Chemosystematics

... pigments, volatiles, and nasty compounds ...
Chemosystematics

= molecular systematics using secondary compounds or micromolecules

Later deal with macromolecules using DNA (and proteins) - although APG classification system is inherently DNA based
Why not use just the diversity of morphological characters to determine the phylogeny or relationships of plants and base classification on this information?
Chemosystematics

1. Unequal rates of morphological divergence in different lineages

- **faboid** (beans, peas) and **mimisoid** (acacia, mimosa) legumes are highly modified
- but descended from the common ancestor of **caesalpinoids**
2. Issues of homology and analogy - character divergence and convergence

- Cacti and spurges show independent origins of swollen and green barrel stems in arid regions

**Barrel cactus**
Cactaceae - American

**Barrel spurge**
Euphorbiaceae - African
2. Issues of homology and analogy - character divergence and convergence

- Cacti and spurges also show independent origins of columnar leafless stems in arid regions
- which is which?
Chemosystematics

2. Issues of homology and analogy - character divergence and convergence
   - evolution predicts descendants of a common ancestor will share homologous features but show divergence through time in these features
   - forelimb of vertebrates composed of homologous bones but modified under different selective pressures
Chemosystematics

3. These problems avoided with molecular systematics or are they? - are there new problems?

will examine plant pigments, volatiles, and nasty toxins

1. how have they been used?

2. what systematic accomplishments result?

3. what problems arise?
Plant Pigments

Nature is predominately green due to **chlorophyll** pigments which absorb in red and blue wavelengths.
Plant Pigments

It is plants or plant parts which are in bright contrast to this green that attract humans and animals.

- pollination
- seed dispersal
- warning coloration
Plant Pigments

Will examine non-green pigments, although chlorophylls and others important at the deepest levels in tree of life.
Plant Pigments

In spite of infinite variety of plant pigments, why have they been used in systematics only during last 60 years?

1. Pigments often unstable - dried in herbarium specimens or even extracted fresh
Plant Pigments

In spite of infinite variety of plant pigments, why have they been used in systematics only during last 60 years?

2. Environmental variation - pH, elevation, UV modifies blue colors

Campanula - bellflower

Cirsium - thistle
Plant Pigments

In spite of infinite variety of plant pigments, why have they been used in systematics only during last 60 years?

3. Chemical mimicry – convergence in pigments

e.g., yellow color within sunflower rays due to two different classes of pigments

- more on this later
Plant Pigments

5 main types of pigments

1. Anthocyanins
2. Yellow flavonoids
3. Colorless flavonoids
4. Betalains
5. Carotenoids

First 3 are flavonoids and unrelated to the others
Plant Pigments

Flavonoids most important source of non-green coloration

Benzene rings structure with side chains = infinite variety

• important in yellow flowers
Plant Pigments

Flavonoids most important source of non-green coloration

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- important in yellow flowers
- important in blue flowers
- important in white flowers
Plant Pigments

Flavonoids most important source of non-green coloration

Benzene rings structure with side chains = infinite variety

- important in yellow flowers
- important in blue flowers
- important in white flowers
- important in “black” flowers

*Lisianthus nigrescens*
Plant Pigments

25% corolla dry weight is delphinidin-3-O-rhamnol(1-6)galactoside and its 5-O-glucoside

- important in “black” flowers

*Photos: Rob Nichols

*Lisianthius nigrescens*
Plant Pigments

Flavonoids are the most important source of non-green coloration. Benzene rings structure with side chains are UV absorbing. Flavonoids appear dark to UV viewing insects - nectar guides!

Flavonol: Phenolic compounds composed of three benzene rings with hydroxyl (OH) groups. Without sugar, the molecule is called an aglycone.

Morning glory: normal and UV views.

Flavonoids appear dark to UV viewing insects - nectar guides!
Plant Pigments

1. Anthocyanin flavonoids

• most important and widespread group of coloring matter in plants

• found in almost all families of angiosperms

• replaced by betalains in all families of a lineage within Caryophyllales (except Caryophyllaceae + Molluginaceae)
2. **Yellow flavonoids**

- 20+ families in distribution
- Give yellow color to flowers (in part); also found in leaves but masked
- Works in conjunction with yellow carotenoids - chemical mimicry
Plant Pigments

2. Yellow flavonoids

- **black-eyed Susan - normal light**
  - yellow flavonoids
  - UV absorbing

- **- UV colorized**
  - yellow carotenoids
  - UV reflecting

- **- UV black/white: closer to how UV-sensitive insects view in this range of spectrum - bull’s eye**

http://www.naturfotograf.com/UV_flowers_list.html
### Plant Pigments

2. **Yellow flavonoids** - utility in classification of Gesneriaceae

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African violet family
## Plant Pigments

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## Plant Pigments

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**Biogeography, not gynoecium, consistent with chemical signal + later DNA evidence**
Plant Pigments

3. Colorless flavonoids

- most important secondary compound in systematics
- contributes to “body” or expression of anthocyanins

• absorbs strongly in UV - thus detectable with gas/gel/paper chromatography, MS
Plant Pigments

3. Colorless flavonoids

- spot leaf/flower extract (methanol) in one corner
- aqueous acetic acid diffuses (with flavonoids) through paper in 1-D

- absorbs strongly in UV - thus detectable with gas/ gel/paper chromatography, MS
Plant Pigments

3. Colorless flavonoids

- **Spot** leaf/flower extract (methanol) in one corner
- **Aqueous acetic acid** diffuses (with flavonoids) through paper in 1-D
- **Non-polar solution** diffuses through gel/paper in 2-D

- **Absorbs strongly in UV** - thus detectable with gas/ gel/ paper chromatography, MS
Plant Pigments

3. **Colorless flavonoids**

- **2-D spot pattern specific for each flavonoid**
- **related species have similar although different spot patterns**

• absorbs strongly in UV - thus detectable with gas/ gel/ paper chromatography, MS
Plant Pigments

3. Colorless flavonoids - systematic utility

- Is *Physalis lanceolata* (ground cherry) a hybrid between *P. heterophylla* + *P. virginianum*?

- No! - not additive pattern
Plant Pigments

4. Betalains - named after *Beta* (beet)

- structurally different from flavonoids - N containing red/violets yellow/oranges
4. **Betalains** - named after *Beta* (beets)

- found only in families of “core” Caryophyllales (beets, cacti, pokeweeds, amaranths)

- **anthocyanins** and not betalains found in Caryophyllaceae + Molluginaceae
Plant Pigments

4. Betalains - systematic conundrum

• explaining the presence of betalains in most, but not all, families of Caryophyllales has been a heated debate

• bigger issue: “do you trust chemosystematic data?”

• scenario #3 supported based on DNA/biochemical evidence today
Plant Pigments

Samuel Lopez-Nieves & Hiroshi Maeda, 2017
Volatile Compounds

Smell, like green pigments, is ever pervasive in nature and in song . . .

parsley

thyme

sage

rosemary
Volatile Compounds

Volatile compounds often restricted to families, genera, or even species - Simon and Garfunkel were chemotaxonomists!

Animals, in turn, are attracted or repulsed by the odors

- parsley
- sage
- thyme
- rosemary

families Lamiaceae and Apiaceae
Volatile Compounds

Classical taxonomists used plant odors consciously or unconsciously in classifying plants into groups.

- Pinaceae - conifers
- Lamiaceae - mints
- Apiaceae - carrots
Volatile Compounds

Linnaeus’ “Sensual System” of classification

1. Aromatic
2. Fragrant
3. Musk-like
4. Garlic-like
5. Goat-like
6. Foul
7. Nauseating

Camellia - fragrant
Volatile Compounds

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Stapelia – goat-like

“flore pulchre fimbriato”
“odor hircinus aphrodisiacus lascivus”
Volatile Compounds

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1. Aromatic
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Amorphophallus - nauseating
Volatile Compounds

Six major volatile groups

1. Terpenes - pinenes, menthol, catnip
2. Aliphatic oils - *Magnolia*, amyl acetate
3. Aromatics - wintergreen
4. Aminoid (N) - offensive, Aristolochiaceae, Araceae
5. Sulphides (S) - onions
6. Glucosinolates (S) - mustard

Aliphatic oil pheromone in orchids
Volatile Compounds

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The Mustard Oil Story

Glucosinolates → Isothiocyanates or mustard oils

- Anti-herbivore defense - except Pieridae (cabbage) butterflies

- Pierids show great radiation

Garden nasturtium - mustard oil family
The Mustard Oil Story

Systematic issue: 15 different looking families share mustard oils - are they related?
The Mustard Oil Story

Systematic issue: 15 different looking families share mustard oils - are they related?

Dalhgren - yes!

- mustard oil character evolved once (or twice)
- Capparales (Brassicales) order
- Drypetes (Euphorbiaceae)?
The Mustard Oil Story

Systematic issue: 15 different looking families share mustard oils - are they related?

Cronquist - no!
The Mustard Oil Story

Systematic issue: 15 different looking families share mustard oils - are they related?

DNA: Two origins!
14 in Brassicales & 1 in Malpighiales

Read Edger et al. 2015

one (of several) events that escalated the butterfly-plant chemical arms race?