Terpenoids

- what they are
- how they are made
- major kinds
- plants & their terpenoids -- monoterpenoids
- larger terpenoids

The first big group of compounds = terpenoids

- isolated from turpentine from pine resin
  - "oid" means "like" as in "like turpentine"
- also called isoprenoids
  - produce isoprene at high temperature
  - terpenoids are not made of isoprene
  - misleading name
- backbone is isopentane units
  - 5 carbon
  - not made from isopentane
  - can be combined in different ways
  - many different compounds produced

[24.2]

Some nomenclature

- the basic unit is the terpene
  - 10 C
  - 2 isopentane units
- monoterpenes have 10 C
- diterpenes have 20 C
- triterpenes have 30 C
- sesquiterpenes (1.5) have 15 C
- polyterpenes have lots of terpene units

A little bit of biochemistry to get started

- actually isopentane is not in cells
  - not water soluble
  - too stable to react with anything
  - volatile
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- start with Acetyl CoA [24.4--not on handout]
  - 2 carbons with their hydrogens + oxygen (acetyl) on a CoA carrier
  - 3 of these combine to make mevalonic acid (6-C)
  - too stable to do much chemistry
- mevalonic acid is phosphorylated twice (two steps)
  - this makes it more reactive
  - usual biochemical way to get reactivity
- this is modified to get the basic building block
  - decarboxylated and dehydrated
  - makes IPP
  - \( = \text{isopentenyl diphosphate} \)
- one of the enzymes is also used in cholesterol synthesis
- this all goes on in the cytosol and on the ER
- produces \( n*15-C, n*30-C, \) polyterpenes

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IPP is made a second way

- in plastids
  - pyruvate + gyceraldehyde-3-P (PGA)
  - result is same: IPP

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Elongation

- IPP + IPP = monoterpenes
- monoterpene + IPP = sesquiterpene
- sesquiterpene + IPP = diterpene
- sesquiterpene + sestquiterpene = triterpene
- diterpene + diterpene = tetraterpene
- these are all backbones to be modified

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Further reactions

- cyclization (make into cyclic compound)
- further modifications (lots)
- many enzymes specific to particular kind of terpenoid

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Hemiterpene (5 C) of interest

- plants do emit lots of isoprene
- made in leaves
- light-dependent
- major atmospheric pollutant
- big player in making ozone, using \( \text{NO}_x \)
- role in plant unknown
Monoterpenes of interest (10 C)[24.10]

- flower odors
- "essential" oils in herbs & spices (up to 5% d.w.)
  - limonene a common building block (lemon oil)
  - made into menthol in peppermint
  - made into carvone in spearmint
- essential = "characteristic," not "necessary"
- insecticides
  - monoterpenes ester: pyrethrins (insecticides)
  - alpha-pinene, beta-pinene
    - main constituent of terpentine
    - toxic to bark beetles & their fungi
    - extra made when under attack
- pollinator attractants (1,8-cineole)
- anti-herbivore compounds (camphor, 1,8-cineole) [24.3--not on handout]
- myrcene
  - myrrh -- plant resin
  - incense
  - medicine (mouthwash, antiseptic)
  - perfume
  - one of traditional gifts to Jesus
  - closely related to guggul (lowers cholesterol?)
- monoterpenes lactones (lactone from diterpene)
  - nepatalactone
    - catnip
    - aphid pheremone
- tea tree "oil"
  - antifungal
  - antibiotic
- thujone [thujone structure]
  - in cedar (Thuja), many other plants
  - recall cedar used for storage to keep insects out (cedar chests)
  - actually an anti-plant compound, too (allelopathy)
  - wormwood used in alcoholic drinks
    - absinthe, vermouth (from German "wormwood")
    - problematical due to thujone (at least)
      - neurotoxin
      - addictive, too (bad combination)
      - famous artist in France went crazy
      - fashionable around 1900
      - now outlawed in many countries (substitutes found)
    - has other (medicinal) uses

Now more terpenoids (bigger ones)

- plants & their terpenoids -- above monoterpenoids
- genetic engineering
- second-hand defenses
- detoxifying defense compounds
Sesquiterpenes of interest (15 C)

- essential oils
- phytoalexins
  - antibiotics produced with microbial challenge
  - antifeeding compounds
- juvabione
  - from fir tree
  - insect hormone
- sirenin
  - attracts sperm (as Sirens attract men)
  - from water mold
- artemisin
  - antimalaria
  - traditional Chinese
    - of new interest (much resistance to other drugs)
- gossypol
  - cotton defense compound
  - maybe male contraceptive

Diterpenes of interest

- phytol tail of chlorophyll
- gibberellin hormones (makes plants grow tall)
- resin acids (conifers & legumes) -- make rosin for string players, gymnasts & pitchers
- phytoalexins
- taxol (0.01% d.w.)

Triterpenes of interest (30 C)

- brassinosteroids (hormone present in some plants)
- phytosterols in membranes
- phytoalexins
- liminoids - bitter part of citrus rind (cleaning agent)
- other toxins & feeding deterrents
  - azadirachtin A
    - from neem tree -- insecticidal
- many of these have low toxicity to mammals
- some surface waxes (on grapes)
- ecdysones
  - insect hormones
  - affect molting
- saponins (soap-like) & cardenolides
sugar attached
• toxic to vertebrates
  - saponins may hemolyze blood cells
  - cardenolids overstimulate heart
• includes fish poisons, snail poisons (schistosomiasis control)
• digitoxin from Digitalis used for congestive heart failure
• saponins used as shampoo by native Americans in US Southwest
• licorice (real licorice) -- anti-inflammatory (can be toxic)

Tetraterpenes of interest (40 C)
• carotenoids (several kinds)
• absorbs short wavelength light
  - some energy passed to chlorophyll
  - some energy dissipated, protecting chlorophyll
• humans cleave in half to get Vitamin A
  - important for night vision
  - important for immune system function
  - important for development

Polyterpenes (>40 C)
• plastiquinone & ubiquinone
• rubber (many, many terpenes)

Bits of terpenoids stuck on other things
• vincristine, vinblastine
  - anti-cancer drugs (childhood leukemia)
  - terpenoid fragments in structures
• some proteins have terpenoid bits to anchor them in membranes

Plants usually contain mixtures of terpenoids
• conifers make alpha- and beta- pinene and much more
• cardamon (spice)
  - camphor, pinene, terpinine, eucalyptole
  - many more
• clove (spice)
  - eugenol (< 85% of oil)
  - pinene
  - other terpenoid, and other compounds
• the same compounds occur in many plants
• a particular plant produces multiple compounds
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directly on to more defense