

Pigment Palette

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Autumn tree colors grace our landscapes. The palette of potential colors is as diverse as the natural world. The climate-induced senescence process that trees use to pass into their Winter rest period can present many colors to the eye. The colored pigments produced by trees can be generally divided into the green drapes of tree life, bright oil paints, subtle water colors, and sullen earth tones.

Unveiling

Overpowering greens of summer foliage come from chlorophyll pigments. Green colors can hide and dilute other colors. As chlorophyll contents decline in fall, other pigments are revealed or produced in tree leaves. As different pigments are fading, being produced, or changing inside leaves, a host of dynamic color changes result. Taken altogether, the various coloring agents can yield an almost infinite combination of leaf colors. The primary colorants of fall tree leaves are carotenoid and flavonoid pigments mixed over a variable brown background.

There are many tree colors. The bright, long lasting oil paints-like colors are carotene pigments producing intense red, orange, and yellow. A chemical associate of the carotenes are xanthophylls which produce yellow and tan colors. The short-lived, highly variable watercolor-like colors are anthocyanin pigments producing soft red, pink, purple and blue. Tannins are common water soluble colorants that produce medium and dark browns. The base color of tree leaf components are light brown. In some tree leaves there are pale cream colors and blueing agents which impact color expression. Figure 1.

Perceiving Fall

The forest landscape and trees have five major pigment color sets which can define autumn colors. (Table 1) These tree pigments have chemical structures which modify light as it passes by or is reflected away. Some wavelengths of light are absorbed by these pigments due to physical and chemical properties. Each pigment has a single or several peak wavelengths of light which are absorbed, with the rest of the wavelengths relatively unimpacted.

Humans see these unabsorbed wavelengths of light in the visual spectrum as a dominant color. Color can only be observed by a human in the visible spectrum wavelengths of roughly 380nm (violet) to 730nm (red). The wavelength number is a measure taken in nanometers (nm), or a billionth of a meter. People with modified color vision (various types of "color-blindness") will still register light across the visible wavelengths but not always perceive a color, or the same color as everyone else. Color is truly in the eye, mind, and genes of the beholder.

Chlorophyll Green

Chlorophylls are the green color pigments seen in tree leaves. Chlorophyll is the centerpiece (literally and figuratively) of light capture and food production in trees. Chlorophyll is bound to special membranes inside



carotinoids



anthocyanins



tannins

Figure 1: Graphical color expression range of the three major pigment groups in Fall senescing trees. Note white/cream color blending and brightening agents will impact color expression, as will chlorophyll green.

Table 1: Pigments groups responsible for major color expression in trees during Fall senescence.

1. Chlorophylls
2. Carotenoids
 - A. Carotenes
 - B. Xanthophylls
3. Flavonoids
 - A. Flavones & Flavonols
 - B. Anthocyanins
 - C. Proanthocyanidins (condensed tannins)
4. Tannins (sugared tannins)
5. Betalins (betacyanins & betaxanthins)

chloroplasts within leaf cells. Chloroplasts are transformed through senescence into gerontoplasts, or aged chloroplasts with declining chlorophyll maintenance machinery. Chlorophyll has a medium green color (it absorbs red and blue wavelengths of light) and is produced in such quantities as to dominate or mask other leaf pigments.

Chlorophyll is a light gathering antenna consisting of a porphyrin ring “head” structure with a magnesium atom center, and a long phytol “tail” (tetrapyrrole). It is chemically similar to the iron containing haem pigment of animal blood, and to vitamin B12. Chlorophyll is expensive for tree cells to make, difficult to maintain, and easily torn apart by far blue and ultraviolet light. In most tree leaf cells, a chlorophyll molecule only exists for an average of 26 hours, depending on the biological environment of the leaf. Chlorophyll is only produced when leaf tissues are stimulated by light.

A's & B's

The two types of chlorophyll in trees are called chlorophyll “a” (*chla*) and chlorophyll “b” (*chlb*). Chlorophyll b differs from chlorophyll a by having an additional double bonded oxygen atom attached to one corner, making *chlb* absorb slightly different wavelengths of light than *chla*. *Chlb* is called the shade chlorophyll and *chla* is called the full sun chlorophyll, even though both are present in any tree leaf with only the proportion of molecules changing. For example, the *chla* / *chlb* ratio in shaded tree leaves is about 2.5, where this ratio is about 4.2 in full sun leaves, on average.

If light excites chlorophyll, the energy captured can be quickly stolen by cellular machinery and used to make food. If chlorophyll is excited by light and can not quickly hand-off the energy to other cellular machinery, a highly reactive form of oxygen and peroxides can be generated which disrupt and destroy cell membranes. Tree leaf cells have several means for protecting chlorophyll molecules and for quenching any misdirected energy to minimize internal damage. Several types of colored pigments assist in this process. Some of these protective pigments are seen as Fall leaf colors.

Killing Chlorophyll

In senescence, chlorophyll is detoxified and broken-down. This process occurs along a material conserving pathway. Chlorophyll b is converted to chlorophyll a providing a spike of chlorophyll a and slightly changing leaf color to a darker green. Sometimes this deepening green color can be noticed just before yellowing begins in late Summer / early Fall. Figure 2. Next the long phytol tail is cut-off chlorophyll followed by the magnesium atom being liberated and shipped away. Finally, the large ring structure (porphyrin) of the chlorophyll head is straightened out. All these now colorless building blocks of chlorophyll are stored, further broken down, and shipped out of the leaf.

Carotenoid Oil Paints

Carotenoids (isoprenoids / tetra-terpenes) are some of the most common pigments made by plants and microbes, and stolen by animals. Carotenoids were discovered in 1831, and found to be essential to plants and always found in tree leaves. Carotenoids are non-nitrogen containing, fat-soluble pigments contained on membranes inside plastids, either with chlorophyll (in chloroplasts) or by themselves (in chromoplasts). Carotenoids are represented by more than 700 pigments - each presenting a slightly different color.

Carotenoids are tough, “oil paint-like” pigments that are familiar in everyday things such as the color of carrots, corn, bananas, egg yolks, and butter. Animals conserve and use a number of the carotenoids in their own coloration. Some chickens are fed yellow carotenoids to produce a pleasing golden-yellow skin color. To see a common set of carotenoid pigments, just lay a piece of cardboard over green grass for a few days. The grass will lose its chlorophyll, leaving the yellow of the carotenoids behind.

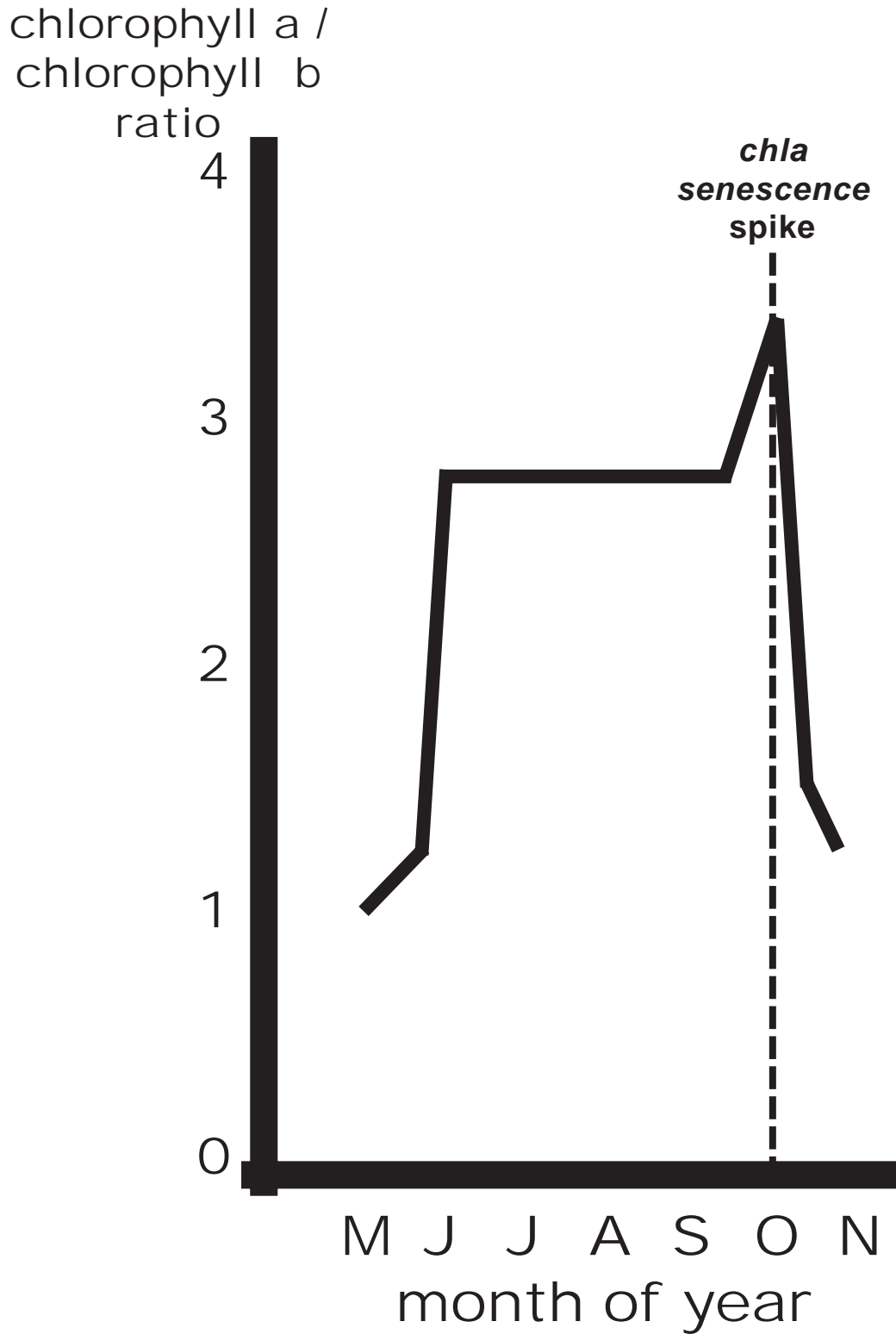


Figure 2: Change of chlorophyll ratio (chl a / chl b) in mixed oak leaves over time. (from Sanger, 1971)

Tough Color

Carotenoids are built with forty carbons strung together and are called tetraterpenes (40C). Other important plant materials come from this same chemical line including the sesquiterpene (15C) abscisic acid (ABA), and many types of diterpene (20C) gibberellic acids. Both groups are important plant growth regulators. The carotenoids all share a long carbon chain structure which has alternating single and double carbon bonds (conjugated) with or without two types of terminal rings or loops.

Carotenoids are energy-expensive for a tree to manufacture and not easily broken apart. Unlike chlorophylls which are only manufactured or maintained when light is present, carotenoids can be generated in the dark. Carotenoids do more than just add color, they play three critical functions within tree leaves: blocking excessive light from sensitive chlorophyll systems; harvesting light beyond chlorophyll wavelengths; and, quenching energy paths leading to free radicals.

Light Antenna

The light capturing and processing machinery in a tree are dependent upon chlorophyll. Carotenoids help protect the light gathering system of trees from overexposure to light especially blocking some blue and violet light which damage chlorophyll molecules. Carotenoids, being more stable and tougher than chlorophyll, help shield valuable but fragile chlorophyll. In other words, carotenoids function as a sunscreen in leaves.

Carotenoids act as antenna for capturing certain wavelengths of light. Because the carotenoids and chlorophylls are attached to membranes close to each other, the carotenoids can easily transfer any captured energy to chlorophyll molecules. This “accessory pigment” role for carotenoids helps to funnel more energy to chlorophylls to process. Alternatively, when chlorophyll captures energy and can not quickly pass it onto surrounding energy conserving machinery, carotenoids can remove this energy, preventing chlorophyll damage. Carotenoids vent energy away, disposing of extra energy as heat. If not vented away, unused energy would generate damaging oxygen radicals.

Anti-Oxidant

Probably the most important role for carotenoids in a tree is preventing light powered oxidation (destruction) of chlorophyll, surrounding molecules, and membranes by oxygen radicals. This type of oxidation can be extremely damaging to the light capture system and individual cells in a leaf. Carotenoids function as an anti-photo-oxidant. Anywhere in the tree where there is chlorophyll, light, and oxygen, carotenoids are pre-positioned to help protect light gathering systems from damage. Figure 3.

With & Without Oxygen

Carotenoid pigments comes in two forms, non-oxygenated forms called carotenes and oxygenated (alcohol) forms called xanthophylls. The pigment color expressed by carotenes and xanthophylls depend upon light wavelengths absorbed as shown in Table 2. Most carotenoids have three closely clustered light absorption peaks which cover an absorption range averaging roughly 70nm.

Carotenoids brightly color many tree parts with red, orange and yellow. The amount of carotenoids present in leaves is roughly one-twelfth the amount of chlorophyll present at the beginning of senescence. Figure 6. Xanthophylls comprise roughly 66-75% of all carotenoids in a leaf. Carotenoids usually outlive chlorophyll pigments by 3-5 weeks in tree leaves. New carotenoid pigments are also manufactured as leaf, light, and temperature conditions change.

Carotene Orange

Carotenes range in color from bright oil-paint-like yellow, orange, red-orange, and red. They are the pigments coloring oranges, tomatoes, carrots, pineapples, citrus, paprika, apples, saffron stigmas, strawberry, yams, mangoes, apricots, peaches, sweet potatoes, and pumpkins. The carotenes are long carbon chains with two, one or no carbon loops on their ends, like all carotenoids. For example, lycopene (pinkish-red) helps generate the bright red color of tomatoes and has no terminal loops.

relative leaf carotenoid concentration

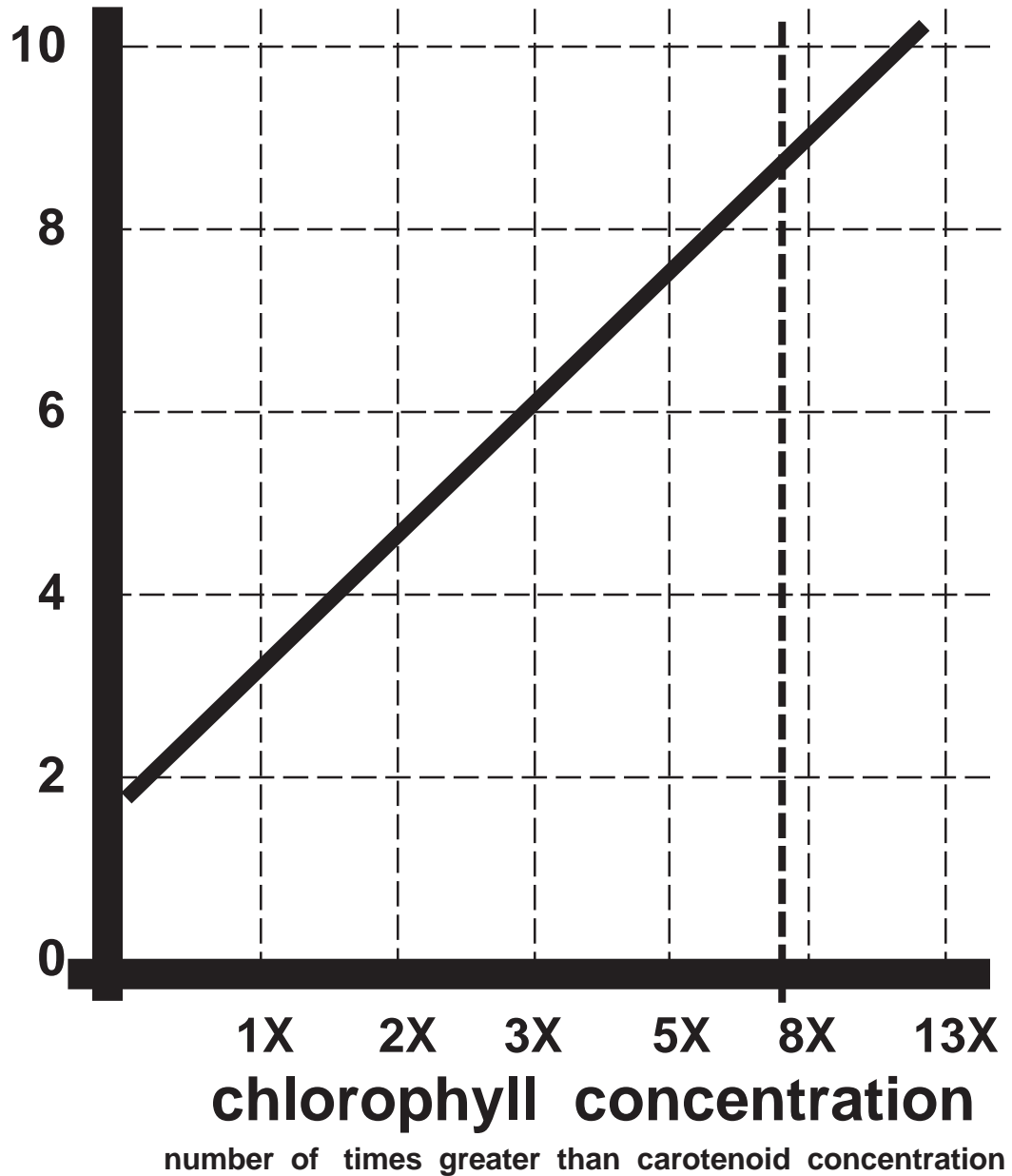


Figure 3: Estimated relative chlorophyll concentrations compared with carotenoid concentrations in tree leaves. Left of the bold dashed line are senescence levels of chlorophyll.

(derived from Lee et.al. 2003)

Table 2: Color expressed, average peak absorption wavelength (nm), and primary absorption wavelength range (nm) for a variety of carotene and xanthophyll pigments.

color expressed	average absorption peak	absorption range
clear / colorless	--	<360
pale yellow	400	378-425
yellow	443	414-475
yellow-orange	451	421-488
orange	455	432-490
pink	469	435-505
red	494 nm	451-540 nm

A carotene with one terminal beta loop on the carbon chain is called a gamma form (a pink pigment and precursor to beta-carotene). A long chain of carbons with two identical beta loops on each end is called the beta form (orange colored beta-carotene). The delta form (yellow-orange pigment) has one alpha loop on its carbon chain (precursor to alpha-carotene). Two alpha loops on each end of the carbon chain is the alpha form (alpha-carotene, a yellow pigment).

Every tree species and individual may generate different amounts of different carotenes. Each carotene differs every so slightly from its chemical family members, but these small differences change light reflectance and so color expressed. Generally, beta-carotene is most common in chloroplasts and the lycopene is most common in chromoplasts. Both gamma-carotene and alpha-carotene are precursors to vitamin A (20C), a product of a split carotene and essential for animals.

Reflected Colors

Carotenes serve to protect chlorophyll from too much or the wrong wavelengths of light, and so act as a selective filter. *Chla* has general light absorption peaks around 670nm and 430nm. *Chlb* has general light absorption peaks around 640nm and 460nm, just inside the *chla* peaks allowing it to be more efficient in the shade of *chla*. Beta-carotene (orange) has absorption peaks between 420nm and 480nm, shielding chlorophyll from too much light at the blue end of the spectrum.

Every carotene theoretically, due to the long chain of carbons, can exist chemically as many hundreds of different isomers (i.e. 1,056 isomers for lycopene; 272 isomers for beta-carotene). In the tree, only one or two isomers usually exist. Extracting carotenes from tree cells usually disrupts and changes the isomer mix. The most common of the carotenes include pro-lycopene (orange), lycopene (pinkish-red), neuroxanthin (yellow), torulene (red), tetrahydrolycopene (red), zeta-carotene (pale yellow), gamma-carotene (pink), delta-carotene (yellowish orange), beta-carotene (orange), and alpha-carotene (yellow). There has been a number of positive human health values associated with consumption of many of the carotenes.

Xanthophyll Yellow

Xanthophyll (xanthoxanthin) pigments were discovered in plants in 1837. As mentioned above, xanthophylls are oxygenated carotenoids. Xanthophylls are more strongly bound to cell membranes and more polar chemically than carotene carotenoids. Light is not needed to initiate or maintain xanthophyll pigments. Xanthophylls generate yellow, gold, yellow-tan, and yellow-orange colors in trees. They are found pigmenting marigold petals, citrus, peaches, nectarines, and papayas. The bright red of peppers are from capsanthin and capsorubin, unique red xanthophylls with modified end loops on each molecule. Animals can not generate xanthophylls and must utilize ingested plant pigments for coloration of feathers, egg yolks, and eye color, for example.

Cycling Up Protection

Xanthophylls are an important component of the light harvesting machinery in tree leaf chloroplasts. They absorb light in wavelengths chlorophylls can not and pass captured energy to primary chlorophyll reaction centers. Xanthophylls also serve a photo-protective role, protecting other tissues and the photosynthesis process from overexposure to light by acting as a filter of blue spectrum light and actively dissipating extra energy captured but not used. A part of this specialized progressive protective process is called the xanthophyll cycle.

In tree leaf cells much of the xanthophyll in the morning is in the form of a large violaxanthin pigment pool within plastids. As light intensity and ultraviolet light increases, violaxanthin (yellow) is converted to antheraxanthin (yellow) which provides greater light screening and cell protection. As sunlight intensity peaks, zeaxanthin (orange) is generated from antheraxanthin providing even more protection for photosynthetic machinery. Cells become more acidic at high light intensities which facilitates the quickening of the xanthophyll

cycle toward zeaxanthin. Overnight most of the xanthophylls are converted back to violaxanthin. Xanthophylls (specifically zeaxanthin) have also been cited as a blue light sensor for stomate opening in the morning and for helping tree tissues sense directional differences in lighting, generating phototropism (directional growth response to light).

Naming Names

Some of the xanthophylls include flavoxanthin, rubixanthin, rhodoxanthin, canthaxanthin, zeaxanthin (orange), alpha- and beta-cryptoxanthin (yellow-orange pigments converted to Vitamin A in animals), zeinoxanthin (yellow), fucoxanthin, canthaxanthin, and astaxanthin (red), violaxanthin (yellow), lutein (yellow), neoxanthin (yellow), and antheraxanthin (yellow). Not all xanthophylls are involved with every xanthophyll-cited task within a tree leaf. Violaxanthin and lutein (yellow pigments) help capture light energy for photosynthesis (photosystem II) and dissipate excess energy for chlorophyll. Neoxanthin (yellow) does not capture light nor can it dissipate energy by eliminating energized radicals.

Lycopene (straight-line pinkish-red pigment) is the starting point for both carotenes and xanthophylls using two physiological processes. One process uses lycopene to generate beta-carotene with its two identical end rings eventually forming a number of xanthophylls. The other process generates alpha-carotene with its two different end rings eventually forming the xanthophyll lutein. As in the carotenes, small differences in end rings can change color expression. Lutein (yellow) and zeaxanthin (orange) are the same except for two bonds on one end ring.

Flavonoid Water Colors

There are more than 7,000 flavonoids -- phenolic compounds (having carbon rings) discovered in 1664. The pigment forms are found in angiosperms, especially in fruits and flowers, and in gymnosperms. All are water soluble and found dissolved in the cell vacuole solution. The flavonoids are here divided into two primary tree pigment groups: flavones and flavonols (pale yellow, cream, ivory, white, colorless); and, anthocyanins (dark yellow, orange, red, blue, pink, purple).

Flavo-Pale

Flavones and flavonols (sometimes called the “yellow flavonoids”) are unique materials found in small amounts in tree leaves. They absorb selectively in the ultraviolet part of the spectrum, never interfering with photosynthetically active radiation wavelengths. They absorb much farther into the far blue end of the spectrum than anthocyanins. Some generate the yellows (chalcones) and bright yellows (aurones) of flowers. Many are visible to humans only when concentrated, then appearing milky or cloudy. Flavones and flavonols are visible to insects and utilized in some flowers to facilitate insect pollination. The value of flavones and flavonols to tree leaves are as selective light filters, filtering out the damaging UV light while allowing valuable wavelengths into cell machinery.

Some of the colorless flavone and flavonol pigments are maintained in cells and converted into anthocyanins when needed for protection of young tissues or of senescing tissues in Fall. The color expression value of flavones and flavonols are in how other colors are softened or modified. White creamy coloration provides additional depth and breadth for other colors. Colorless flavones and flavonols can form pigment complexes with highly colored anthocyanins and metal ions to form unique colors in a process called copigmentation. Some of the vivid blues arise from this process.

Anthocyanin Purple

Anthocyanins (meaning “blue paint” or “blue flower”) are one form of water soluble (“watercolor-like”) plant pigment discovered in 1913. They are usually concentrated just under the upper epidermis in the palisade parenchyma cells of the leaf. Anthocyanins are stored inside cell vacuoles and sometimes isolated in protein

inclusions within vacuoles called anthocyanoplasts. In Fall, anthocyanins are synthesized in leaf cells from a pool of colorless flavonoids in vacuoles. Figure 4. They do not have nitrogen chemical components and so do not interact with nitrogen mobilization in the leaf. Anthocyanins are common in all trees and found in other terrestrial plants. These pigments are not essential to trees but perform many important functions. There are more than 630 anthocyanins known.

Anthocyanins are the pigments found in bronzed or dark-leaved trees in Summer. Anthocyanins also color some tree flowers, fruits, and new tissues. The red colored blush of new growth in many trees is the result of anthocyanin pigments. Anthocyanins make cherries, cranberries, and apples red while making grapes, blueberries and plums blue. The range of colors is great, producing dark yellow, orange, red, crimson, scarlet, dark red, blue, violet, pink, purple, burgundy, and purple-red colors. Anthocyanins can also be colorless.

Chameleon Changes

Each anthocyanin does not have a single base color. Color ranges widely depending upon conditions of the cell where dissolved over the course of the senescence season. Anthocyanins are not stable for long periods dissolved in the cell solution. Anthocyanins change color as cells age. They are sometimes mistaken for the water soluble betalain alkaloid pigments found in beet roots, spinach leaves and rhubarb stalks.

Technically, there are two forms in the tree, usually not clearly differentiated: anthocyanins have a sugar attached; anthocyanidins are the pigment rings without a sugar attached. Usually glucose or rhamnose are the sugars comprising an anthocyanin. The sugar attachments make the anthocyanin more water soluble (and osmotically active / water conserving / frost resistive), and shifts the color of the pigment farther toward the blue end of the spectrum. Senescence greatly increased starch breakdown and sugar mobilization. Sugars greatly increasing within leaf cells in Fall include sucrose, fructose and glucose as anthocyanins concentrations peak.

Protective Services

In senescing leaves, anthocyanins serve a protective role. Anthocyanins provide sun-blocking, light filtering, and antioxidant services within leaf tissues containing chlorophyll. They can be induced in tissues by stress (cold, light, pests, element deficiency). Young shoots of Spring and senescing tissues in Fall may be colored with anthocyanins for protection. Summer leaves usually do not generate anthocyanins, but succulent shoots, petioles, and buds may show anthocyanin coloration. Anthocyanins help absorb damaging free radicals generated by inefficient photosynthesis reactions. Anthocyanins also provide limited protection against radiative frost damage while conserving leaf water.

Anthocyanins minimize photo-destruction of cell machinery by blocking damaging wavelengths of light in the 475-575nm wavelength range. Anthocyanins in tree leaves function as “blue blockers,” filtering out ultraviolet (UV) light to protect surrounding tissues from UV damage. Anthocyanins are generated following two pathways inside trees -- one initiated by ultraviolet light (UV) light reducing flavones, and one with no light required from a clear material called leuco-anthocyanin. Senescing leaves in full sun generate and maintain anthocyanins to assure successful reabsorption of valuable leaf materials.

Band on the Titanic

Anthocyanins are generated in response to many leaf stress conditions. One stress initiating anthocyanin production is essential element shortages. Senescence processes in a tree attempt to recover valuable nitrogen, sulfur, potassium, and phosphorus (and other elements) from leaves before leaves are abscised. As element deficiencies develop in a leaf, protective anthocyanins are generated to shelter the declining remnants of cell processes and machinery. Senescence is a living tissue process and requires some food production as fuel. Some waning level of photosynthesis is critical through the Fall, and anthocyanins help protect this last food production and remobilization process.

As starch is being dismantled into sugars, and sugars are being transported out of the leaf, anthocyanin

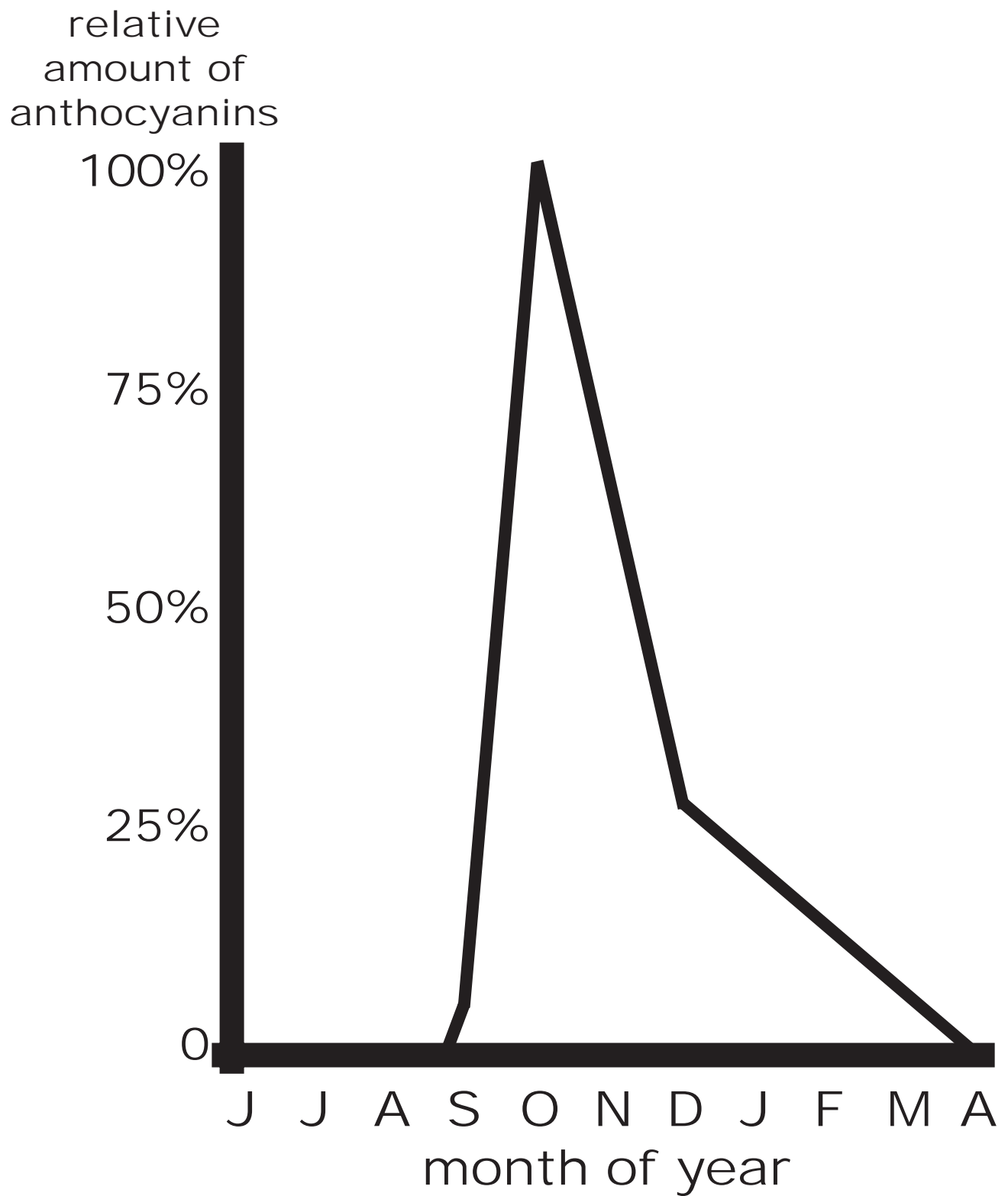


Figure 4: Changes of anthocyanins in oak leaves over time. (from Sanger, 1971)

content and forms greatly increase. Because anthocyanins are bound to a sugar molecule (the combined unit is called a glycoside) within a cell, sugar supplies are required for anthocyanin production and presentation. In Fall as low temperatures and a developing abscission layer slow material movement out of leaves, sugar enrichment and anthocyanin production result.

Red & Blue States

Every tree and species will have a different combination of anthocyanins generated depending upon genetic and environmental interactions. For example, as senescence of leaves continue into the Fall, cells become more acidic. As pH within a leaf becomes more acidic, the same anthocyanins become more red while a more basic pH in cells (early season cell contents) will generate more blue color expression from the same anthocyanins. The amount and form of iron (Fe) and aluminum (Al) in leaf cells also modify the range of anthocyanin colors.

Anthocyanins have a standard color gradient ranging across dark red, red, orange-red, purple-red, purple, bluish-purple, and blue. The chemical modifications which shift color along this color range are summarized in three statements: 1) as chemical attachments to the basic molecule change from OH (hydroxyl) to OCH (methyl), the color expressed becomes bluer; 2) as more small chemical attachments are added to the molecule, the color expressed becomes bluer; and, 3) the more basic cellular pH the bluer color expressed. See Table 3.

Variability!

Anthocyanin contents vary greatly from year to year in tree leaves while carotenoids stay relatively constant. Seasonal environmental and biological differences greatly change anthocyanin formation and color expression. Anthocyanin formation is greatly increased by, and color expression is impacted by:

- leaf deficiency of nitrogen (N), boron (B), sulfur (S), potassium (K), and phosphorus (P);
- water content (drying);
- salt content (increasing);
- starch to sugar conversion rate (accelerating);
- sugar content (high);
- ultraviolet (UV) light intensity (bright sunshine);
- cool temperatures (non-freezing);
- reduced precipitation (dry weather) causing less leaching of leaf materials;
- wounding or infection of tissues
- number of OH and OCH chemical attachments (more blue);
- presences of chelating metals like aluminum (Al) and iron (Fe) (more blue);
- presence of flavone or flavonol pigments (cloud and soften);
- pH of cell vacuole (acid = red); and,
- method of storage and cell shape.

Tannin Khaki

The death of leaf cells form oxidative products which are dark in color (melanins). These brown materials are various forms of phenolics like tannins. Tannins are found within and around leaf cells. Tannin, or tannic acid, was used to tan leather in the past concentrated from wood and bark. Tannins are water soluble and help color black tea. Tannins give red wine a darker color and a bitter taste. Tannins can be orange-brown, amber, yellow-brown, pale yellow, and light to medium brown in color. Tannins are polymers of phenolic rings combined in complex ways and found in two general forms in trees leaves: condensed and sugared.

Table 3: Example of colors expressed for selected anthocyanins with different chemical attachments (OH = hydroxyl group; OCH = methyl group), and at different cellular pH values.

name	attachments	pH 5 acid	pH 7 neutral	pH 9 basic
pelargonidin	1OH	dark red	orange-red	purple
cyanidin	2OH	red	purple-red	bluish-purple
delphinidin	3OH	purple	bluish-purple	blue
peonidin	1OH/1OCH	dark red	red	purple-red
petunidin	1OH/2OCH	red	purple-red	blue

Condensed tannins are laid side by side and can be precursors of anthocyanins (proanthocyanidins) under strong acidic conditions. Sugared tannins, or hydrolyzable tannins, are complexly interconnected with each other and sugars in small pieces. These two groups of tannins are not related to each other in how each are formed. From a color standpoint, they both generate dark colors. The sugared tannins are more water soluble than condensed tannins, and can form anthocyanins under weak acidic conditions. Tannins are reactive materials and can bind proteins together, disabling critical cellular, decay and digestive enzymes. Because tannins are dangerous to cell proteins, they are kept in cell vacuoles till cell death.

Betalain Special Red

Betalains (betacyanins or chromo-alkaloids) are water soluble, bright, alkaloid pigments stored in cell vacuoles. They were discovered in 1919. Betalains, like anthocyanins, are not essential to tree cells. Betalains are found in only one order of angiosperms called the *Caryophyllales* (*Chenopodiales*) and in some basidiomycete fungi. Within the *Caryophyllales* order there are several plant families, including the *Caryophyllaceae* and *Molluginaceae* which do not have betalains. If a plant has betalains, they will not have anthocyanins, and if they have anthocyanins they will not have betalain pigments. Trees with betalains are generally from the Mediterranean basin, Madagascar, and South Asia. Trees with betalain pigments are usually salt and drought tolerant.

Common plants with betalains include many carnivorous plants like pitcher plants, cactus, many succulents, seagrapes, pokeweed, jojoba, smartweed, sorrel, dock, buckwheat, rhubarb, salttree, bougainvillea, portulaca, ombu-tree, spinach, sugar beets and beets. The shirt-staining, water soluble pigment of a cut beet root is a betalain, not an anthocyanin. Notably, the carnations, pinks, campions and mouse-ears within this order of plants have anthocyanins not betalains.

Betalains are made from the amino acid tyrosine and has four carbon rings, many oxygens, and two nitrogens. Light is not required for inducing or producing this pigment. As an alkaloid, it is kept out of the way in the vacuoles of cells tethered to a sugar. Because it contains nitrogen, the pigment is part of a reabsorption process in the senescing leaf. Like anthocyanins, betalains reflect different colors depending upon pH conditions in the cell. Betalains are red to violet under basic pH conditions (called betacyanins), and yellow to orange under acidic pH conditions (called betaxanthins). Betalains have little impact on fall foliage coloration in the trees of Eastern North America, but can be found in understory and forest edge plants.

Pigment Summary

Fall colors herald Winter and approach of the following Spring. No new or unique mechanisms are used in generating fall colors, just the pigments and colorants trees use for other functions. The “watercolor,” “oil paint,” and “earth tone” colors all provide a fantastic show that humans around the temperate areas of the globe have long appreciated. Figure 5. The chemistry of tree life can be colorful.

Figure 5: Generalized color range for major pigments comprising the autumn tree color expression palette.

