I. Plant biochemical pathways: Primary and Secondary Metabolism

II. Types of Secondary Compounds
   • Terpenes
   • Alkaloids
   • Phenolics

III. Roles in Plant Biology
• **Primary metabolism**: functions essential for life
  – Used in normal cell functioning.
  – Energy storage and release.
  – In general, these compounds are not toxic to predators.
  – Most living things share a common primary biochemistry.
    • Glycolysis, TCA/Krebs cycle, electron transport, ATP as energy currency.

• **Secondary metabolism**: processes that create molecules that are **not** required for the general functioning of the organism, but have more specialized functions
  – Secondary metabolites are highly diverse
  – Compounds involved in plant defenses are typically secondary metabolites; they are often toxic to other organisms
  – Most medicinal/drug compounds are secondary metabolites.
• Products and intermediates from primary metabolism (photosynthesis, respiration) feed into 2° pathways

Calvin cycle intermediate product

glycolysis intermediate product

First step in Calvin cycle

Product of glycolysis

Citric acid cycle intermediate

MEP = methyl erythritol phosphate
• Use radioisotopes to label precursors (1950s)
  – Follow radioactivity to identify sequence of products
• Use plant cell cultures to produce pathway enzymes (1970s)
  – Provides abundant material to isolate, purify, and characterize enzymes
• Use molecular techniques (1990s)
  – Isolate, characterize, and manipulate genes encoding biosynthetic enzymes
Amino acid bioynthesis

- 20 amino acids (a.a) found in proteins.
- 9 essential amino acids in humans

Amino acids are precursors to many secondary (2°) compounds.

Biochemistry and Molecular Biology of Plants; ASPP 2001
Shikimate Pathway: produces 2 essential a.a.

- Produces the essential aromatic amino acids tryptophan, phenylalanine

Tryptophan: precursor in synthesis of auxins (plant hormone)

Phenylalanine: precursor in synthesis of flavonoid pigments

Herbicide Round-Up blocks their synthesis.
- without these a.a., plants die.
Pharmacologically active compounds found in plants are usually secondary metabolites (produced from secondary metabolic pathways)

- Primary and secondary pathways are directly connected
- Secondary metabolites are often derived from precursors made from primary metabolic pathways
- These compounds are only ‘secondary’ in that they are not essential for the basic function of the plant. They are still extremely important.
• **Mevalonic Acid Pathway and MEP (non-mevalonic acid)**
  – *Terpenes*

• **Shikimic Acid Pathway**
  – Produces aromatic amino acids
    • These are precursors for many *alkaloids* and some *phenolics*

• **Malonic Acid Pathway**
  – *Phenolics*
    • More prevalent in fungi and bacteria than in plants
I. Plant biochemical pathways: Primary and Secondary Metabolism

II. Types of Secondary Compounds
   • Terpenes
   • Alkaloids
   • Phenolics
   • Roles in Plant Defense

III. Properties of Water; Water Potential.

IV. Cell Wall

V. Intro to how plants grow: tissues and tissue systems
• Largest class of secondary metabolites
  • 25,000 described

• Some act as primary metabolites for the plant and are necessary for cell function
  – Cell growth modulation, light harvesting, photoprotection, control of membrane fluidity
    • Examples: gibberellins (hormones), carotenoids (pigments), sterols

• Components of “essential oils” (i.e., “essences” of plants... not “necesseties”)
• Numerous applications in medicine.
• Formed from acetyl CoA via mevalonic acid pathway
  – Acetyl CoA is converted into mevalonic acid
• Formed using different intermediates via the MEP pathway
  – This usually occurs in chloroplasts
• Compounds are made based on the isoprene rule
  – Terpenes are built by combining 5 carbon units, creating structures with 10, 15, 20, 30, 40 carbons
    -- Basic unit is 5-Carbon Isoprene

\[
\begin{align*}
\text{CH}_3 \\
\text{H}_2\text{C} & \text{C} & \text{H} \\
\text{CH} & \text{C} & \text{CH}_2
\end{align*}
\]

Isoprene (C\textsubscript{5}H\textsubscript{8})
Types of Terpenoids

- **Monoterpenes** = 10 carbons
- **Sesquiterpenes** = 15 carbons
- **Diterpenoid** = 20 carbons
- **Triterpenoids** = 30 C
- **Tetraterpenoids** = 40 C

All can be broken down into 5-carbon units (isoprene)

*All with Carbon atoms in multiples of 5*
• Structurally, there are linear terpenes and cyclic terpenes
  – Cyclization requires the action of specific enzymes

• Geraniol, non-cyclic terpene
  – Geraniums

• Limonene, cyclic terpene
  – Orange peels

• Both are examples of monoterpenes, containing 10 carbons
• Second largest, most structurally diverse, most medically important group of plant compounds
  – Defined generally as plant compounds containing a nitrogen atom in a ring structure
    • Many have basic chemistry (as opposed to acidic)
    • Many are bitter
    • Morphine was the first alkaloid identified (1806)
    • Over 10,000 different alkaloids are now known.
    • Important defensive molecules in plants.
    • Toxic/repellent effects against many animals.
2-22 Some physiologically active alkaloids (a) Morphine is contained in the milky juice released by slititng the seed pods of the opium poppy (*Papaver somniferum*); (b) cocaine is present in the leaves of the coca plant (*Erythroxylum coca*); (c) coffee (*Coffea*) beans and tea (*Camellia*) leaves contain caffeine; and (d) cultivated tobacco (*Nicotiana tabacum*) plants contain nicotine.
- Specific alkaloids often named for the plant they are first identified in.

- Atropine, from *Atropa belladonna*, the deadly nightshade
- Cocaine, from *Erythroxylum coca*
Classes of alkaloids are named based on the type of ring structure they contain.

Atropine and Cocaine are both Tropane alkaloids.

*All have N atoms incorporated into a ring structure.*
Carbon metabolism process diagram showing the primary and secondary carbon metabolism pathways. The primary metabolism includes photosynthesis, which leads to the formation of carbon compounds like Carbonyl pyruvate, 3-Phosphoglycerate (3-PGA), and Acetyl CoA. The secondary metabolism involves the conversion of these primary metabolites into various secondary products such as Phenolic compounds, Nitrogen-containing secondary products, Aromatic amino acids, Aliphatic amino acids, Shikimic acid pathway, Malonic acid pathway, Mevalonic acid pathway, and MEP pathway. Additional metabolites like Terpenes are also produced.
• Composed of one or more phenol groups with various other groups attached.

• Weakly acidic, simple, aromatic molecules with a hydroxyl group attached to an aromatic ring
  – Sometimes the hydroxyl is ‘lost’ or replaced

• Phenolic compounds account for 40% of organic compounds found in the biosphere

• Many thousands of different natural phenols are known.
• Phenolics are a plant adaptation that allow for survival on land
  – Most phenolic compounds have cell wall structural roles (impermeable, rigid)
  – Provide wood and bark characteristics
  – Roles in flower color, plant taste and odor
    • These are important characteristics for plant reproduction
  – Roles in plant defense
- Lignins and lignans
- Flavonoids
  - Include anthocyanins, isoflavonoids, chalcones, proanthocyanidins
- Coumarins (sweet grass smell)
- Tannins
  - color/taste of tea, wine

Aromatic (smelly) Phenolic Compounds
**Terpenoids**
- Linear or cyclic (often polycyclic)
- Multiples of 5 carbons
- Produced by **Mevalonic acid pathway (MAP)** and **MEP** (non-mevalonic) pathway
- Volatile essential oils, toxic resins, some pigments

**Alkaloids**
- One or more ring structures
- Nitrogen atoms included in the rings
- Produced by several pathways, including **shikimate** pathway, which converts aromatic amino acids into alkaloids.
- Typically toxic to herbivores by a variety of mechanisms.

**Phenolics**
- One or more ring structures
- At least one ring is “aromatic” (has 3 double bonds)
- Extremely stable structures
- Produced via **shikimate** and **malonic acid pathways**.
- Numerous roles in plant reproductive and defensive strategies.
Which is the alkaloid? The terpenoid? The phenolic?

A. \[
\begin{align*}
\text{CH}_3 & \\
\text{C} & \\
\text{H}_3 & \\
\text{C} & \\
\text{CH}_3 & \\
\text{CH}_2 & \\
\text{OH} & \\
\end{align*}
\]

B. \[
\begin{align*}
\text{CH}_3 & \\
\text{C} & \\
\text{H}_3 & \\
\text{C} & \\
\text{CH}_2 & \\
\text{CH}_2 & \\
\end{align*}
\]

C. \[
\begin{align*}
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{N} & \\
\text{O} & \\
\text{CH}_3 & \\
\text{H}_3 & \\
\end{align*}
\]

D. \[
\begin{align*}
\text{O} & \\
\text{H} & \\
\text{O} & \\
\text{CH}_3 & \\
\end{align*}
\]
A. Attract pollinators/fruit dispersers
   • Less reliance on water for fertilization.

B. Direct Defense
   – Defense against herbivores: insects and vertebrates
   – Photosensitive and activated compounds
   – Defense against fungi, bacteria, viruses
   – Instigated insect evolutionary responses

C. Communication
   • plant/plant – cooperative or competitive
   • plant/animal – attract insect predators
Compounds attract pollinators

- Pollinators are attracted by floral shape, **color**, **scent**.

- Pollinators are rewarded with nectar (sugars) or other essential nutrients (amino acids, **volatiles**).

Some flowers are generalist, while others have highly modified forms adapted to specific pollinators.
- Specialist flowers have co-evolved with effective pollinators.

- **Secondary Compounds** (phenolics, terpenoids) involved.
• Flower color and smell is often the product of phenolic compounds like anthocyanins
2° compounds: chemical adaptations for biotic dispersal of seeds

- Attractive colors, scents, rewards (sugars/nutrients)

- Often combined with thick/hard seed coats or other structures to protect embryos from chomping teeth (i.e., the peach pit protects the seed inside)

- Seeds may be dropped away from the parent plant either before or after passing through the animal...

- Seed dispersal is important:
  - removes offspring from competition with parent.
  - potentially introduces plant species to new areas, expands range.
  - plants that disperse widely safer from local extinction?

- Biotic seed dispersal is potentially less random than abiotic.
• Fruits are brightly colored to attract birds or mammals
  – Phenolic pigments (flavonoids, anthocyanins)

• When seeds are developing
  – Fruit is not as palatable and lacks color (= green)
  – Unripe fruit may contain secondary compounds to deter feeding.
  – Change in taste and color (ripening) occur when seeds are ready to be dispersed.

• Fruits may contain compounds that deter insects, but are still edible for birds and mammals
• Cretaceous Period: Dinosaurs have developed strategies to deal with protective plant surfaces
  – Teeth adapted for grinding tough leaves
  – evolved gizzards, swallowed stones to help disrupt plant tissue

• Fraenkel 1959
  – Article in *Science* suggests secondary compounds arose as a means for plant defense
  – As with physical features, we see evolution of many different secondary compounds with defensive roles, as well as convergent evolution of biosynthetic pathways to create similar secondary compounds in different plants.
Plants produce secondary compounds to reduce grazing
- Predators include bacteria, fungi, insects, mammals

Secondary compounds work due to a variety of characteristics
- Bad taste or smell (repellent effect/deterrents)
- Physiological effect (toxins)

Insects, in particular, have co-evolved their own counterdefenses against the plant compounds
• Grazers avoid coca plant (coca) and coffee leaves (caffeine) due to the presence of toxic alkaloid compounds.

• Glycoalkaloids penetrate cell membranes of skin cells on mouth and tongue and break down tissues lining mouth and stomach
  – Sprouted potatoes (*Solanum tuberosum*)
  – Unripe tomatoes (*Lycopersicon esculentum*)
  – Woody nightshade (*Solanum dulcamara*)

• Glucosinolates (2° organic compounds containing nitrogen and sulfur) give some vegetables (cabbage, brussels sprouts) their strong flavor.
Glycoalkaloids = alkaloid with sugar molecules attached.

- Produced in tubers when exposed to light – natural defense against herbivores. Chlorophyll content also increases (=> greening of the potato), but bitter taste indicates solanine buildup.

- Disrupts cellular ion balance, leads to cell death. Symptoms include vomiting, diarrhea in vertebrates.
• *Solanum tuberosum*: the potato

• In addition to alkaloid production, leaves damaged by insects increase their production of protease inhibitors
  – These disrupt the insect’s digestion and development

• Damaged leaves also send chemical messages to other leaves and ‘tell them’ to do the same
Plants emit volatile terpenes that attract the herbivore’s enemies

Zea mays (maize) is damaged by butterfly larvae

1. Plant emits terpenes that attract parasitic wasps
2. Wasps lay eggs on larvae
3. Only occurs when plant is damaged by larvae

• Milkweed contains toxic cardiac glycosides (terpenes)
• Monarch butterfly larvae eat milkweed leaves and store toxins
• After metamorphosis, the monarch butterflies contain toxins and are unpalatable to birds
- Birds that eat monarch butterflies become violently ill.
- Young birds quickly learn to recognize Monarchs, and won’t eat them.
• Viceroy butterfly mimics the Monarch butterfly

• Birds avoid the viceroy even though it does not contain terpenoid cardiac glycosides