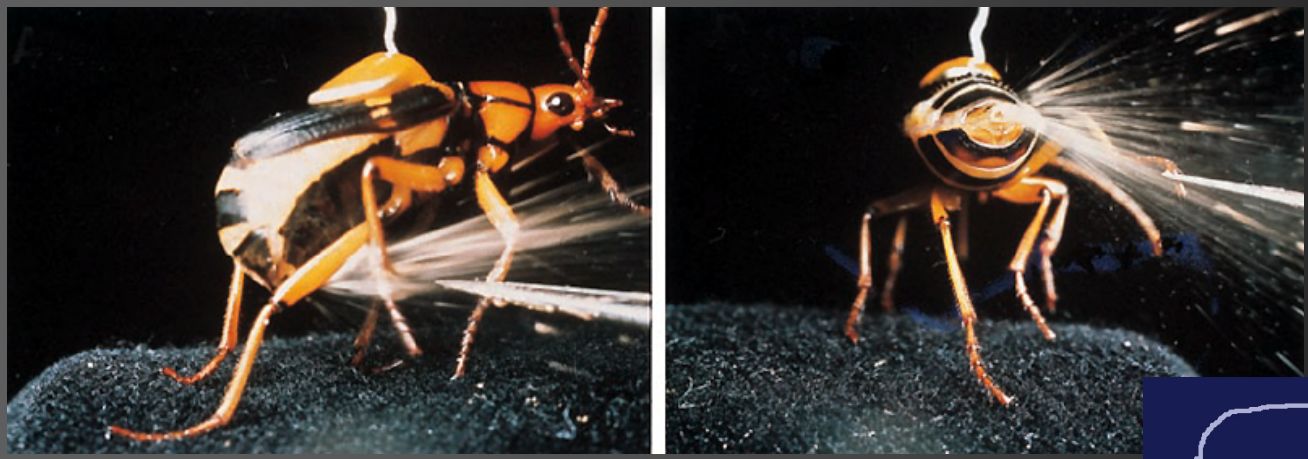
Carabus coriaceus

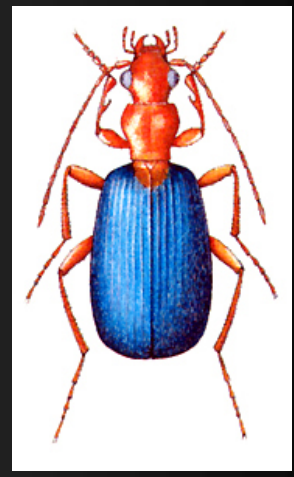
- massive insect predators (2-6 cm)
- enemies: vertebrates
- defense: strongly stinking secretion
- composition: lower fatty acids

$CH_3(CH_2)_2COOH$ – butyric acid
$CH_3(CH_2)_3COOH$ – valeric acid

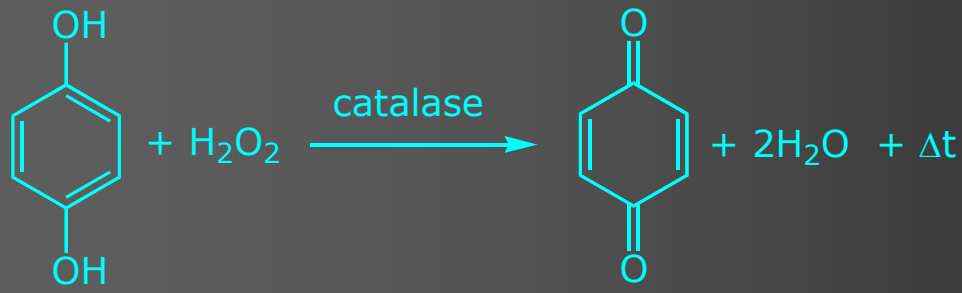
Carabus intricatus

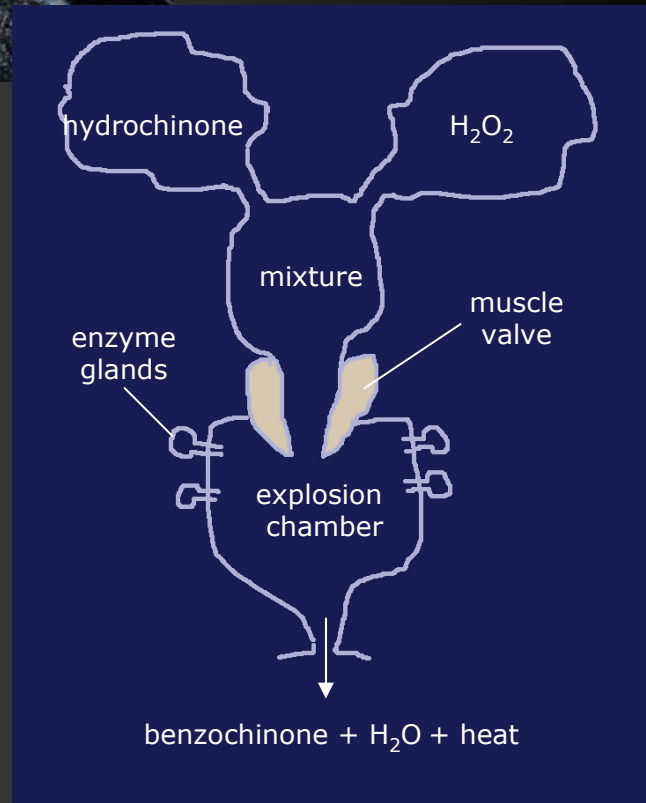
Bombardier beetles - Brachinus genus





- unique & efficient system of chemical defense
- well audible and visible "explosion"
- temperature at chamber exhaust: 100 °C

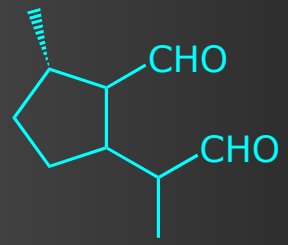




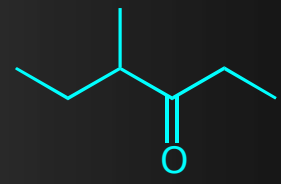
Rove beetles (Staphylinidae)

Ocypus olens (The Devil's Horse)

- the biggest European rove beetle, strong predator
- produces stinking defensive secretion



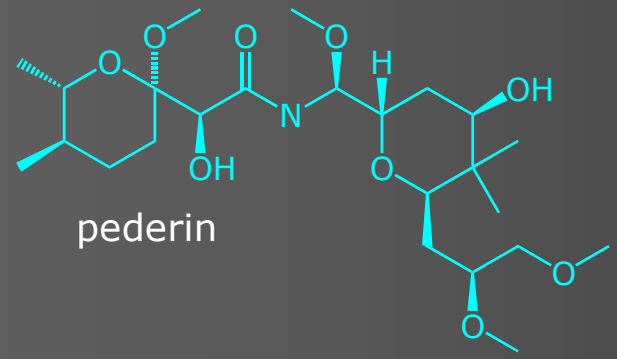
iridodial



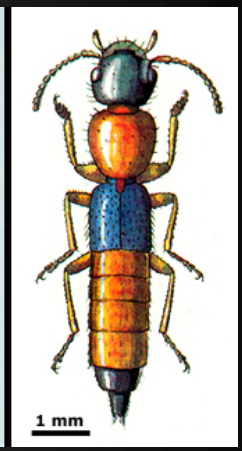
4-methylhexan-3-one

Females of *Paederus* sp.

- very strong toxin & DNA inhibitor
- bacterial biosynthesis in guts



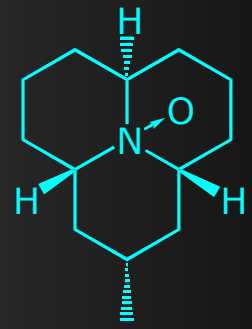
pederin



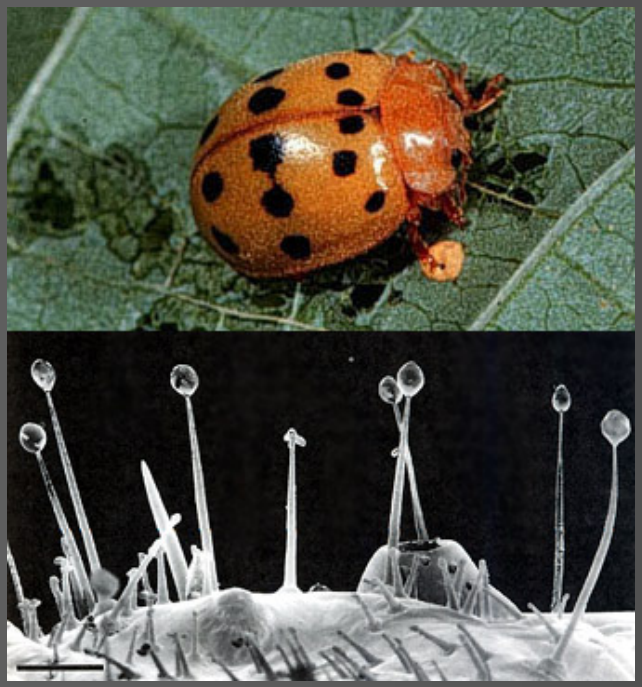
Ladybugs (Coccinellidae)

Coccinella genus

- reflexive bleeding after irritation
- defensive compounds in lymph
- major component: coccinelline
- efficient against predators

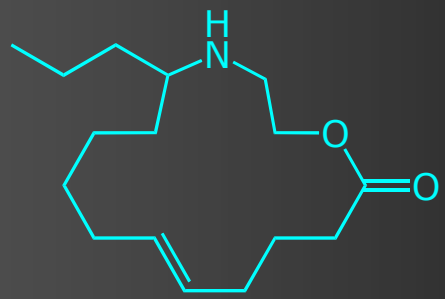


coccinelline

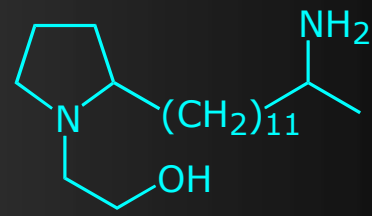


Epilachna varivestris

- adult: reflexive bleeding after irritation
- pupa: gland-hairs excrete defensive secretion
- toxin: number of structurally interesting alkaloids



pupa (epilachnene)

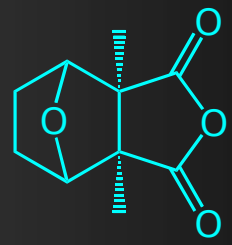


adult's lymph

Blister beetles (Meloidae)

Spanish fly (*Lytta vesicatoria*)

Toxic compound: cantharidin
(biosynthesis, only in males!)



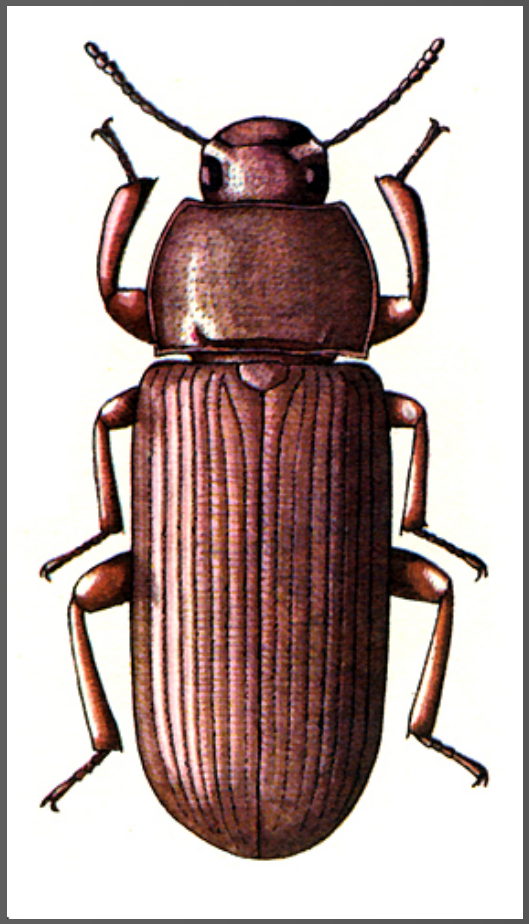
Function:

- defense of adults
- defense of eggs (transfer)

Effects:

- nephro- and hepatotoxic
- strongly irritating skin
- known aphrodisiacal effects
- popular poison (*Aqua toffana* in Medici family, Italy)

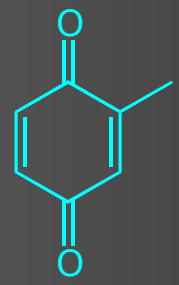
Darkling beetles (Tenebrionidae)

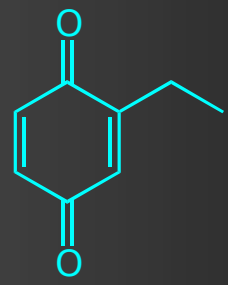


Yellow mealworm
(Tenebrio molitor)

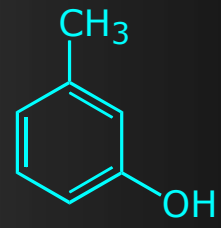
Confused flour beetle
Tribolium confusum

- most species excrete strongly stinking secretions
- distinct phenolic odor
- composition: chinones and phenols





2-methyl & 2-ethyl benzochinone

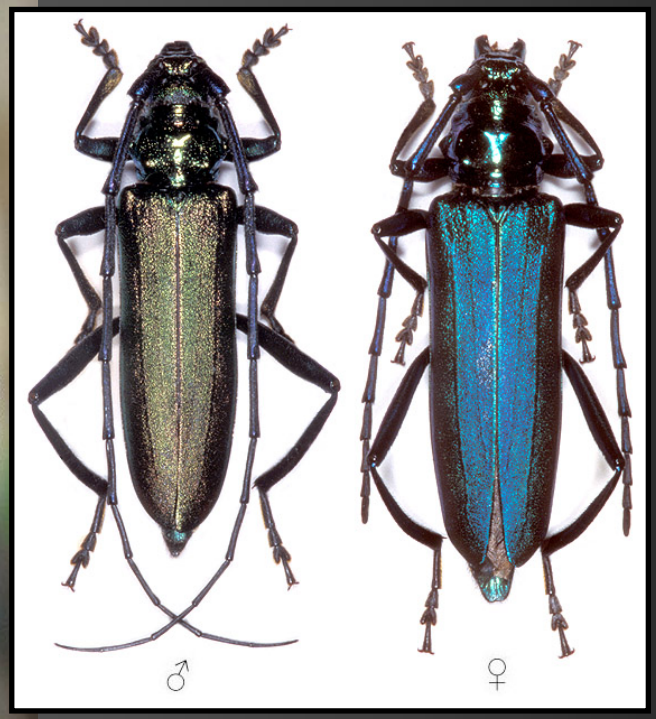


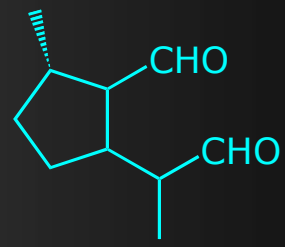
m-cresol

Longhorn beetles (Cerambycidae)

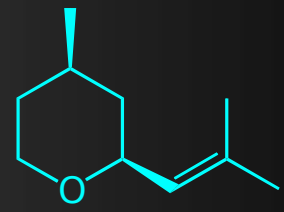
Musk longhorn (Aromia moschata)

- well visible orifices of thoracal gland
- irritated excretes intensively smelling secretion
- probably for defense and alarm communication
- isomer mixture of rose-oxide and irodial





iridodial

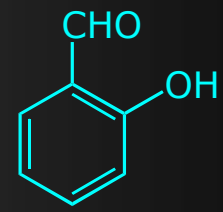


rose oxid

Poplar & willow leaf beetles of genus Chrysomela

Chrysomela saliceti

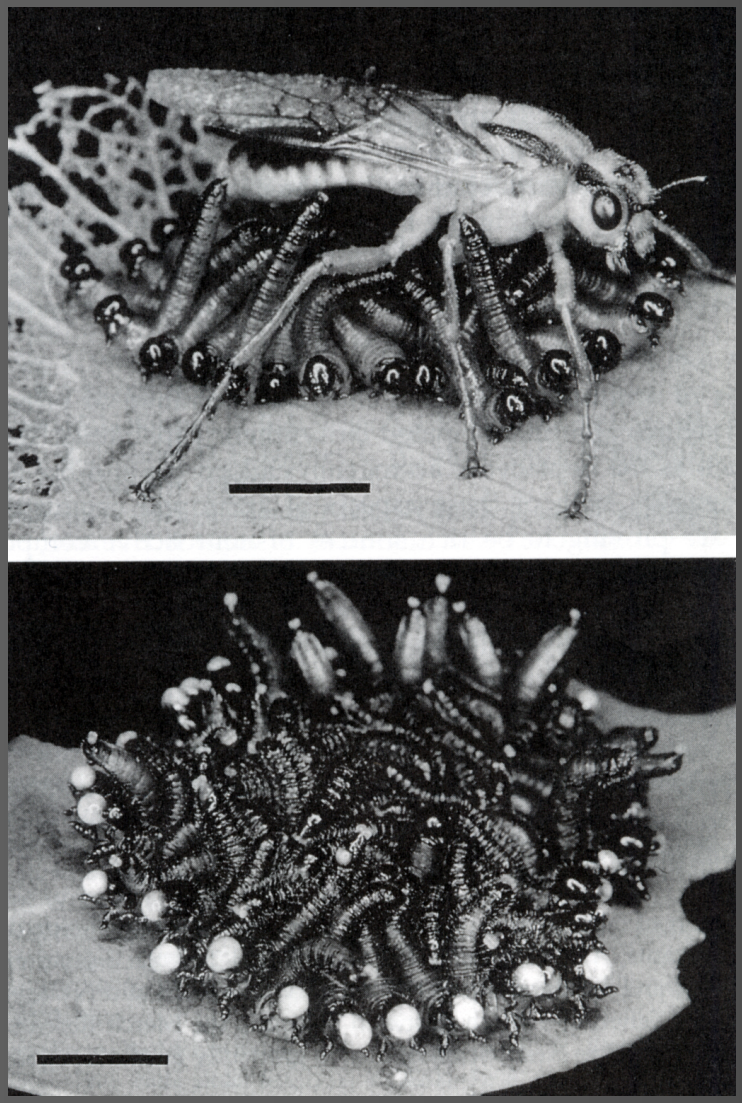
- larvae & adults excrete defensive secretions
- both species feed on poplars and willows
- both species sequester glycoside salicine and metabolize it to salicyladehyde (active compound of defensive secretions)



salicyladehyde

Chrysomela vigintipunctata

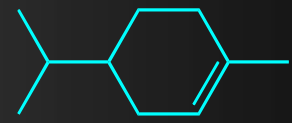
Herbal wasps - sawflies (Pergidae family)



Australian sawfly Pseudoperga guerini

- mother physically protects young larvae
- irritated older larvae use defensive secretions
- sequestration of active compounds from food
- defensive secretion – eucalypt oil (terpenes)

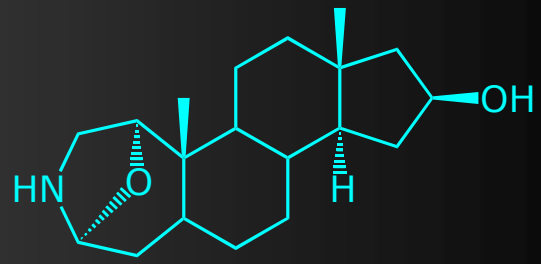
cineol



limonene

Fire Salamander (Salamandra salamandra)

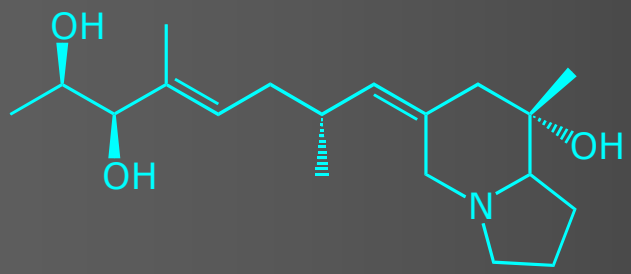
- small, slowly moving and vulnerable vertebrate
- defense: toxins in skin slime = samandarine
- steroid with cytotoxic and antibiotic effects
- is rather disgusting than toxic for predators
- not dangerous for humans



samandarine

Dart frogs of genera Dendrobates and Phyllobates

- "Dart frogs" (South and Central America)
- defense: alkaloids in slime skin secretion
- some of them are the most toxic substance known yet
- origin unknown – sequestration ?



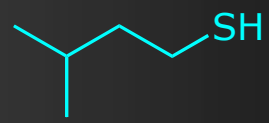
pumiliotoxin B (*D. pumilio*)

Dendrobates pumilio

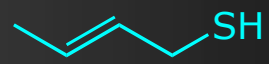
Skunks (Mephitidae)

- small or medium carnivores (40-70 cm long)
- all 14 species of family Mephitidae use chemical defense
- anal glands spraying powerfully stinking oily secretion (2 ppm in air)
- composition: sulphur compounds (thiols, thiolacetates…)
- great defense against another carnivores (volves, foxes, badgers…)
- not so efficient against birds of prey (poor-to-nonexistent sense of smell)

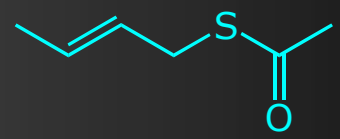
Striped skunk (*Mephitis mephitis*)



3-methylbutane-1-thiol



(*E*)-but-2-ene-1-thiol (70%)



(*E*)-but-2-enyl thioacetate

Literature

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