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

Chemosystematics

Why not use just the diversity of morphological characters to determine the phylogeny or relationships of plants and base classification on this information?

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

- Cacti and spurges also show independent origins of columnar leafless stems in arid regions

- Which is which?

3. These problems avoided with molecular systematics

will examine plant pigments, volatiles, and nasty toxins

1. How have they been used?
2. What systematic accomplishments result?
3. What problems arise?

- 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
Plant Pigments

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

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.

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

3. Chemical mimicry – convergence in pigments

e.g., yellow color within sunflower rays due to two different classes of pigments
- more on this later

5 main types of pigments

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

Flavonoids most important source of non-green coloration

Benzene rings structure with side chains = infinite variety

- important in yellow flowers

Flavonoids:
- Phenolic compounds composed of three benzene rings with hydroxyl side groups.

- Important in dyes, as antioxidants, in plants.
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

Lisianthus nigrescens

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

2. Yellow flavonoids - utility in classification of Gesneriaceae

- black-eyed Susan - normal light
- - UV colorized
- - 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

<table>
<thead>
<tr>
<th>Subf.</th>
<th>Ovary position</th>
<th>Distribution</th>
<th>Pigments</th>
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<tbody>
<tr>
<td>Gesnerioideae</td>
<td>Inferior</td>
<td>New World</td>
<td>Yellow flavonoids + carotenoids</td>
</tr>
<tr>
<td>Cyrtandroideae</td>
<td>Superior</td>
<td>Old World</td>
<td>Carotenoids only</td>
</tr>
</tbody>
</table>

Columnea Superior New World Yellow flavonoids + carotenoids

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

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

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Plant Pigments

3. Colorless flavonoids

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

- 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

Plant Pigments

3. Colorless flavonoids

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

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

Physalis colorless flavonoids
Plant Pigments

4. Betalains - named after *Beta* (beet)
- found only in families of “core” Caryophyllales (beets, cacti, pokeweeds, amaranths)
- anthocyanins and not betalains found in Caryophyllaceae + Molluginaceae

“core” Caryophyllales

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

Volatile Compounds

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

thyme

rosemary

sage
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.

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

- Pinaceae - conifers
- Lamiaceae - mints
- Apiaceae - carrots

Linnaeus’ “Sensual System” of classification

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

Camellia - fragrant

Stapelia – goat-like
“flore pulchre fimbriato”
“odor hircinus aphrodisiacus lascivus”
Volatile Compounds

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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

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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?
Dalhgren - yes!
• mustard oil character evolved once (or twice)
• Capparales (Brassicales) order
• Drypetes (Euphorbiaceae) ?

Cronquist - no!

The Mustard Oil Story

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

Cronquist’s distribution of mustard oil families
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?