Chemosystematics

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

Chemosystematics

= molecular systematics using secondary compounds or micromolecules

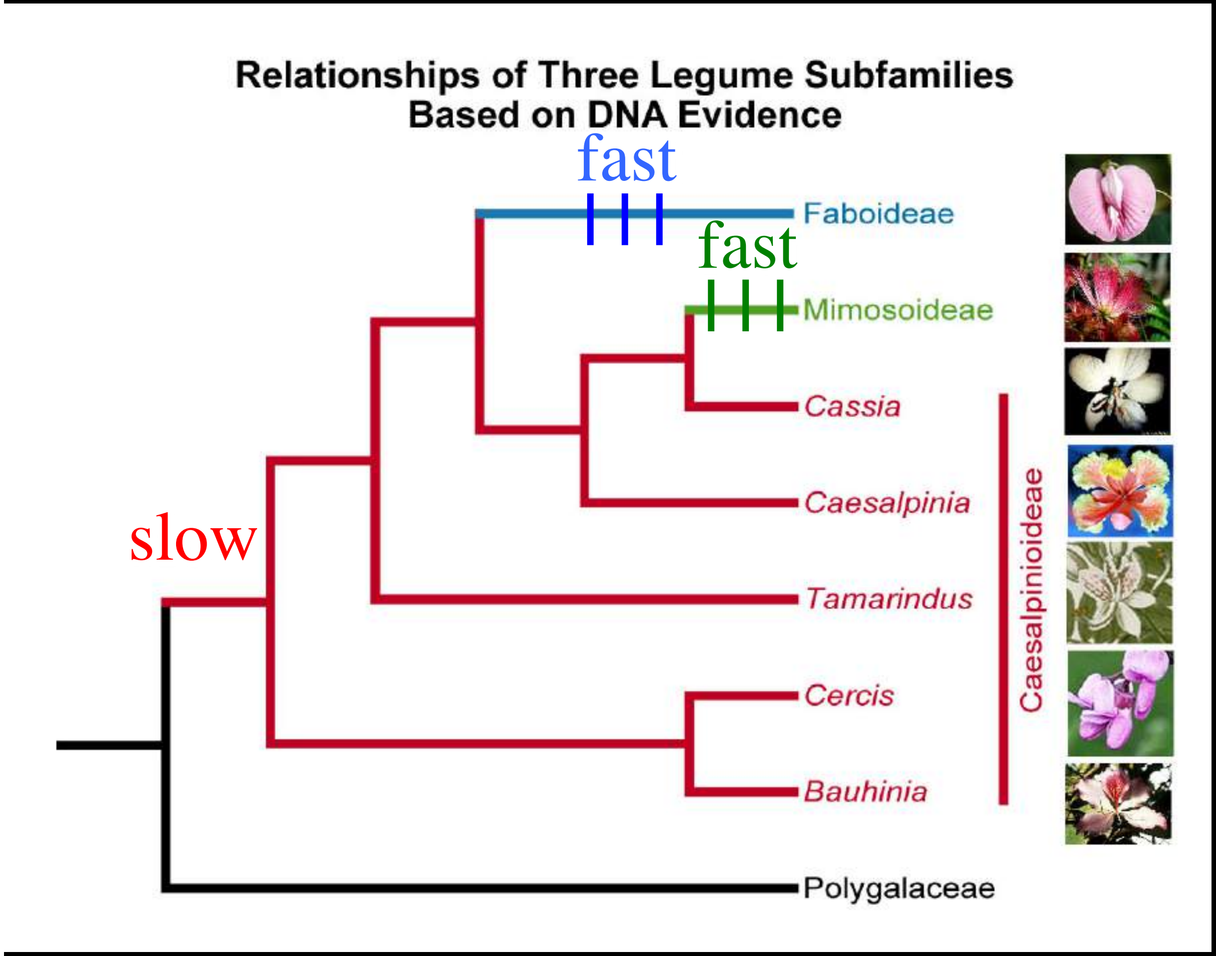
Later deal with macromolecules using DNA (and proteins) - although APG classification system is inherently DNA based

Chemosystematics

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

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

Chemosystematics

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

Chemosystematics

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?

Euphorbiaceae

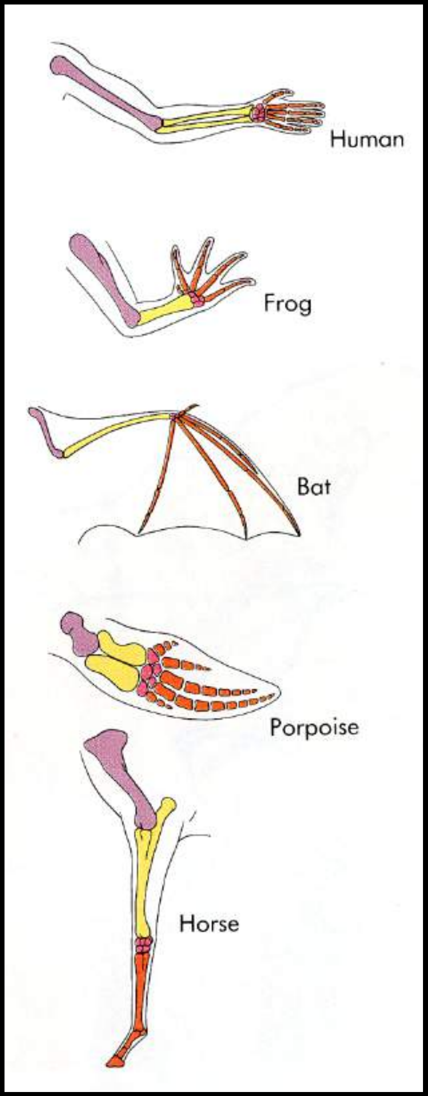
Cactaceae

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



grasping

leaping

flying

swimming

running

Chemosystematics

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

will examine plant pigments, volatiles, and nasty toxins

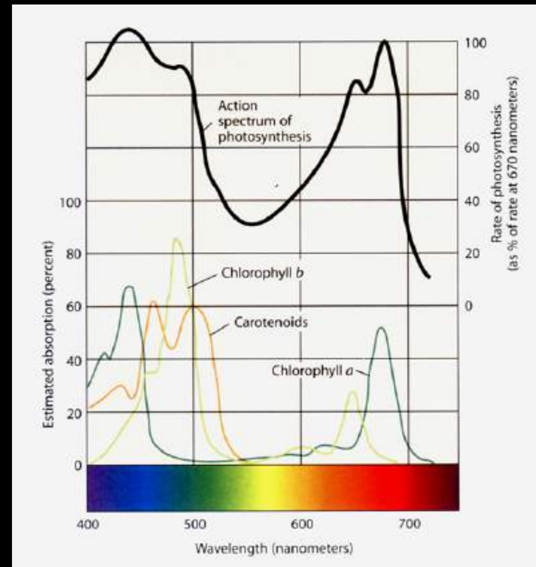
1. how have they been used?

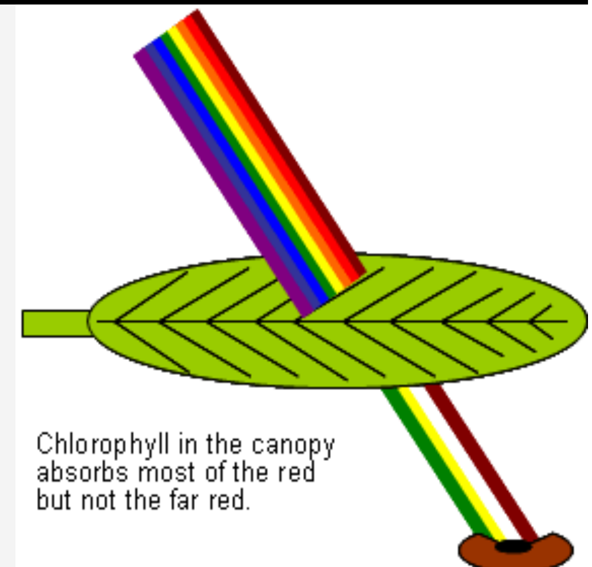
2. what systematic accomplishments result?

3. what problems arise?

Plant Pigments

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





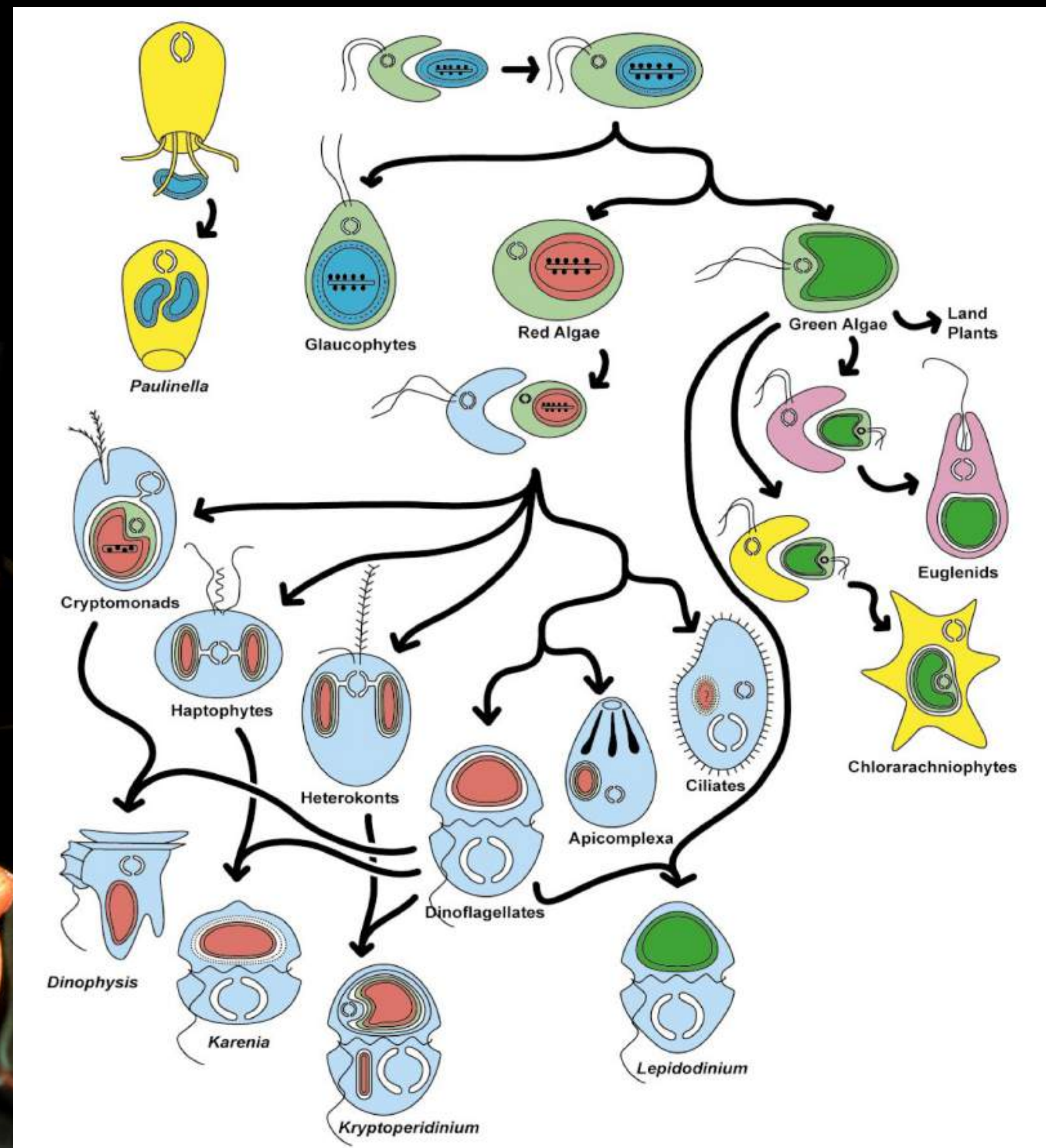
Plant Pigments

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

sunflower

Plant Pigments

5 main types of pigments

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

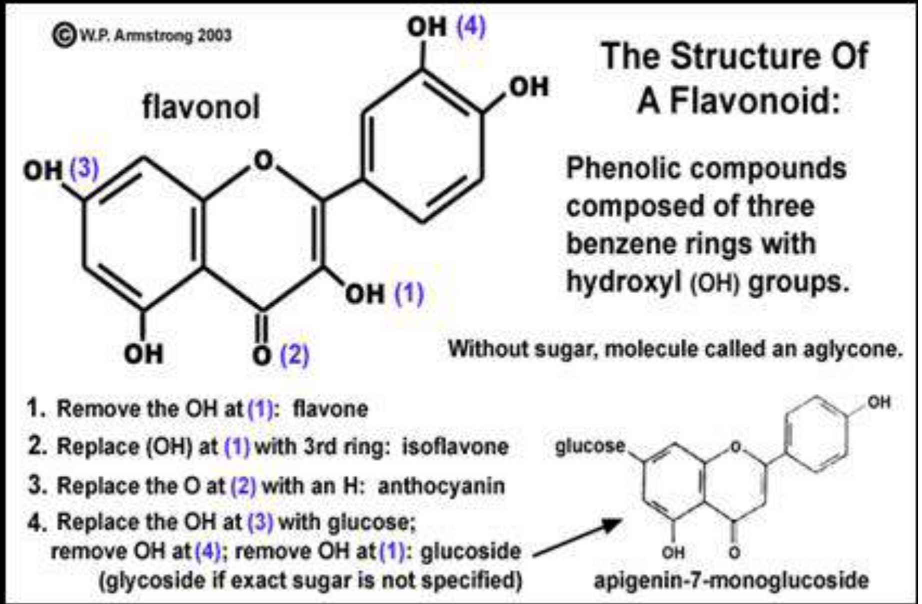
First 3 are flavonoids and unrelated to the others

Plant Pigments

Flavonoids most important source of non-green coloration

Benzene rings structure with side chains = infinite variety

- important in yellow flowers




sunflower

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

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

Lisianthius nigrescens

Plant Pigments

Photos: Rob Nichols

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

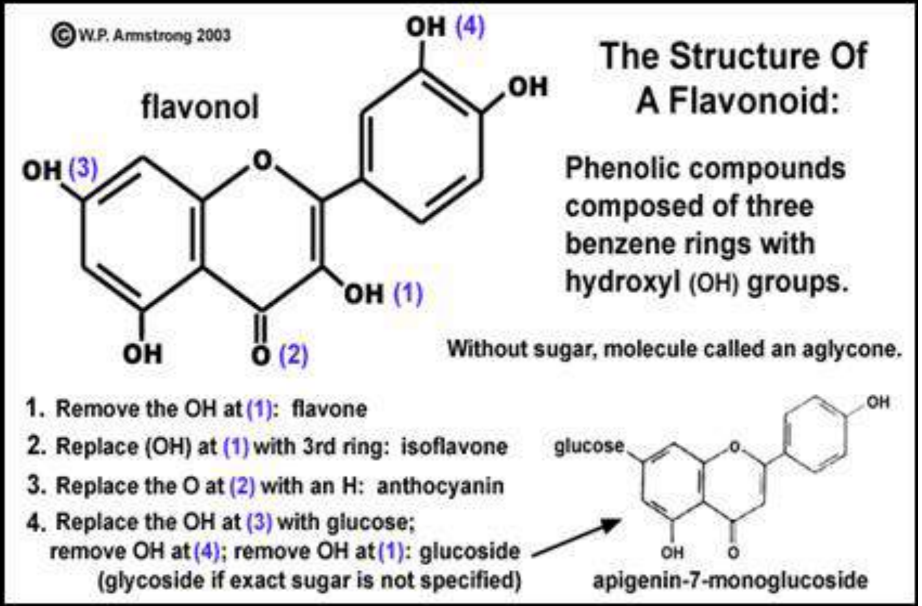
- important in "**black**" flowers

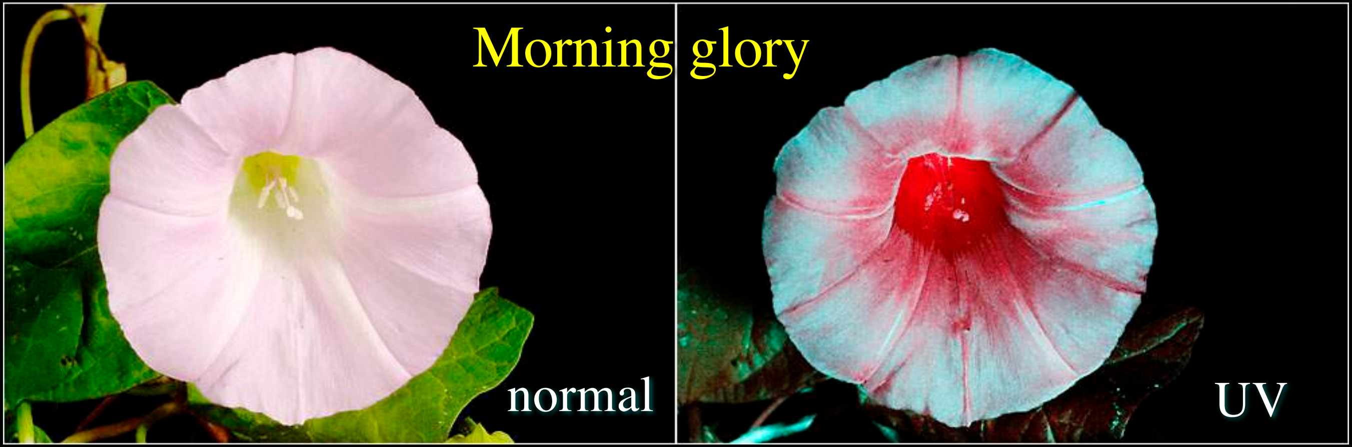
Lisianthius nigrescens

Plant Pigments

Flavonoids most important source of non-green coloration

Benzene rings structure with side chains = UV absorbing





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)

Plant Pigments

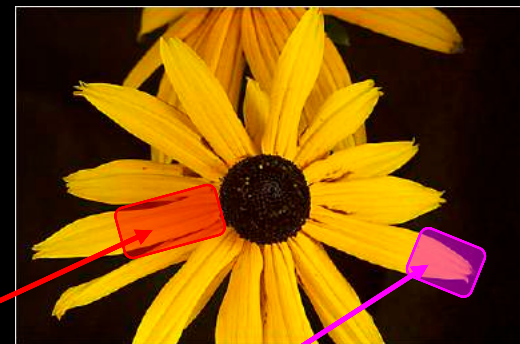
2. Yellow flavonoids

- 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

African violet family

	Ovary position	Distribution	Pigments
Subf. Gesnerioideae	Inferior	New World	Yellow flavonoids + carotenoids
Subf. Cyrtandroideae	Superior	Old World	Carotenoids only

Plant Pigments

2. Yellow flavonoids - utility in classification of Gesneriaceae

African violet family

	Ovary position	Distribution	Pigments
Subf. Gesnerioideae	Inferior	New World	Yellow flavonoids + carotenoids
Subf. Cyrtandroideae	Superior	Old World	Carotenoids only
Columnea	Superior	New World	?

Plant Pigments

2. Yellow flavonoids - utility in classification of Gesneriaceae

African violet family

	Ovary position	Distribution	Pigments
Subf. Gesnerioideae	Inferior	New World	Yellow flavonoids + carotenoids
Subf. Cyrtandroideae	Superior	Old World	Carotenoids only
Columnea	Superior	New World	Yellow flavonoids + carotenoids

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

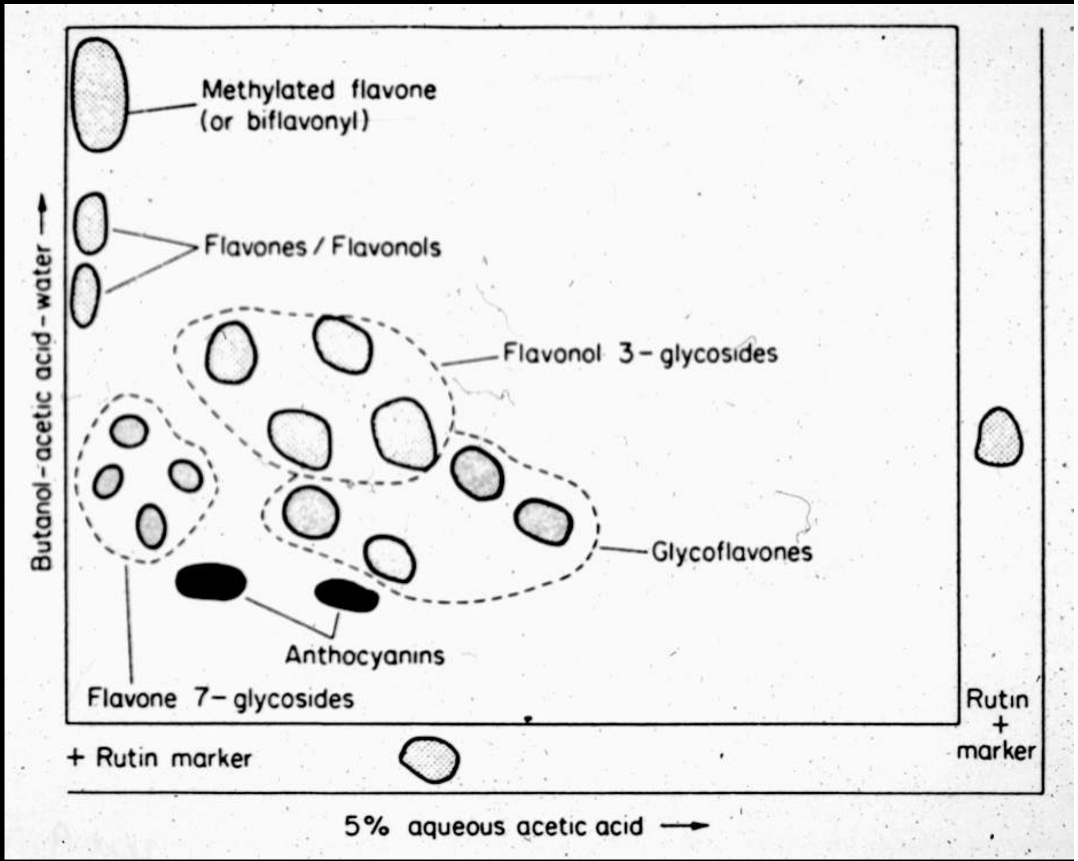
Plant Pigments

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

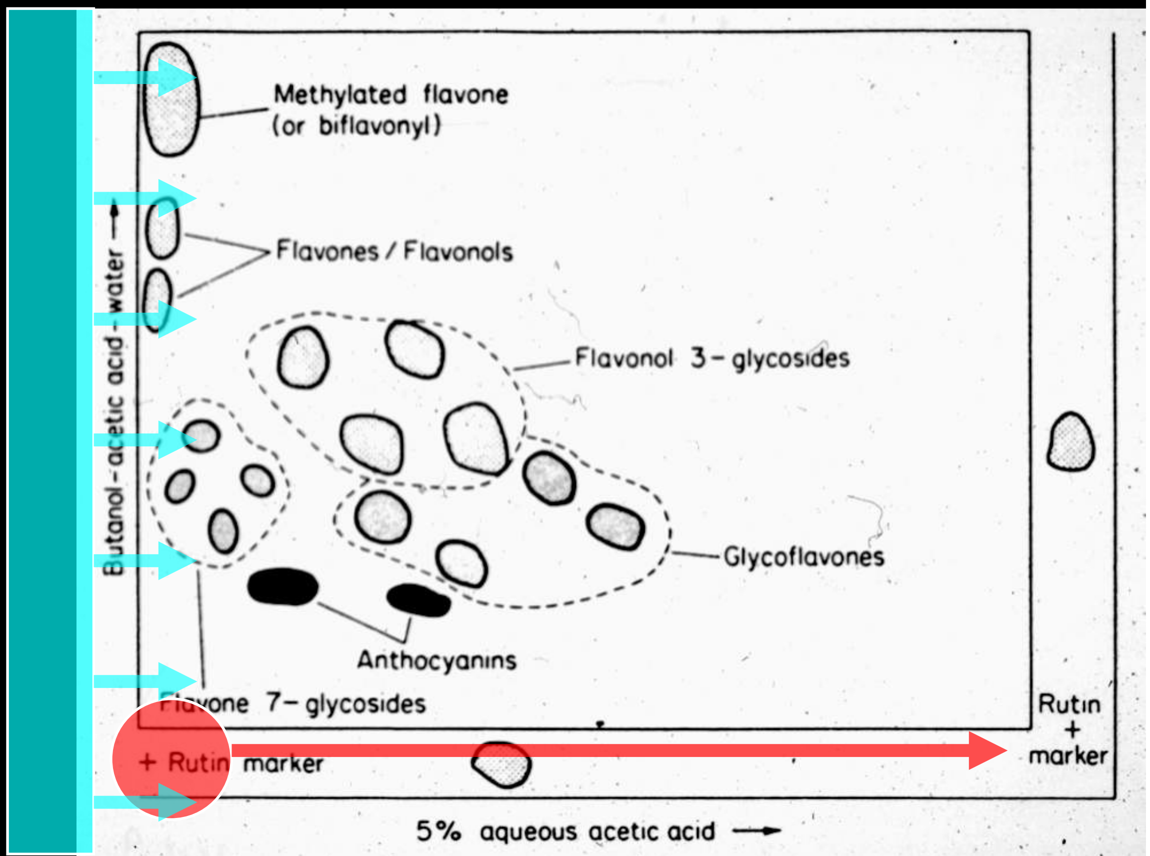


Plant Pigments

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

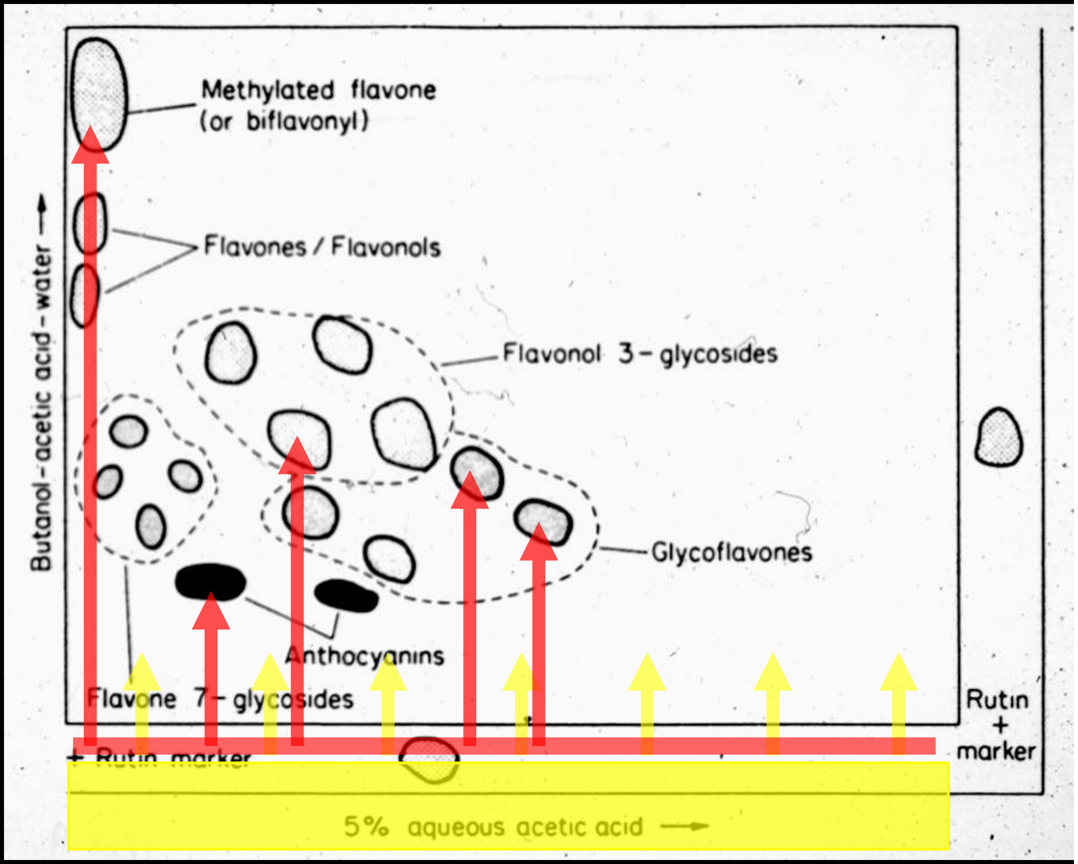
3. Colorless flavonoids

• 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



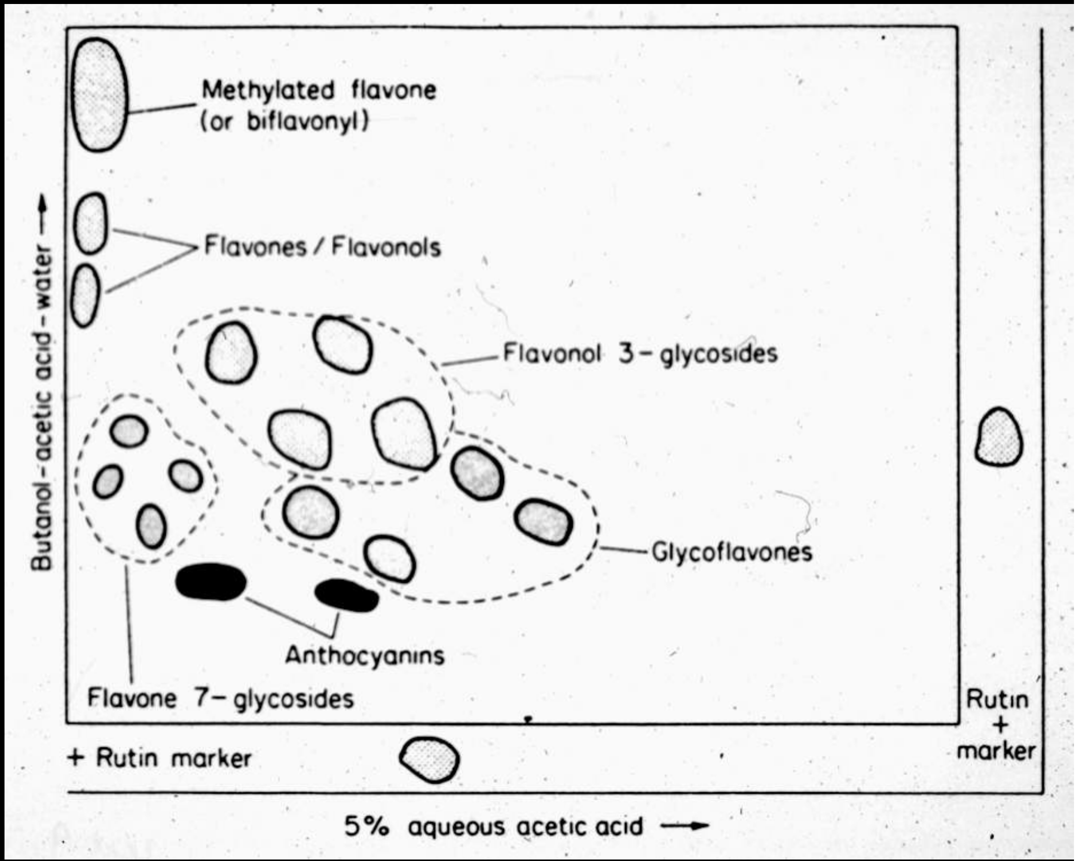
Plant Pigments

3. Colorless flavonoids

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

• 2-D spot pattern specific for each flavonoid

• related species have similar although different spot patterns

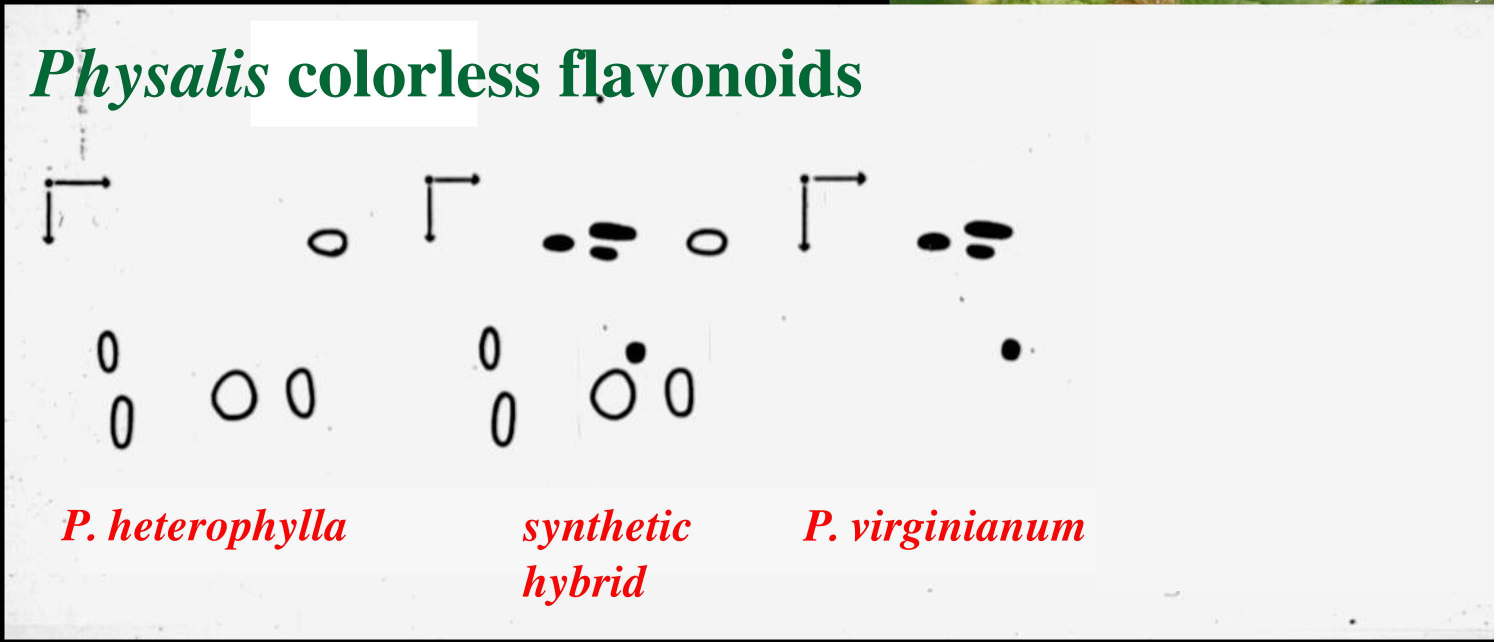


Plant Pigments

3. Colorless flavonoids - systematic utility

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

- No! - not additive pattern



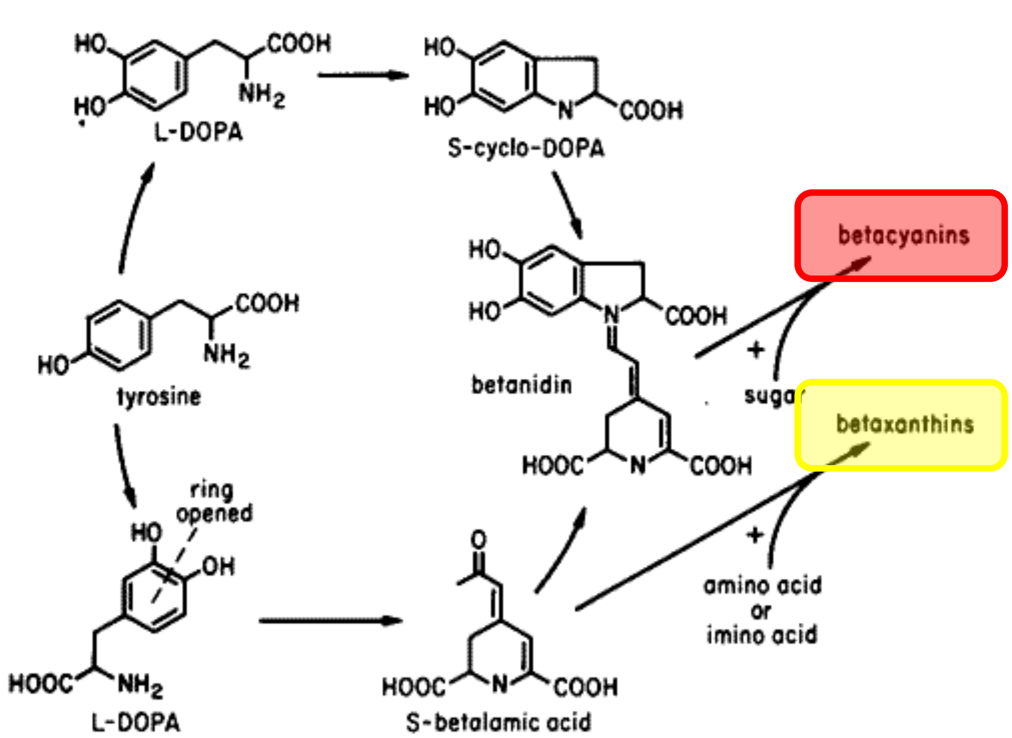
Plant Pigments

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

- structurally different from flavonoids - N containing

red/violets

yellow/oranges

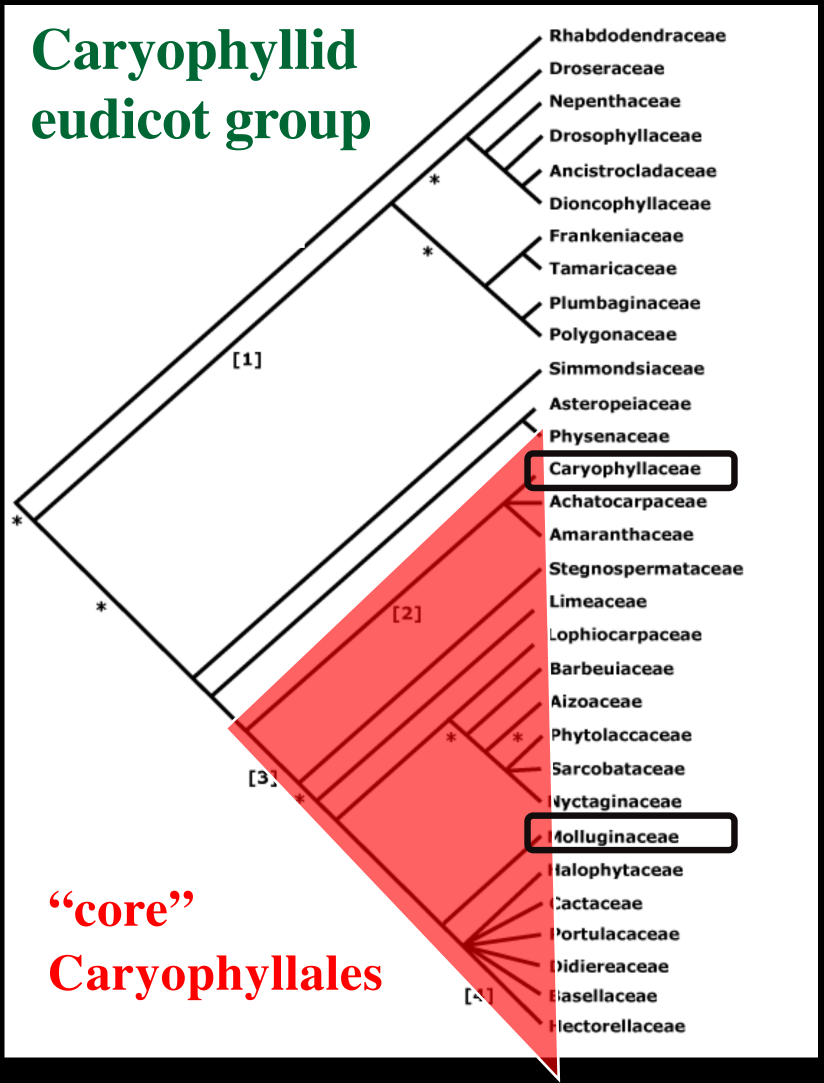


Plant Pigments

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



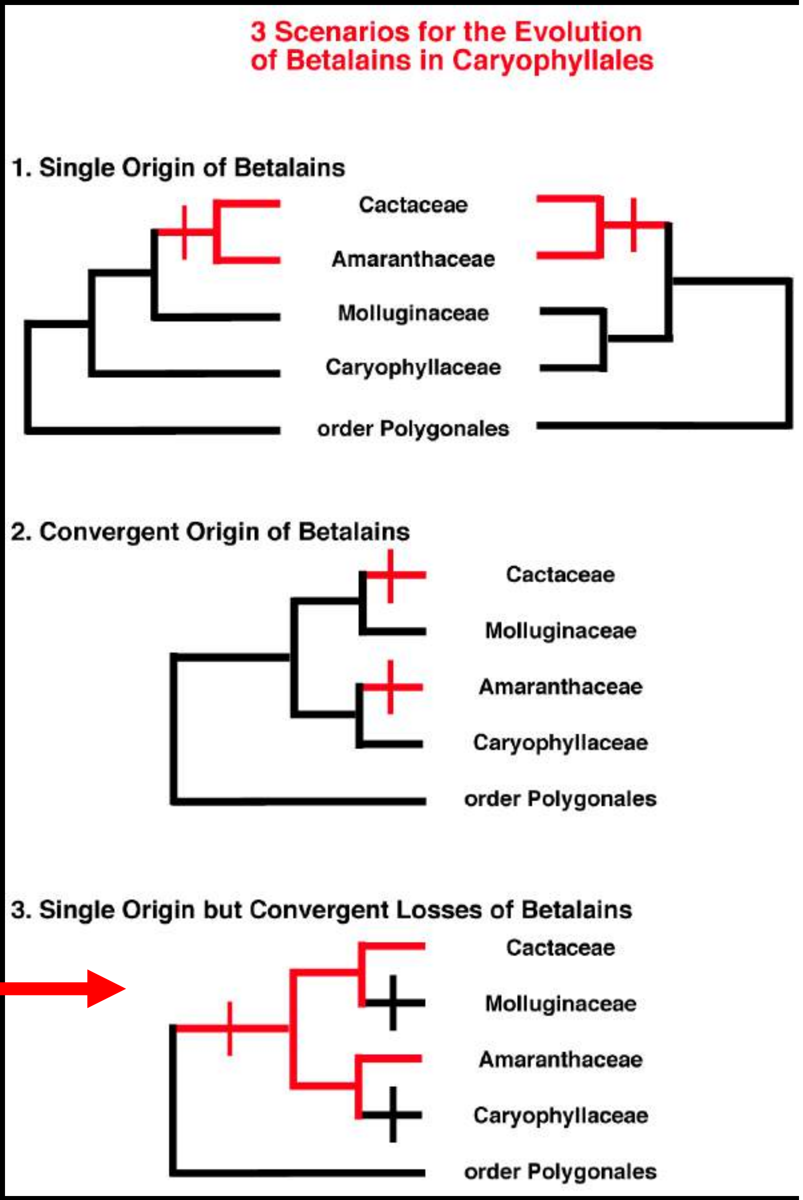
Plant Pigments

4. Betalains - systematic conundrum

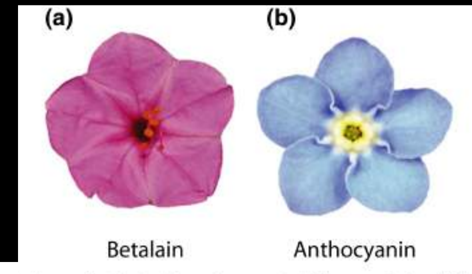
- explaining the presence of betalains in most, but not all, families of Caryophyllales has been a heated debate

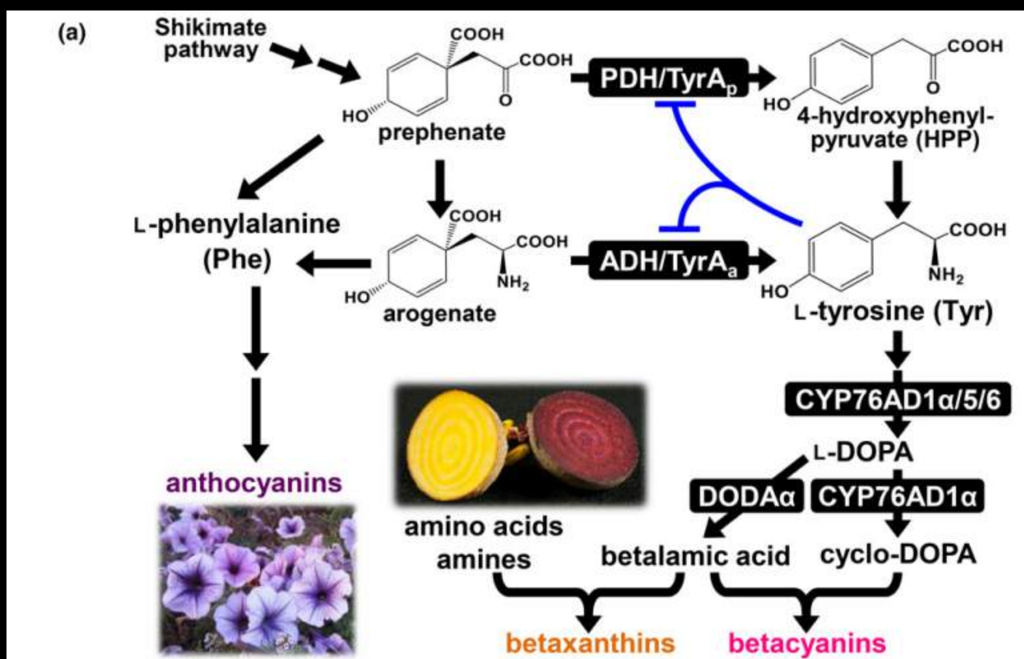
- bigger issue: "do you trust chemosystematic data?"

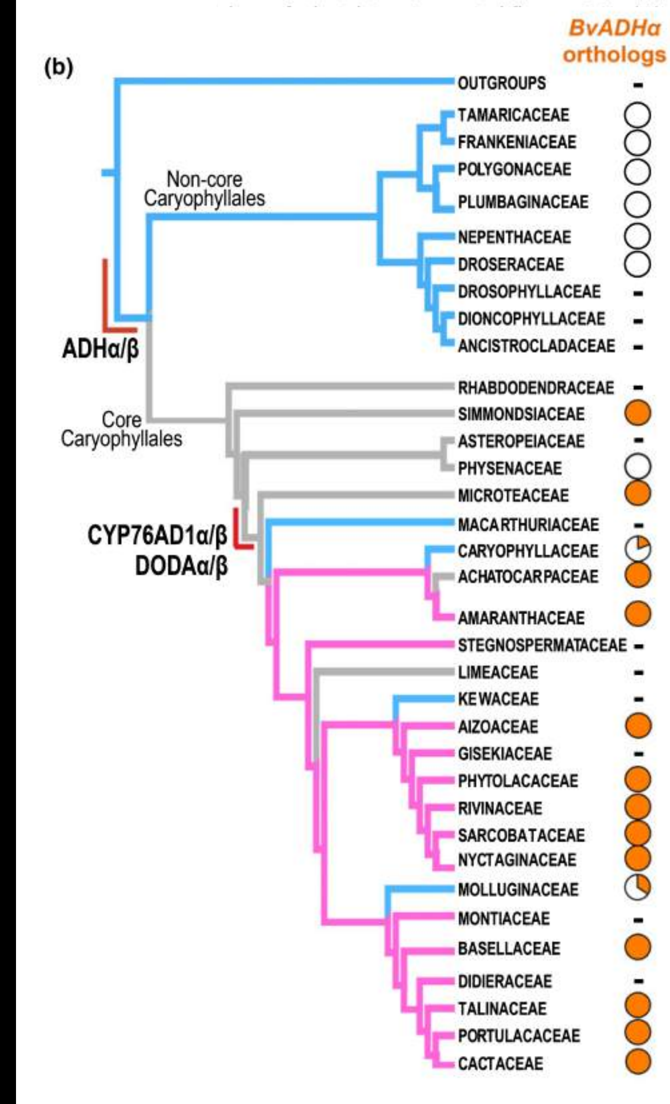
- scenario #3 supported based on DNA/biochemical evidence today



Plant Pigments







Samuel Lopez-Nieves & Hiroshi Maeda, 2017

Volatile Compounds

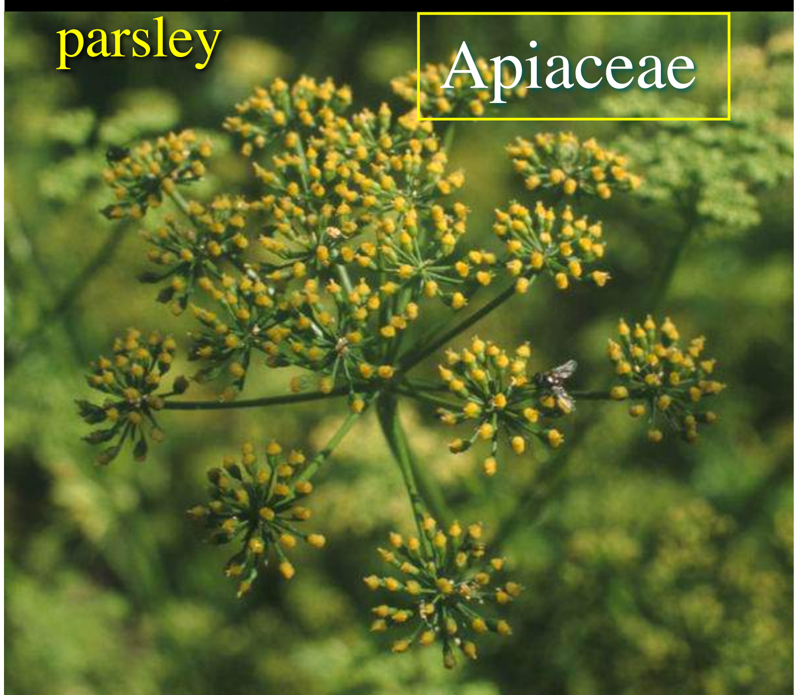
Smell, like green pigments, is ever pervasive in nature

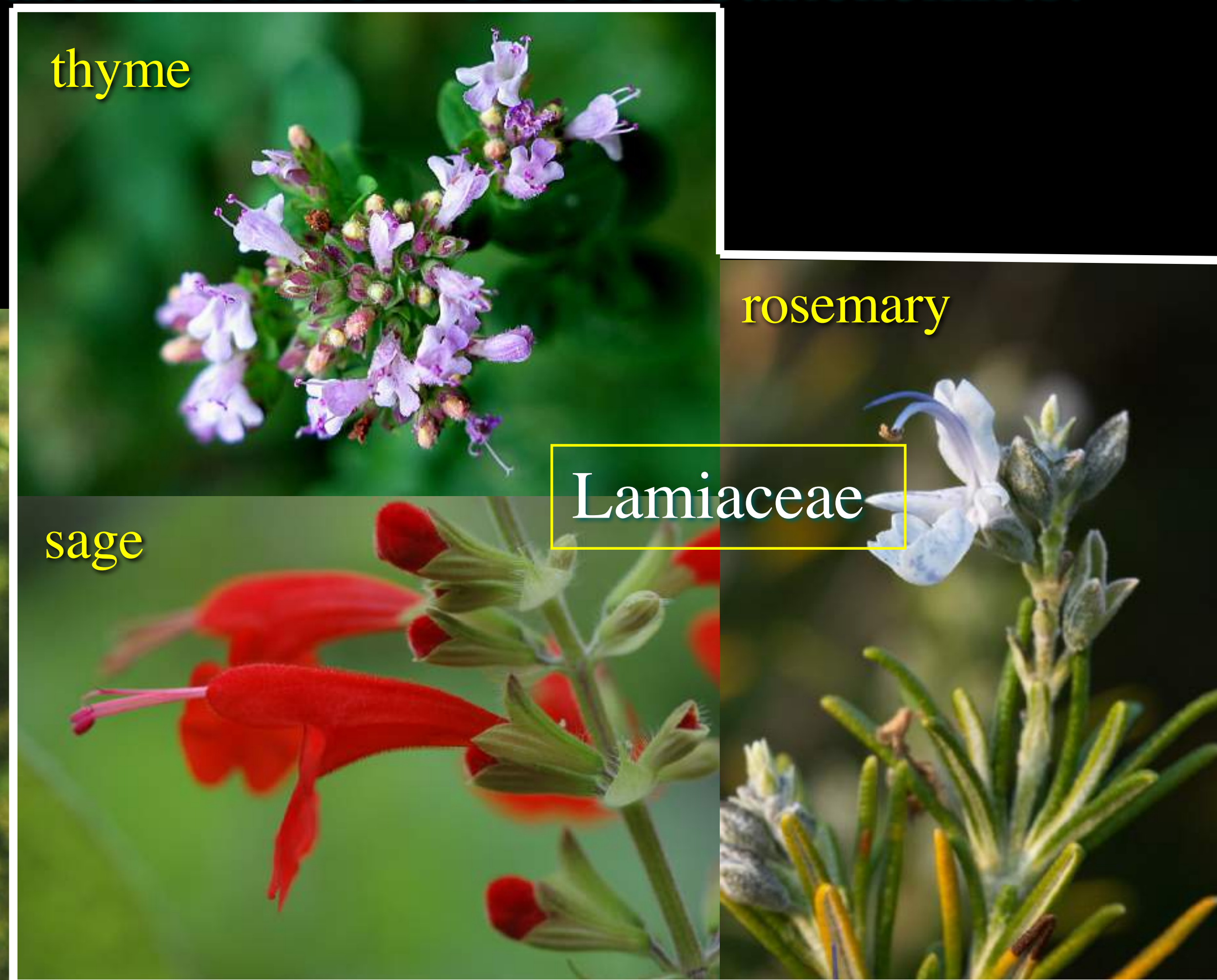
and in song . . .

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

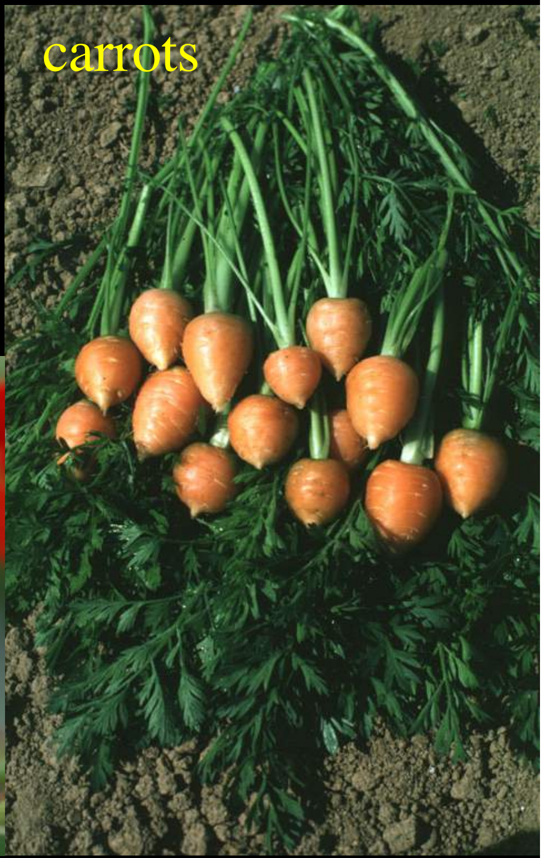




Volatile Compounds

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

Linnaeus' "Sensual System" of classification

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

Stapelia – goat-like

"flore pulchre fimbriato"
"odor hircinus aphrodisiacus lascivus "

Volatile Compounds

Linnaeus' "Sensual System" of classification

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

'Big Bucky'

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

Six major volatile groups

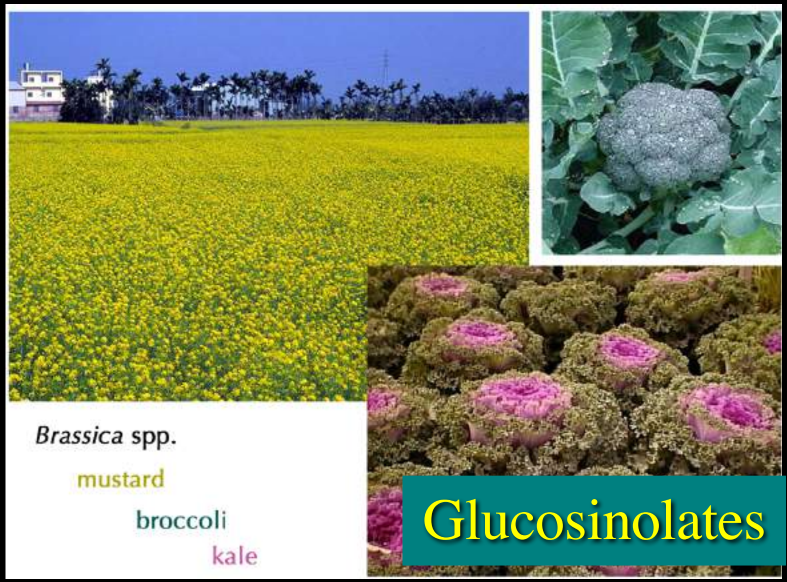
1. Terpenes - pinenes, menthol, catnip
2. Aliphatic oils - *Magnolia*, amyl acetate
3. Aromatics - wintergreen
4. Aminoid (N) - offensive, Aristolochiaceae, Araceae
5. Sulphides (S) - onions
6. Glucosinolates (S) - mustard

Aminoid

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



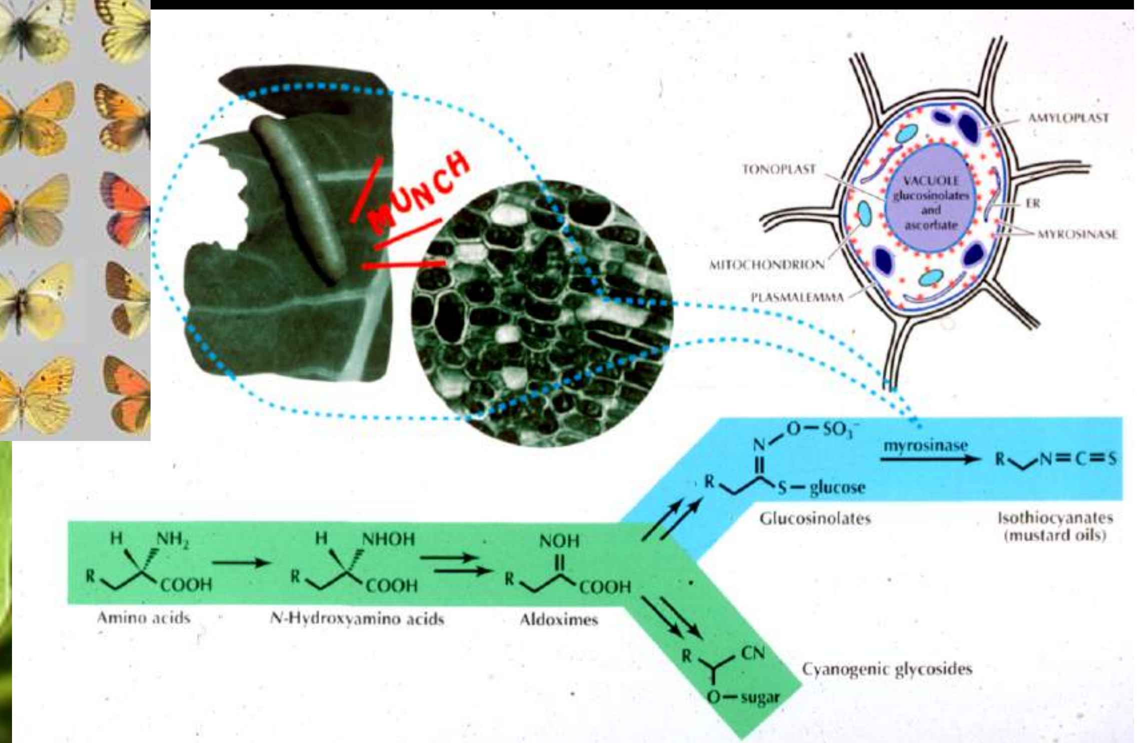
The Mustard Oil Story

Glucosinolates ⟶ Isothiocyanates or mustard oils

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

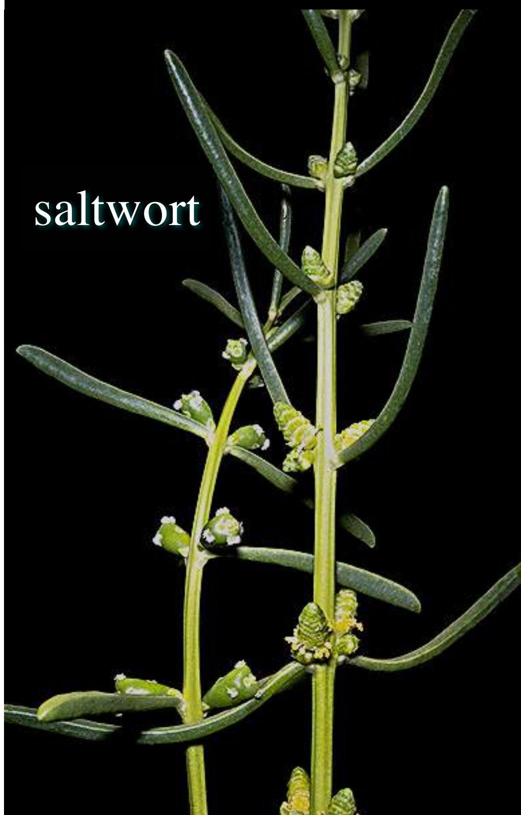
- Pierids show great radiation

Garden nasturtium - mustard oil family



The Mustard Oil Story

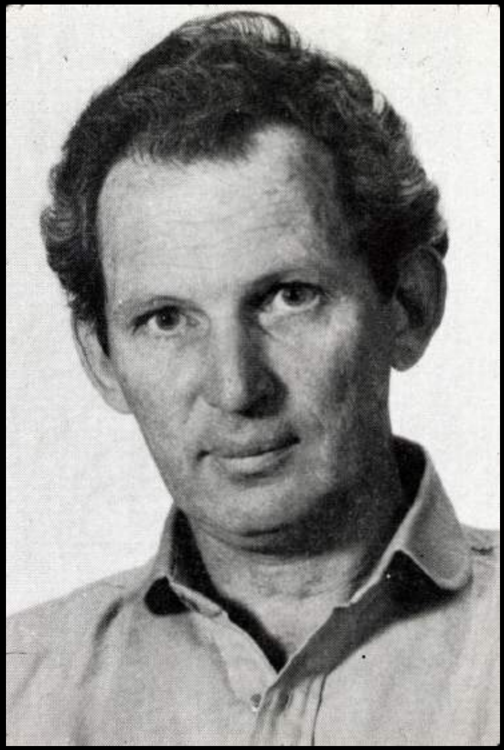
Systematic issue: 15 different looking families share mustard oils - are they related?



The Mustard Oil Story

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

Dalhgren - yes!



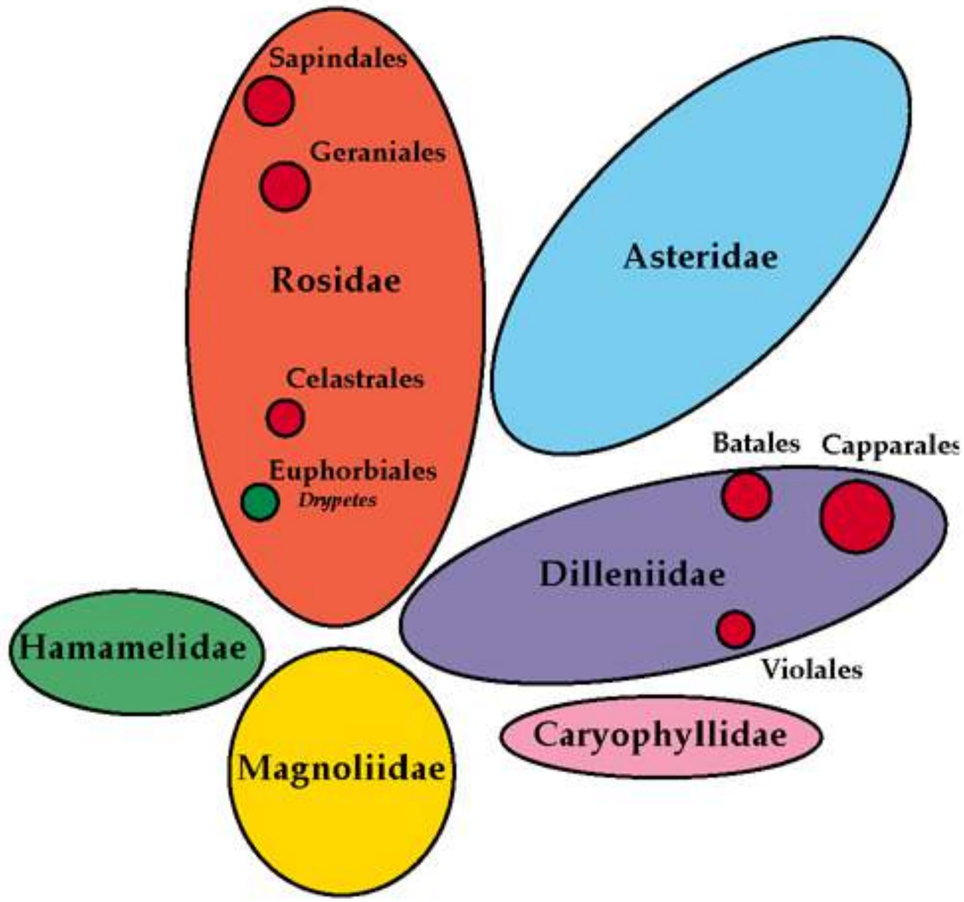
- mustard oil character evolved once (or twice)
- Capparales (Brassicales) order
- *Drypetes* (Euphorbiaceae) ?

The Mustard Oil Story

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

Cronquist - no!

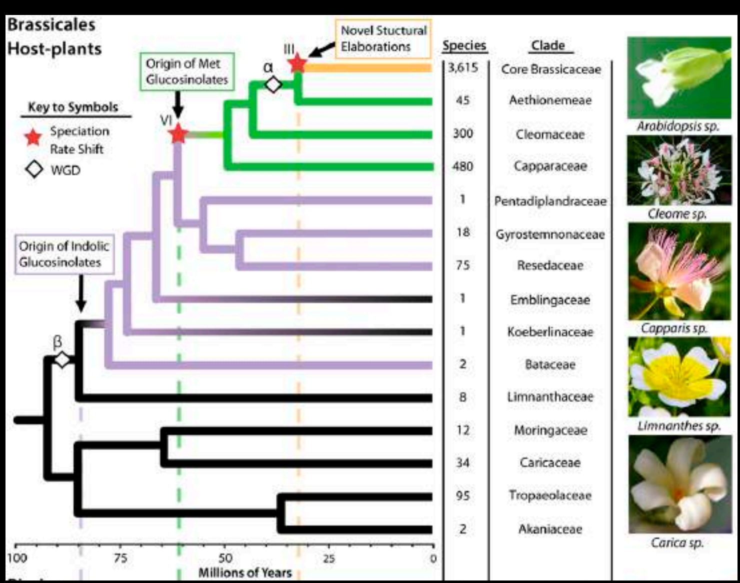
Cronquist's distribution of mustard oil families

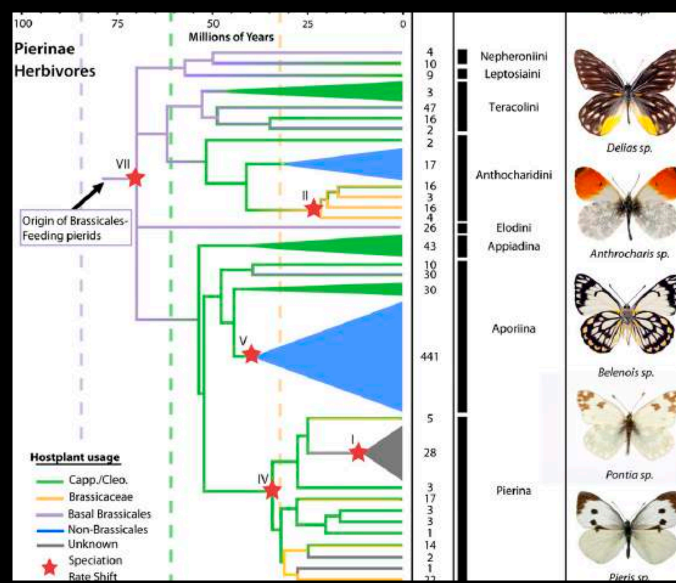


The Mustard Oil Story

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?