SAFER CHEMISTRY THROUGH BIOMIMICRY:
REDUCING POTENTIALLY HARMFUL IMPACTS OF TRI CHEMICALS

Report prepared by the Biomimicry Guild
for the U.S. Environmental Protection Agency,
Region 8

October 2010

BIOMIMICRY
GUILD

Biomimicry is the ***conscious emulation of nature's genius****.* Conscious *implies that we intentionally ask nature for advice.* Emulation *means that we are not directly copying nature, but rather abstracting deep design principles from the strategies found in the natural world and applying them to our challenges.* Nature's genius *recognizes the inspiration we can gain from 3.8 billion years of R&D currently represented by 30 to 100 million species living on this planet.*

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Original Patent Holders
We fully recognize that we are not the originators of these ideas, but rather they belong to the individual species whose unique strategies are presented here in this report. As such, the Biomimicry Guild donates a portion of our profits annually to the Innovation for Conservation program, which promotes habitat conservation as a means to protect the well-spring of nature's genius. To learn more about this program as you develop ideas from this report and others, please contact The Biomimicry Institute (www.biomimicryinstitute.org).

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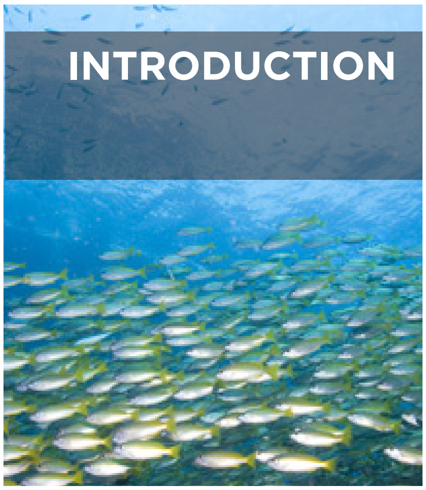
SUMMARY

The U.S. Environmental Protection Agency (EPA), Region 8 office, partnered with the Biomimicry Guild to test biomimicry as a methodology to identify innovations for reducing the potentially harmful effects of Toxics Release Inventory (TRI) chemicals. Bisphenol-A (BPA) was selected as the target chemical based on environmental release quantities reported to TRI for 2008 and its status as an EPA chemical of concern. BPA's use as a color-developer in thermal and carbonless paper was chosen as the target chemical application.

A comprehensive survey of the scientific literature revealed almost two-dozen natural strategies for color change in organisms ranging from crab spiders that change from white to yellow, tomato hornworms that change from black to green, sugar maple leaves that change from green to red, tropical flatfish that turn from beige to dark brown/black, and squids that can turn to almost any combination of color, iridescence, and texture. Color change strategies include oxidation to colored compounds, hormone control of the motion of pigment-containing organelles within individual color cells, and pigment-free layered structures that play with incoming light to produce color.

This broad but "shallow dive" into nature's color-changing strategies is an early step in the biomimicry process. "Deep dives" into a subset of the strategies presented in this report would reveal more detail of the chemistry involved and allow a set of deep patterns to emerge that are common across taxa. Design ideas for a BPA color developer substitute or for a new color development technology for thermal and carbonless paper would be generated based on these common patterns and principles. Ultimately, proof of concept prototyping in partnership with a chemistry laboratory would follow.

INTRODUCTION



Biomimicry is the conscious emulation of life's patterns to solve human challenges. Rather than enslave organisms to do our chemical processing and extract nature's bounty, biomimicry spurs the creation of new, life-friendly technologies based on the wisdom extracted from nature by an informed scientific research community. Life must synthesize, use, and dispose of chemicals in the same environment in which it eats, sleeps, and rears its young. By necessity then, life's chemistry follows a set of principles: it is water-based, uses self-assembly at ambient conditions, a subset of elements in the Periodic Table, renewable feedstocks, freely available energy sources, catalysis, and chemical specificity, among others. In a nutshell, life creates conditions conducive to life. These principles mesh well with the twelve Green Chemistry Principles that seek to transform commercial chemical products and processes into sustainable practices. What better source for inspiration than nature's time-tested elegant and sophisticated chemistries?

Thermal and carbonless paper consists of a layer of color-development chemicals covering the whole surface on the side to be printed. The color-development chemicals include a leuco dye (crystal violet lactone) in its colorless form, a color developer (BPA), and a solvent. The leuco dye and BPA are each micro-encapsulated to prevent reaction until heat or pressure causes the capsules to rupture, allowing BPA to react with, and darken, the leuco dye. Thermal and carbonless printing papers are regularly used as cash register receipts, luggage tags, faxes, and labels. Experiments conducted with cash register receipts suggest that ten times more BPA can be transferred to wet or greasy skin compared to dry skin; BPA may penetrate to depths where it can no longer be washed off. Daily exposures from handling receipts for a period of 10 hours results in doses below the current tolerable daily intake (TDI) of 0.05 μg/kg body weight (Biedermann 2010). Additional sources of BPA exposure include food stored in cans lined with epoxy resins, polycarbonate plastic beverage containers and infant feeding bottles, and PVC stretch films used for food packaging where BPA is added as an antioxidant or inhibitor (Lopez-Cervantes 2003).

Doses below the currently accepted TDI are an issue because BPA has been shown to mimic natural estrogens that may impact the endocrine system even at very low doses; the major concern is exposure of the developing fetus to low-doses of BPA.

METHODOLOGY

Choosing the target chemical

EPA's primary TRI contractor, Abt Associates, analyzed 2008 TRI data and provided the Biomimicry Guild with a database including air and water release quantities, waste management quantities, and toxicity-weighted release quantities per North American Industry Classification System (NAICS) sector for four TRI chemicals that are also included in EPA's Action Plans: Decabromodiphenyl ether (Deca) (Chemical Abstracts Services Registry Number, CASRN 1163-19-5), Dibutyl phthalate (DBP) (CASRN 84-74-2), Di(2-ethylhexyl)phthalate (DEHP) (CASRN 117-81-7), and BPA (CASRN 80-05-7). The Biomimicry Guild chose BPA as the target chemical because it is (1) the highest in disposal and release quantities, (2) the only chemical with increasing percent change in disposal and releases from 2007 levels, (3) the highest in waste management quantities, and (4) the second highest in air emissions.

Choosing the chemical function

At the heart of the biomimicry methodology is the function question: *How does nature _____?* Whatever the challenge, it has to be broken down into one or more function questions in order to most effectively approach the biological literature and coax out the strategies used in the natural world to achieve the same function.

To identify the target function for this challenge, we first looked at the NAICS industrial sectors reporting BPA to TRI. Since NAICS categories are not always sufficiently detailed to indicate where and how BPA is used, we created a 5-part analysis to home in on the most important of the industrial sectors reporting BPA. We sorted NAICS by: (1) rank of total TRI disposal and release pounds, (2) rank of TRI waste management pounds, (3) BPA-associated product used or produced in that sector, (4) desired attribute of the BPA-associated product, and (5) likelihood that BPA serves a primary role in achieving the desired attribute. Ultimately, this analysis led to selecting controlled color change for thermal and carbonless paper as the target function for further research, and BPA's antioxidant/inhibitor function for PVC products as a back up.

Biological literature search

A search of both the primary and secondary literature resulted in the attached list of 21 ways that nature changes color. For each strategy, we provide the common and scientific name of the organism, a brief description of the strategy, the color changes that occur, whether or not the change is reversible, the color change trigger, colorant, and citation where available.

Three major types of color-change strategies emerge from the shallow-dive research: (1) pigment-based color changes, (2) pigment-free, structure-based color changes, and (3) combination pigment-based and structure-based color changes. Chemical triggers are the most often cited initiators of color-change including hormones, neurotransmitters, oxidizing agents, sugars, and acids/bases. Other color change triggers include light (UV, visible, and polarized) and temperature changes. Anthocyanins (flavonoids) and melanins are, not surprisingly, the most often mentioned colorants followed by carotenes (terpenes).

Nature-inspired alternatives to BPA in thermal paper might take one of two routes. The first is to develop a non-toxic substitute for BPA while preserving the current two-chemical encapsulation technology triggered by heat or pressure. The shallow dive done for this project suggests melanin or anthocyanins might be promising candidates as colorants, so the next step would be to select several of the melanin and anthocyanin strategies for more detailed study of their color change chemistry (what we call a "deep dive" into the primary scientific literature).

The second route is to develop a completely new technology for use as cash register receipts, luggage tags, faxes, labels, etc. Imagine a technology that requires no pigment, no color developer, and no solvent, but instead relies on modification of the nano-structure of the substrate to create the desired pattern. In this case, the next step would be to select one or more of the pigment-free, structure-based strategies for deep dive research.

The results of the deep dives would be used to identify any common principles at work across strategies and taxa. Once identified, these common principles help formulate plans for biomimetic innovations to be shared with a collaborating laboratory that could develop a proof of concept prototype.

Natural Strategies for Color Change

1

Bothus ocellatus

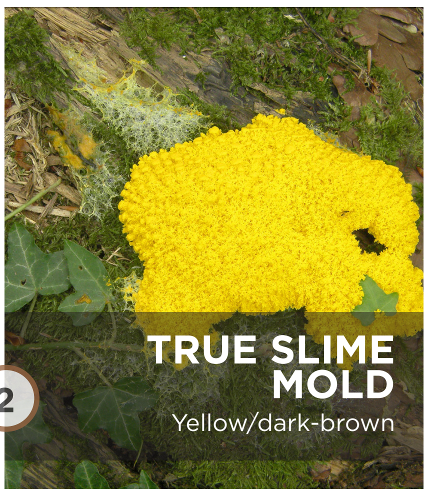
The tropical flatfish can achieve pattern-matching with surprising fidelity. By adjusting the contrast of different sets of ‘splotches’ of different grain size (or spatial frequency) on the skin, the fish can blend into a wide range of background textures in just 2-8 seconds.

Reversible Change
Yes

Color Change Trigger

Colorant
Melanin

2



Fuligo septica

Acellular (true) slime moulds are capable of a transition to the stage of sclerotium – a dormant form of plasmodium produced under unfavourable environmental conditions. Darkening of the sclerotia (a vegetative, resting food-storage body composed of a compact mass of hardened mycelia) is most probably a pathological phenomenon connected with the impairment of water balance during sclerotization.

Reversible Change
No

Color Change Trigger

Colorant
Melanin

3

In many species of fish, melanosomes (tissue-specific organelles specialized in biosynthesis and storage of melanin and present in cells known as melanophores or melanocytes) are highly motile, leading to visible changes in color. The bidirectional translocations of melanosomes are fast and synchronized, and regulated by hormones or direct innervation. Molecular motors carry melanosomes along the cytoskeleton to disperse them throughout the cell or to aggregate them in the cell center.

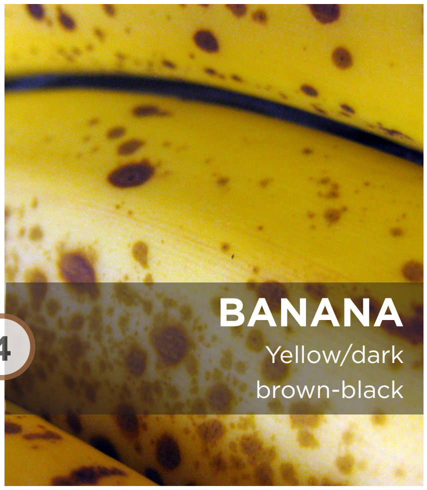
Reversible Change
Yes

Color Change Trigger
Noradrenaline, melatonin

Colorant
Melanin

Natural Strategies for Color Change

4



A yellow, catechol-based pigment in banana skins reacts with oxygen in the air to convert to a dark form of melanin.

Reversible Change
No

Color Change Trigger
Oxygen

Colorant
Melanin

5

In amphibian melanophores, molecular myosin-V motors carry melanosomes along actin filaments that make up the cytoskeleton to disperse them throughout the cell (darker color) or to aggregate them in the cell center (lighter color). Darkening occurs by elevating cAMP/PKA; PKA is linked to melanosomes via Rab32.

Reversible Change
Yes

Color Change Trigger
Protein kinase A (PKA)

Colorant
Melanin

6

Persea Americana
Skin of 'Hass' avocados changes color from green to purple/black as fruit ripen. Total anthocyanins in skin tissue increase during ripening, but this increase is due almost entirely to a single anthocyanin: cyanidin 3-O-glucoside. It is also influenced by the ripening temperature.

Reversible Change
no

Color Change Trigger
Temperature

Colorant
Cyanidin 3-o-glucoside

Natural Strategies for Color Change

7

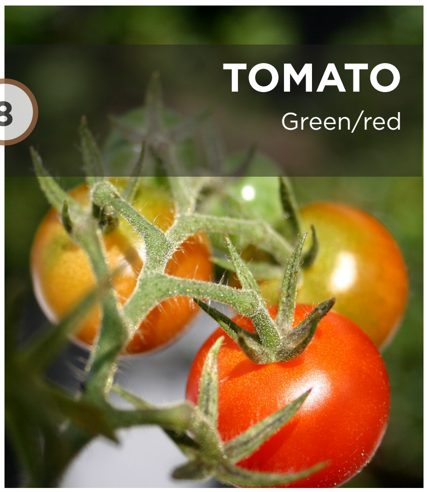
The rice stink bug places its eggs in clusters on plants. Each cluster consist of two rows. Freshly deposited eggs have a pale green color but develop a reddish tinge before hatch.

Reversible Change

Color Change Trigger

Colorant

8



Lycoperskon esculentum
During normal ripening of pericarp in intact tomato fruit, tissue color changes from green through orange to red, ethylene biosynthesis and respiration undergo a climacteric rise.

Reversible Change
No

Color Change Trigger
Ethylene?

Colorant
Lycopene

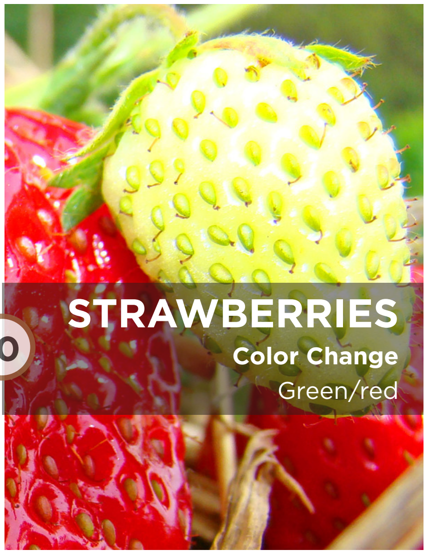
9

Pentapodus paradiseus
This fish has distinct reflective stripes on its head and body. The reflective stripes contain a dense layer of physiologically active iridophores, which act as multilayer reflectors. The wavelengths reflected by these stripes can change from blue to red in 0.25 s. Iridophore cells contain plates that are, on average, 51.4·nm thick. This thickness produces a stack, which acts as an ideal quarter-wavelength multilayer reflector (equal optical thickness of plates and spaces) in the blue, but not the red, region of the spectrum. Color change is associated with changes in the distance between adjoining reflecting plates. Reflective changes are controlled by the sympathetic nervous system; noradrenaline (norepinephrine) causes the reflected wavelengths to change to the longer end of the spectrum, adenosine causes the reverse effect.

Reversible Change
Yes

Color Change Trigger
Noradrenaline, adenosine

Colorant
Structural (no pigment)



In strawberries, color change, the loss of the green color and the appearance of the red color, is the result of the synthesis of anthocyanin. These compounds are flavonoids and are synthesized from the aromatic amino acid phenylalanine. Two key enzymes were described for the synthesis of these compounds: phenylalanine ammonia- lyase (PAL) and chalcone synthase. In the particular case of PAL, it has been demonstrated that this enzyme is synthesized de novo during ripening of the strawberry.

Reversible Change
No

Color Change Trigger

Colorant
Anthocyanin

Misumena vatia
The crab spider can change its color reversibly from white to yellow, matching the color of the flowers on which it perches. The change of color is based on a complex physiological process that still is not understood, but ommochromes pigments are major players. These pigments range from yellow (xanthommatin), red (ommatin), purple, violet, to black. The chemically characteristic property is their redox behavior, absorption of ultraviolet and visible light, and low solubility in aqueous medium. The reduced forms are red, while the corresponding oxidized form is usually yellow. Compounds such as tryptophan, kynurenine, and kynurenic acid occurred only or mainly in white crab spiders. In contrast, compounds such as 3-hydroxy-kynurenine, xanthommatin, and ommatin D occurred only or mainly in yellow crab spiders.

Reversible Change
Yes

Color Change Trigger

Colorant
Ommochromes

Natural Strategies for Color Change

Aloe arborescens
Under sustained intense light, *Aloe arborescens* plants, grown in the Negev Desert, Israel, accumulate rhodoxanthin inside chloroplasts, in the place of chlorophyll: hence the color change from green to red.

Reversible Change
Yes?

Color Change Trigger
UV light

Colorant
Rhodoxanthin

Acer saccharum
The timing and extent of red leaf coloration was consistently correlated with both foliar nitrogen (N) concentrations and starch or sugar concentrations. Leaves of trees with low foliar N concentrations turned red earlier and more completely than those of trees with high foliar N concentrations. During the autumn development of red leaf coloration, foliar starch, glucose and fructose concentrations were positively correlated with red leaf color expression.

Reversible Change
No

Color Change Trigger
Decreasing temperature, photo-period, and N concentration; increasing starch concentration

Colorant
Anthocyanin

Ophiocoma wendti
Brittlestars produce color by chromatocytes (cells with fixed pigment granules) and by chromatophores (cells with pigment granules that disperse in response to light). *Ophiocoma wendti* is dark brown during the day, and is banded gray and black from dusk to dawn. The transformation occurs over a 3 to 4 hour period. The color depends on the distribution of chromatocytes, the density of chromatophores, and the aggregation or dispersion of pigments in chromatophores.

Reversible Change
Yes

Color Change Trigger
Daylight

Colorant
Pigment(s) not specified

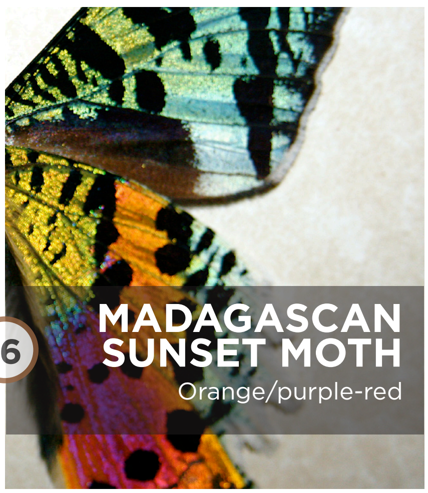
Natural Strategies for Color Change

Nomadacris septemfasciata
The hindwing color of red locusts changes with age, turning from hyaline (glassy or transparent) to light pink, pink-red, and finally purple-red, thus darkening with time. During most of adult reproductive diapause—a period of hormonally controlled quiescence—the proportion of pink, pink-red, and purple-red wings remained relatively constant. However, a change occurred at the end of diapause at the beginning of the summer rainy season.

Reversible Change

Color Change Trigger
Hormones

Colorant



Chrysiridia rhipheus
The Madagascan sunset moth wings exhibit a striking iridescence. The optical properties of the wing are consistent with those of a stack of 5-10 thin layers of structural elements called ridge, crossrib, microrib, trabeculae which lie in the basal part of the scale. When at least one of those elements is modified into a periodical structure comparable with the wavelength of light, it can cause optical interference to result in beautiful iridescence. The scale of the Madagascan sunset moth is also highly curved along its longer side—it has the shape of a longitudinally curved rectangular plate having a length of about 250 mm, a width of 100 mm and a thickness of several mm. The strong curvature produces an unusual polarization effect of the wing through the inter-scale dual reflection. Therefore, the structural color of this moth does not solely come from the multilayer optical interference, but from the cooperation between the two structural modifications in completely different sizes. The wing color changes between orange and purplish red depending on light polarization.

Reversible Change
Yes

Color Change Trigger
Polarized light

Colorant
Structural (no pigment)

Natural Strategies for Color Change

17

Anthocyanins, found in vegetables as well as flowers and fruits, can be red to purple depending on pH. The resonating flavylium structure accounts for anthocyanins' depth and intensity of color. While there are six common anthocyanidins, more than 540 anthocyanin pigments have been identified in nature.

Reversible Change
Yes

Color Change Trigger
Sugar, pH

Colorant
Anthocyanins

18

The lobster is black when alive but becomes red when boiled. The black color is caused by the pigment alfachrustacyanine composed of two parts: the red carotene part is called astaxanthine and one protein. When the lobster is boiled, the protein is denatured and the red color remains. Carotenes are usually yellow or red, but can come in red, blue or black if they are bound to a protein.

Reversible Change
No

Color Change Trigger
Heat

Colorant
Alfachrustacyanine

19

M. quinquemaculata
Tomato hornworm caterpillars emerge green when it's above 28°C and black below 20°C—a demonstration of how species can mask effects of genetic mutations until an environmental trigger reveals them, an adaptive mechanism that may help organisms survive. Organisms that live in variable environments often evolve traits—called polyphenisms—that change according to particular conditions. In the cooler northern United States, the caterpillars that emerge in the autumn are black to absorb more sunlight, but in the south, where camouflage is more important than heat conservation, they're green. Reduced juvenile hormone secretion results in an increased melanization (darkening) of the larval epidermis.

Reversible Change
Yes

Color Change Trigger
Heat, juvenile hormone levels

Colorant

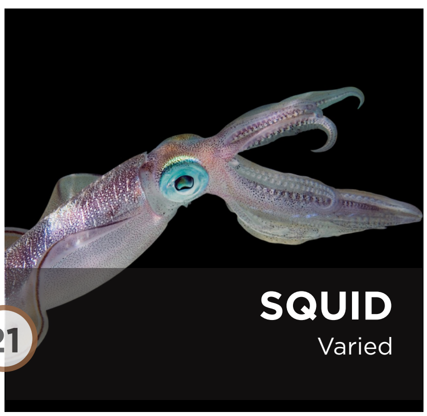
20

Red, purple and blue flower color is mainly due to anthocyanins. The color development and stability of anthocyanins are effected by co-existence of co-pigment and metal ions, and pH. The color is stabilized and varied by formation of a supramolecule. Especially beautiful blue flower colors are developed by a metalloanthocyanin, a stoichiometric supramolecular metal complex pigment. The metalloanthocyanins are composed with six molecules of anthocyanins, six molecules of glycosylflavones, and 2 atoms of metal ion.

Reversible Change

Color Change Trigger
Co-pigment, metal ions, and pH

Colorant
Anthocyanin



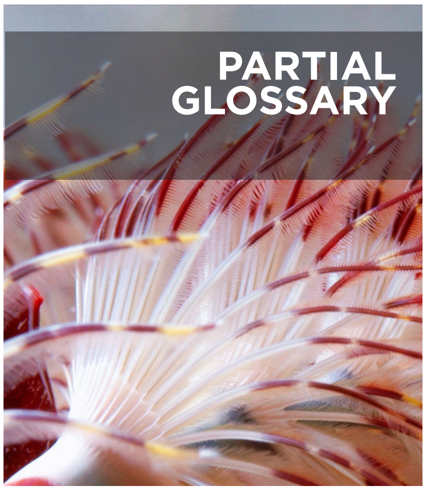
21

Loligo pealeii
Color and pattern changes in squid skin are mediated by the action of thousands of pigmented chromatophore organs in combination with subjacent light-reflecting iridophore cells. Chromatophores (brown, red, yellow pigment) have attached to them dozens of radial muscles that are innervated directly by the brain, and by contracting and relaxing these muscles, the pigmented sac of a chromatophore increases or decreases in area. In the squid, they can quickly expand and retract over underlying iridophore cells (red, orange, yellow, green, blue iridescence) made up of stacks of thin plates that reflect light by thin-film interference. Light reflectance from iridophores can be changed by applications of acetylcholine. Light reflected from iridophores can be filtered by the chromatophores, enhancing their appearance. Three color classes of pigments, combined with a single type of reflective cell, produce colors that envelop the whole of the visible spectrum.

Reversible Change
Yes

Color Change Trigger
Acetylcholine

Colorant
Brown, red, and yellow pigments as well as pigment-free, color-generating structures.



cAMP
(cyclic adenosine monophosphate, cyclic AMP or 3’-5’-cyclic adenosine monophosphate) is a second messenger important in many biological processes. cAMP is derived from adenosine triphosphate (ATP) and used for intracellular signal transduction in many different organisms, conveying the cAMP-dependent pathway. (wikipedia)

Cephalopods
any mollusk of the class Cephalopoda, having tentacles attached to the head, including the cuttlefish, squid, and octopus.

Chromatocytes
biological cells with fixed pigment granules.

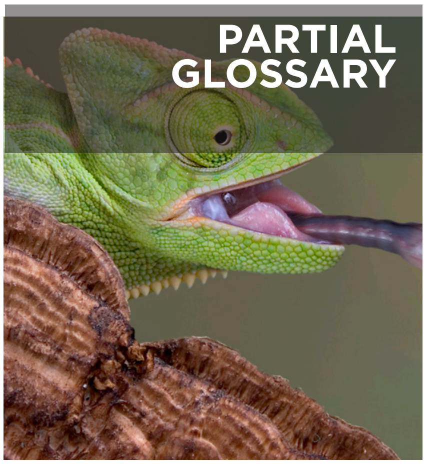
Chromatophores
biological cells with pigment granules that can be dispersed throughout the cell or concentrated in the middle.

Erythrophores
cells that contain pterinosomes producing pteridine pigments (red) (may also contain carotenoid pigments).

Iridophores
unlike chromatophors, iridophores contain no pigment. They produce shiny and iridescent color through a layered structure.

Leucophores
white-pigment chromatophores.

Melanin
In animals melanin pigments are derivatives of the amino acid tyrosine. The most common form of biological melanin is eumelanin, a brown-black polymer of dihydroxyindole carboxylic acids, and their reduced forms. The most common melanin, dopamelanin is a mixed copolymer of polyacetylene, polyaniline and polypyrrole. Another common form of melanin is pheomelanin, a red-brown polymer of benzothiazine units largely responsible for red hair and freckles.



Melanocytes
contain melanin-producing and storing melanosomes in warm-blooded animals. Melanin pigment granules cannot disperse throughout melanocyte cells as they can in melanophore cells present in cold-blooded animals.

Melanophores
chromatophores that house melanosomes.

Melanosomes
tissue-specific organelles specialized in biosynthesis and storage of melanin (black or brown) and present in cells known as melanophores or melanocytes.

Ommochrome
any of a group of biological pigments (biochromes) conspicuous in the eyes of insects and crustaceans as well as in the changeable chromatophores in the skin of cephalopods. Ommochromes are derived from the breakdown of the amino acid tryptophan.

Pericarp
the walls of a ripened ovary or fruit, sometimes consisting of three layers, the epicarp, mesocarp, and endocarp.

Pigment granules
melanosomes, pterinosomes, carotenoid vesicles, and other organelles that produce and store pigments.

Pigment
in biology, any substance whose presence in the tissues or cells of animals or plants colors them.

Xanthophores
chromatophores that contain carotenoid vesicles producing carotenoid pigments (yellow or orange) (may also contain pteridine pigments.

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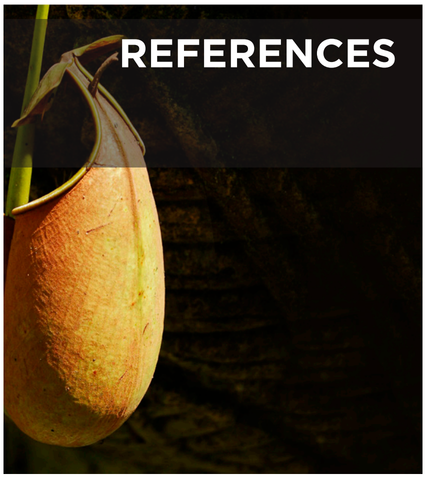

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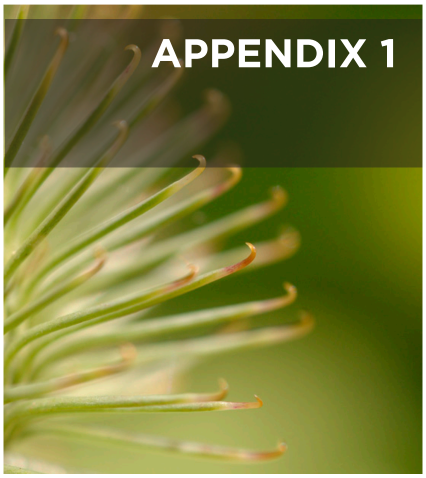
APPENDIX 1



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APPENDIX 2

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