

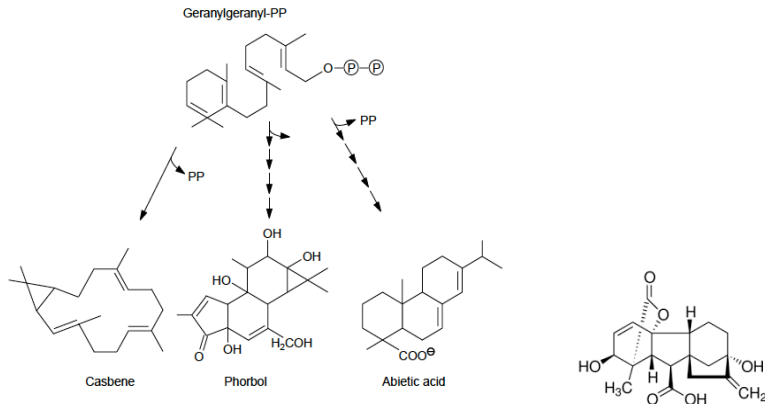
## Isoprenoids II

### 4. Diterpenes: Examples and functions (several toxin and deterrent functions)

i) toxins and phytoalexins: (i.e., casbene in castor bean (*Ricinus communis*), Euphorbiaceae (also phytoalexins in rice roots are diterpenes)

ii) growth regulators (hormones): **gibberellins** (= a primary metabolite)

- gibberellins promote shoot elongation, break dormancy in seeds (*recall seed amylase induction*)



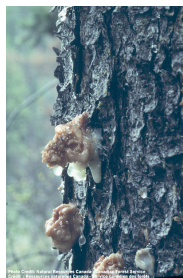
iii) conifer **oleoresin** consists of **diterpene acids** (plus mono- & diterpene volatiles that can disperse)  
 - **constitutive** or **induced**. Typically under pressure so it exudes.  
 - in resin **ducts** or resin **blisters** (i.e., pines, firs)

Oleoresin is the primary defense against **bark beetles** (*Ips*, *Scolytus*, *Dendroctonus*)

- beetle life style and damage to phloem (Mountain pine beetle, *Dendroctonus ponderosae*)
- conifer defense based on **oleoresin** (= *intoxicate, extrude, entrap*)
- roles of oleoresin components (volatiles and diterpene resin acids)
- **mass attack** and **fungal symbiont** (blue stain) contribute to tree death.
- Dead trees for reproduction.

Volatile signals in conifer-beetle interaction

- female beetles attracted to monoterpenes
- **semiochemicals**
  - plant-synthesized beetle attractants (**myrcene** and other monoterpenes)
  - aggregation pheromones (**frontalin** / **exo-brevicomin**) (beetle-synthesized)
  - repellent pheromones (**ipsendiol**, **verbenone**= beetle modified from **myrcene** &  **$\alpha$ -pinene**)



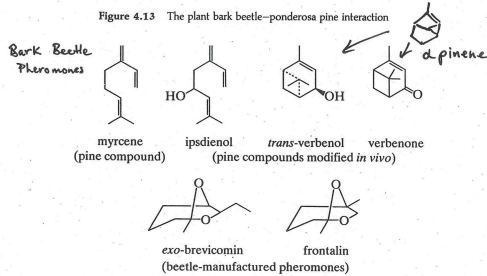
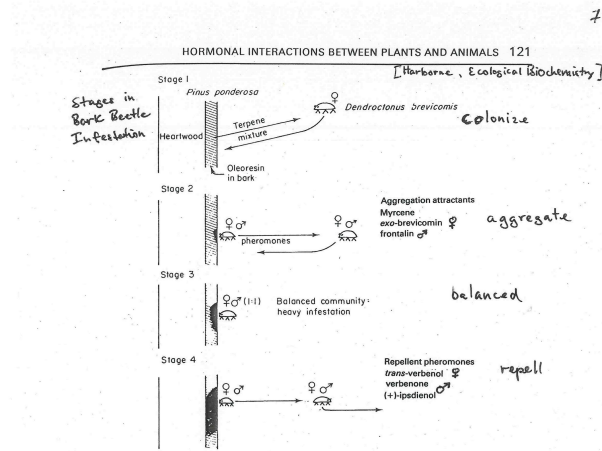
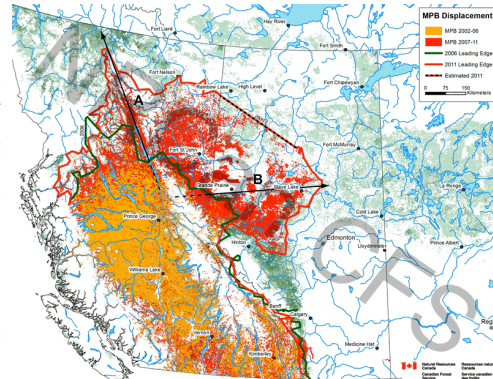


Figure 4.14 Pheromones of the pine bark beetle and their origins



What caused the MPB epidemic in BC? (= massive failure of plant defense?)

- suspected causal factors: host age (older trees), winter weather (climate change)
- host specificity: primarily **lodgepole pine**, but moving to jack pine east of the Rockies (AB)
- Ponderosa pine is attacked (interior BC), Whitebark pine (impact on grizzlies)

### 5. Triterpenes:

Biosynthesis: 2 x FPP = 30 C (*squalene synthase*)

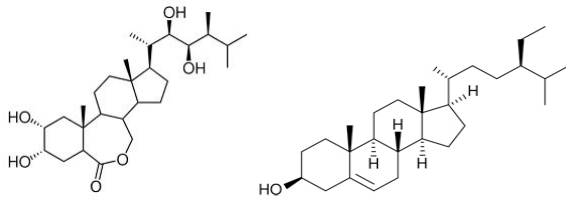
- head to head condensation
- 'wave of cyclization' to close rings

Types of triterpenes: - **sterols** (4 rings, 3' OH)

- other **triterpenes** typically have 5 rings
- **saponins** (glycosylated sterols, **amphipathic**)

**Functions of triterpenes-** primary metabolic roles:

- Plant growth regulators - **brassinolide**, required for **photomorphogenesis (de-etiolation mutants)**
- Phytosterols **campesterol**, **sitosterol** (note branched C-24 chain): structural components in membranes



**Functions of triterpenes** - secondary metabolite roles

iii. Antifeedants, toxins, hormone mimics

**Triterpene-derived toxins**

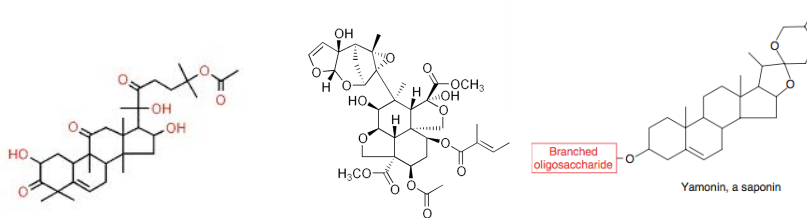
- i) Cucurbitacin from cucumber leaves: most bitter compound known
- ii) Azidarachtin from Neem tree *Azadirachta indica*= "limonoids" (traditional insecticide in India)
  - neem oil contains complex mixtures (up to 100 structures)
  - complex mode of action and effects: anti-feedant, disrupts molting

**Saponins** (glycosylated triterpenes)

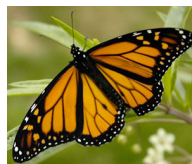
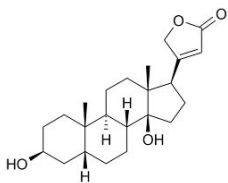
- Hecogenin, Yamonin
- glycosylated with diff sugars (& oligosaccharides)
- lyse cells, toxic, foams (see structure)

**Cardiac glycosides**

- cardiac glycosides (=cardenolines) = a type of saponin, affects cardiac muscle
- extreme toxins (w. medicinal use)
  - i.e.: digitoxin (from *Digitalis*, foxglove)
- > monarch/milkweed/bluejay interaction

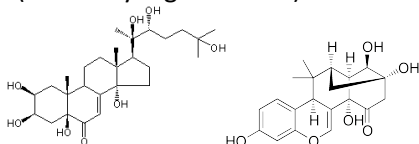


Yamonin, a saponin



**Steroid hormone mimics** (animal steroid-like)

- phytoestrogens: miroestrol from *Pueraria mirifica*
- abortifacant in humans (estrogen activity - traditional knowledge, SE Asia)
- **phytoecdysones**: molting hormone mimics in insects (*Polypodium*, *Taxus* & and other gymnosperms) (relatively high content)



## 6. Tetraterpenes - (Carotenoids)

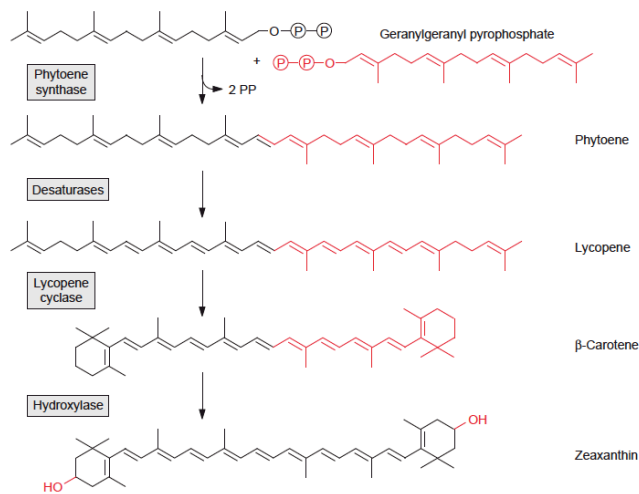
- Recall Biosynthesis: 2 x GGPP = 40 C (*phytoene synthase*)
- subsequent desaturation *desaturases* (-> lycopene)
  - cyclization: *lycopene cyclase* (->  $\beta$ -carotene)
  - hydroxylation *hydroxylase* (-> xanthophyll)

Carotenoid functions:

- accessory pigments for photosynthesis (antennae pigments to help capture light energy)
  - *photoprotection* (oxygen radical scavenger, antioxidant)
  - abscisic acid (ABA) biosynthesis (a sesquiterpene plant growth regulator - drought stress response)
  - color in flowers, leaf, fruit (pepper, tomato)
- xanthophylls* (hydroxylated carotenoids) = yellow color. By contrast, *lycopene* is red

Carotenoid uses for humans and in the diet:

- role in nutrition as anti-oxidant
- spice: Saffron (*Crocus sativus*)
- $\beta$ -carotene is a vitamin A precursor (*retinal*)



Engineering of  $\beta$ -carotene-enhanced food: The story of **Golden Rice**

problem: vitamin A deficiency causes 1-2 million preventable, deaths, blindness.

goal for biotechnology: produce rice with  $\beta$ -carotene (for vitamin A).

strategy: genetic engineering with three genes to be expressed in rice endosperm (*phytoene synthase*, *phytoene desaturase*,  *$\beta$ -carotene cyclase*)

1999 - golden rice produced (1.6 ug) Ingo Potrykos is Time Magazine's Man of the Year.. (great optimism)  
- IP (patents) issues were

2005 - GR2 has boosted carotene content to 37 ug/g, one serving = half of daily requirement

2008 - PR battle still ongoing re: GMO food. Regulatory and legal hurdles because of GM status

S

7. **Polyterpenes:** = high MW isoprenoid polymers (5000-10,000 MW)

- *Hevea brasiliensis* (rubber tree) Euphorbiacia
- latex = milky secretion in vesicles or ducts (often phloem-associated)
- "elastic latex" -> contains rubber particles within the latex

- synthesis: sequential additions of IPP on growing rubber particles

Function of **latex** in plants:

- non-elastic latex can contain alkaloids, other toxins.
- defensive functions of rubber could include wound-sealing
- rubber (*trans* polyisoprene), gutta percha (*cis* polyisoprene)

Industrial applications of plant latex:

- native American discovery of rubber (C. & S. America)
- industrial modifications with S (Goodyear & Firestone)
- some other plants make rubber (*Parthenium argentatum*)

