R. Middleton ✉ (iD) ; M. Sinnott-Armstrong (iD)

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Structural color in fruits: Biomaterials to inspire physical optics Ⓕ

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R. Middleton[1,2,3,a] ⓘD and M. Sinnott-Armstrong[4,5,6] ⓘD

AFFILIATIONS

[1] Dresden University of Technology, 01069 Dresden, Germany
[2] University of Bath, Claverton Down, Bath BA27AY, United Kingdom
[3] University of Bristol, Beacon House, Bristol BS8 1QU, United Kingdom
[4] Max Planck Institute of Colloids and Interfaces, 14476 Potsdam, Germany
[5] Department of Biology, Duke University, Durham, North Carolina 27708, USA
[6] Department of Chemistry, University of Cambridge, Lensfield Rd., Cambridge CB2 1EW, United Kingdom

[a] Author to whom correspondence should be addressed: rm2950@bath.ac.uk

ABSTRACT

This Tutorial introduces structural color in fruits as a phenomenon of diverse optical materials. Originally best known in abiotic materials and animals, structural colors are being increasingly described in plants. Structural colors have already inspired a variety of useful products, and plants are especially attractive as models to develop new bioinspired technologies thanks to the comparative ease of working with them compared with animal systems. Already, human-engineered structural colors modeled after plant cellulose-based architectures have shown promising applications in colorants and sensors. However, structural colors include a far broader group of materials and architectures beyond cellulose. Understanding the new and diverse structures that have recently been described in plants should provoke research into new bioinspired products based on plant optical structures and biomaterials. In this Tutorial, we focus on fruits as new structures have recently been discovered, leading to new opportunities for bioinspired technologies. We bring together a review of optical structures found in fruits from a physical optics perspective, with a consideration of each structure as an opportunity in bioinspired and biomimetic design.

INTRODUCTION

New technologies are constantly needed to tackle emerging and endemic problems in a wide variety of fields, ranging from textiles to healthcare, electronics, food and agriculture, renewable energy, and environmental challenges. One source of such new technologies is the natural world itself. Technologies that incorporate or are inspired by biological solutions to problems that organisms encounter in their environment have many benefits, from inspiring new ideas to utilizing materials that are sustainable, nontoxic, and/or biodegradable. Color-producing materials are of particular interest, not only in the paints and cosmetics industries, but also for their potential applications in other areas of technology (e.g., sensing). In this field, structural color in nature is a powerful model. The development of new colorful materials based on biological solutions requires both an understanding of the diversity of

structures produced in nature and the continual discovery of new structures.

In this Tutorial, we discuss the history of colorful, bioinspired materials and describe the optical properties of recently discovered structural colors in plants. Although we include examples of structural color found in flowers and leaves, the focus here is on fruits and other "dispersules" (e.g., cones, which are not botanically speaking fruits but are also dispersed by animals). We aim to draw attention to light–matter interactions in the diversity of complex hierarchical materials found in unrelated species.

Structural coloration and bioinspiration

Since the earliest historic records, humans have used diverse materials and technologies to color our world, from pigments for painting and writing, to fabric dyes, to cosmetics applied directly

to human skin. Many colorants developed by humans have relied on heavy metals and are highly toxic both to human health and to the environment,[1] such as the use of arsenic to produce green fabrics and wallpapers.[2,3] Even today, many paints, colorants, and dyes are toxic to human health and/or the environment, leading to a continual need for sustainable, environmentally friendly, and non-toxic options.[4] The ability to produce color from new materials—especially non-toxic and biodegradable materials—promises to revolutionize colorants.

This need has led to new interest in characterizing the sources of colors in the natural world as an avenue for designing new colorants. The two primary methods of producing color in nature, pigments and structural colors, have different properties and associated advantages and disadvantages. Pigments provide the majority of coloration in nature, especially in plants, but they have limitations. Pigments tend to fade over time[5] and generally produce a broad-waveband reflectance peak and non-angle dependent hue (although some pigments change color in different chemical environments[6]). Although none of these features make pigments unattractive for their primary applications, structural colors offer a range of additional optical phenomena.

Structural color arises from the interaction between light and nanostructures that vary in refractive index on a wavelength or sub-wavelength scale, usually resulting in constructive interference. These colors can produce a variety of optical effects, ranging from iridescence, polarized light reflectance, as well as (in some cases) close to full reflectance intensity of a single wavelength at a single angle.

One of the most common types of photonic structures in the biological world are layered materials, where light interferes by reflectance from subsequent layers as the wave passes into the material and is reflected at each refractive index boundary. The distance between adjacent layers defines the phase difference between reflected light and, therefore, which wavelengths will constructively or destructively interfere. Interference is defined by the material and optical wavevector. Any periodic refractive index contrast can produce interference effects of this kind, including structures made of a single material (e.g., helicoidal cellulose,[7] which produces index contrast through varying material orientation) or out of alternating materials of differing refractive indices.[8,9] In addition to multi-layered structures, diffraction gratings (periodic ridges, where diffraction occurs due to lateral interference between light waves reflected from adjacent ridges) also occur.[10,11]

Although structural color is strongly associated with uniform periodicities, the biological world is rife with structures that exhibit differing degrees of disorder,[12] which alters the optical effects that a structure can produce. A relatively widespread class of structure is photonic glass, in which the scattering centers are tightly packed as with photonic crystals, but without ordered packing. Such architectures retain short-range order (defined by the distance between scattering centers, which are all near-touching) but lose the long-range order seen in a photonic crystal, meaning that coherent interference can be observed from all directions. This architecture has been identified as particularly widespread in bird feathers.[13]

Increasing disorder, both at the scale of separation between individual refractive indices and in the longer-range orientation of the whole architecture, serves to decrease the prominence of, and broaden, the reflectance peak.[14] Scattering in disordered systems

also introduces a blue shift in the reflectance spectrum.[15] Where there is a great deal of disorder, this increased reflectance of shorter wavelengths results in the reflection of UV/blue color dominating the coloration.[16,17]

From the perspective of designing new bioinspired technologies, structural colors have a variety of advantages over pigments. Structural colors can be used to achieve the same colors as pigments, as well as additional optical effects. For instance, the physical parameters of many photonic structures can be tuned to reflect essentially any hue,[18] including spectacularly intense colors even from very small quantities of material.[19] The introduction of disorder into the system allows further tuning of the intensity and peak of the reflected color to suit a variety of functions. Furthermore, the same nanostructural architectures producing structural colors can be constructed from many different materials, thus escaping the need to use specific dye molecules or toxic ingredients and instead allowing tuning of both color and material to the desired purpose. The ability to make the same colors from a variety of materials also means that such materials can potentially combine color with other functions, such as responsiveness to external conditions like light or temperature for use as sensors and in displays.[20]

This review

Although there are many non-biological structural colors (e.g., labradorite,[21] sedimentary opals,[22] and "thin film effects"[23] like oxide layers and oil films on water), many of the most stunning colors are found in the biological world (Fig. 1). Perhaps the most well-known of these are the feathers of birds[24,25] and the cuticle of beetles[26] and butterflies.[27] In this review, we present an overview of existing research on structural colors in fruits. Structural colors in fruits (see Table I) are of particular interest because their evolutionary adaptations to multiple roles in nature suggest that fruit structural colors may fulfill multiple functions simultaneously, which could be exploited by humans in bioinspired designs. The primary biological function of fruit colors is in visually attracting animals to visit and eat the fruit, thereby removing and dispersing the seed(s).[28] However, the visual function is complex: fruits not only attract legitimate seed dispersers, but also risk attracting seed predators who destroy the seed.[29–31] Fruit colors may also serve alternative functions, such as protection against UV radiation.[32] These multiple biological roles suggest strategies for engineering colorants, which also integrate multiple functions, including more subtle effects such as "hidden" non-visible (e.g., ultraviolet) wavelengths in addition to other human-visible colors, all produced by the same material.[33] Because the study of structural colors in fruits is still in its infancy, new species and structures are being discovered regularly, and new alternative functions that may serve as the basis for bioinspired materials will likely continue to be discovered into the future.

Here, we focus in particular on the physical optics of the three main types of structural coloration in fruits: 1. helicoidal cellulosic cell wall reflectors, 2. lipid layers embedded in the cell wall, and 3. epicuticular wax coatings. For each material, we address the optical mechanism, the biomaterials in which it occurs, how it may be identified, and what application it has in understanding and engineering biomaterials.
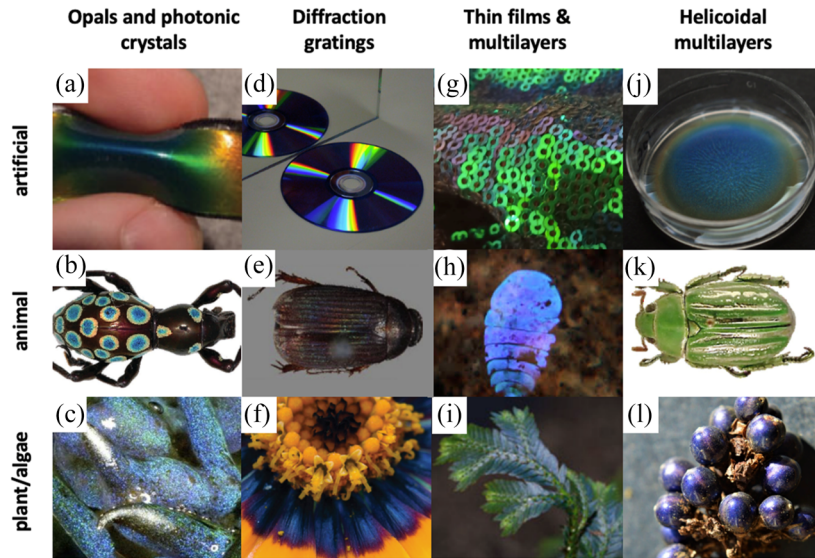
FIG. 1. Examples of structural colors from animals, plants, and human-made (non-biological) materials. (a) Artificial polymer opal,[34] (b) 3d photonic crystals in the weevil *Pachyrhynchus congestus*,[1] (c) opal-type structures in the alga *Cystoseira tamariscifolia*,[35] (d) artificial diffraction grating in a CD,[36] (e) diffraction grating from the cuticle of the beetle *Serica sericea*,[37] (f) diffraction grating from the petals of the daisy relative *Ursinia speciosa*,[10] (g) dichromatic sequins made from thin layers of extruded polymers (plastics),[38] (h) guanine multilayer reflector in the copepod *Copilia mirabilis*,[39] (i) multilayer interference in the spikemoss *Selaginella erythropus*,[40] (j) artificial helicoidal CNC film,[19] (k) helicoidal chitin in the beetle *Chrysina gloriosa* cuticle,[41] and (l) helicoidal cellulose in the fruits of the marble berry *Pollia condensata*.[42] Images in all panels reproduced with permission from original sources. Additional photos (g) and (l) by authors.

TABLE I. List of known species with structural colors in their fruits as of the publication of this Tutorial, organized according to the type of photonic structure. Here, we have divided multilayer reflectors into two categories: Bragg stacks (where the chemical composition of the materials constructing the structure remains unknown) and lipidic reflectors (where lipids of various types alternate with the cell wall).

Helicoidal cellulose	
Pollia condensata, P. japonica (Commelinaceae/Commelinales)	Vignolini *et al.*,[42] Middleton *et al.*[43]
Margaritaria nobilis (Phyllanthaceae/Malpighiales)	Kolle *et al.*,[44] Vignolini *et al.*[45]
Multilayer	
Elaeocarpus angustifolius (Elaeocarpaceae/Oxalidales)	Lee[46]
Delarbrea michieana (Myodocarpaceae/Apiales)	Lee *et al.*[47]
Multilayer (lipidic)	
Viburnum tinus, V. davidii, V. dentatum, V. lautum (Adoxaceae/Dipsacales)	Middleton *et al.*,[9] Sinnott-Armstrong *et al.*,[48] Devide[49]
Lantana strigocamara (Verbenaceae/Lamiales)	Sinnott-Armstrong *et al.*[32]
Epicuticular waxes	
Prunus domestica (including ssp. *intermedia*), *P. spinosa* (Rosaceae/Rosales)	Middleton *et al.*[17]
Vitis vinifera (Vitaceae/Vitales)	
Ribes sanguineum (Grossulariaceae/Saxifragales)	
Vaccinium myrtillus, V. corymbosum (Ericaceae/Ericales)	
Berberis aquifolium, B. darwinii, B. x stenophylla (Berberidaceae/Ranunculales)	
Juniperus occidentalis, J. virginiana (Cupressaceae/Cupressales)	
Abies koreana (Pinaceae/Pinales)	

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Helicoidal cellulose

Helicoidal cellulose nanocrystals, laid down in a periodic pattern, produce polarized reflection of blue light in several species of fruits and seeds (*Pollia* sp., *Margaritaria nobilis*)[42,45] as well as in leaves.[50] During synthesis of the plant cell wall, cellulose is laid down over time.[43,51] In some cases, the synthesis of that cell wall forms pseudolayers, where cellulosic fibrils are laid down consecutively with a regular angular offset to form a helicoidal arrangement (Fig. 2).

Such helicoidal structures are found in the thickened cell walls of surface cells in some structurally colored fruits [Figs. 2(a)–2(d)] and leaves.[50] In structural colors produced by helicoidal cellulose, the periodicity of the helicoid corresponds to a wavelength of visible light, producing resonance [Fig. 2(e)]. The rotation of the fibrils produces a repetitive spatial variation in refractive index, as the fibrils themselves have anisotropic optical density, producing a single layer element with every 180° rotation. The resulting refractive index variation is, therefore, helical and as such structurally reflects only light with a circular polarization that matches the handedness of the cellulosic material and a wavelength that is twice the periodicity in the material [Figs. 2(f) and 2(g)] (where the periodicity of the material is here defined as the single layer element, in which fibrils rotate by 180°).

Helicoidal arrangements of plant cell wall fibrils are common in many plant cells, including in those that do not produce structural color due to insufficient organization and quantity of layers.[52–55] Only in certain species are helicoids sufficiently periodic with enough layers to reflect light; thus, the materials to build this variety of structural color exist throughout plant cells but are only elaborated upon in a few species' fruits and leaves. Reflective helicoidal cellulose was first identified in leaves,[56–60] long before its discovery in fruits of two distantly related genera, *Margaritaria*[44,45] and *Pollia*.[42,43] Other organisms, such as beetles and mantis shrimp, also take advantage of helicoids to create color and other optical effects.[61,62]

Identification of helicoidal materials used as a colorant in nature is, in principle, straightforward because such helicoidal structures reflect circularly polarized light. Observation of materials that reflect circularly polarized light indicates a helicoidal source. A practical method to identify circularly polarized materials in the field is by viewing materials with "3D cinema glasses," which show the color through one circular polarization oriented differently in each eye, which thus allows detection of left- and right-handed polarized reflection. In nature, helicoidal cellulose always reflects left-polarized light (with one exception, in *Pollia condensata*, where left- and-right handed reflecting cells are interspersed[63]). Helicoids may also be confirmed by electron microscopy, either through scanning
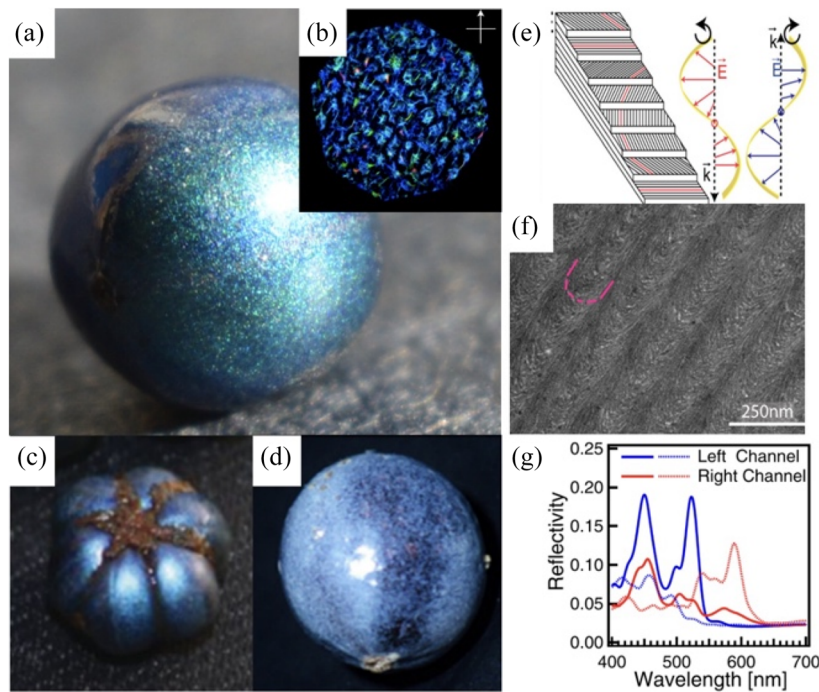
FIG. 2. Helicoidal cellulose has been identified in several species' fruits. (a) Photo of *Pollia condensata* fruit and (b) light microscopy photo of *P. condensata*, showing polarization of individual cells. Photos of additional species with similar helicoidal cellulose nanofibrils, including (c) *Margaritaria nobilis*[45] and (d) *Pollia japonica*.[43] (e) Schematic showing the interaction of light with helicoidal layered cellulose, which results in polarized reflection of light. (f) TEM image showing helicoids in *P. condensata*. (g) Reflectance measurements from individual cells of *P. condensata*, with some cells reflecting only left-polarized light (blue) and others only right-polarized light (red). Images in panels (b),(e)–(g) reproduced with permission from Vignolini *et al.*, Proc. Natl. Acad. Sci. U. S. A. **109**(39), 15712–15715 (2012). Copyright 2012 PNAS. Photo credits: (a), (c), and (d) from Middleton.

electron microscopy (SEM) of cell wall cross sections, where the cell wall can be dried without excessive damage, or through transmission electron microscopy (TEM) of cell wall cross sections.[57]

Helicoidal cellulose nanocrystals (CNCs) extracted from (non-reflective) cellulose fibers, typically from cotton,[64] have already served as the basis for engineered, colorful materials. CNCs self-assemble from suspension to produce a colored helicoidal material, which is flat unless disrupted or patterned. CNCs are very stable materials and demonstrate numerous potential applications of helicoidal cellulose in sensors and colorants.[65]

Although this phenomenon has parallels with the biologically constructed helicoidal cellulose in the structurally colored fruits mentioned here, there are key differences. In the lab, CNCs self-assemble through passive coalescence of the low-energy state arrangement of cellulose nanocrystals. In developing fruits, however, cellulose materials are laid down through an active control process that is yet to be fully understood.[66] The pattern of deposition in *Pollia japonica* has been confirmed by direct imaging of the spectra reflected from the growing cell wall.[43] Unlike the pure cellulose crystals that form CNC materials, the cell wall also includes other materials, such as lignin and hemicelluloses.[67] Another key difference between the helicoids found in CNC materials and those in *Pollia condensata* fruits is the existence of right-hand circularly polarized helicoids, which are not observed in the artificial analog.

It is thought that this handedness reversal may be produced by additional material (along with hemicelluloses) acting as a guide to reverse the handedness.[68] This has been hypothesized because cell walls of left- vs right-handedness have different mechanical properties (which would not be true if the change in orientation were simply a case of the same materials constructed symmetrically in the opposite direction).[63]

Understanding the assembly of helicoidal cellulosic fibrils in plant cell walls, as a phenomenon parallel to self-ordering helicoidal cellulose, might therefore provide insights into engineering prospects for the material. Fruit cells, for instance, eliminate iridescence through hierarchical structuring: the cell walls are curved, which reduces iridescence but retains reflectance in the blue region of the visible spectrum. Artificial engineering incorporating micron-scale curved architectures allows an engineered material to be uniformly colored, rather than iridescent, particulates.[69] Through forming a curved cell wall, helicoidal structural colors achieve the useful properties of being both non-iridescent and particulate, which allows for direct coating of materials.[64,70]

Lipid inclusions in cell walls

A different type of multilayered structural color occurs in the cell walls of several species' fruits (*Viburnum tinus, Lantana strigo-*
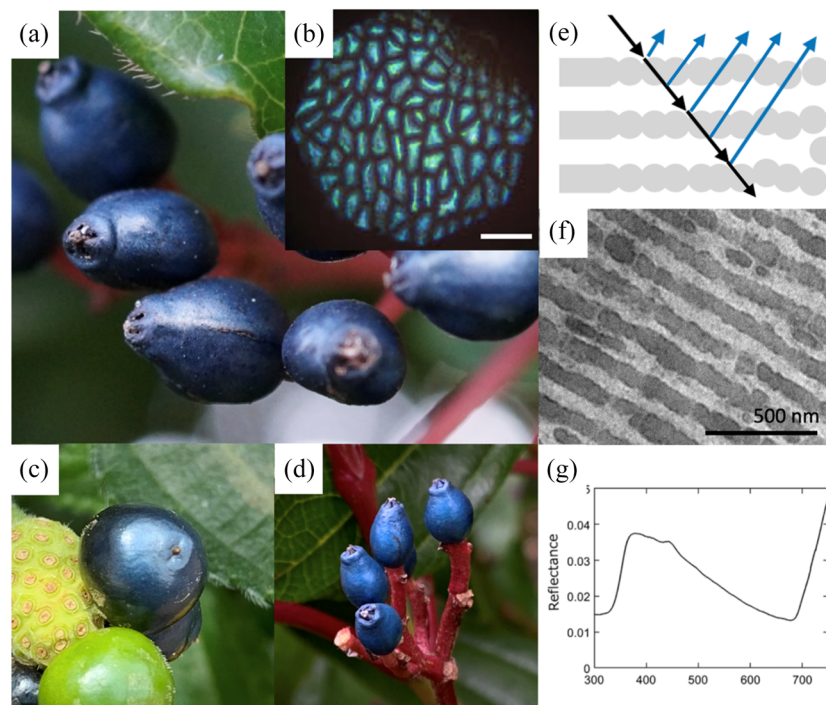
FIG. 3. Layered lipid inclusions embedded in fruit cell walls has also been reported from several species. (a) Photo of *Viburnum tinus* fruit, along with (b) a light microscopy image of *V. tinus* (scale bar = 200 μm). (c) *Lantana strigocamara* and (d) *Viburnum davidii* also produce similar layered lipid inclusions. (e) The structural colors of these species are produced by layered lipid globules arranged as a multilayer reflector. (f) TEM imaging shows that the layers alternate between lipid globules and a cellulosic matrix. (g) Average reflectance from *V. tinus* fruits demonstrates a peak in reflectance at ~400 nm, in the blue region of the visible spectrum. Images in panels (b) and (g) reproduced with permission. Photo credits: (c), (d), and (f): Sinnott-Armstrong.

camara; Fig. 3). Similar-looking structures occur in *Elaeocarpus angustifolius*[46] and *Delarbrea michieana*,[47] although whether the globules are made of lipids or some other material remains unclear in these species and as such we refrain from a full discussion of these species here.

In *V. tinus* and *L. strigocamara*, globular lipid bodies embedded within the cell wall[9,48] produce a brilliant blue color [Figs. 3(a)–3(d)]. The globular bodies are of a photonic lengthscale (roughly 150–200 nm thick in these species) and alternate with a matrix of a similar thickness [with some variation between species; Figs. 3(e) and 3(f)]. Although the refractive index contrast between the lipid globules and the cellulosic matrix is low, there is nonetheless sufficient contrast that the globular multilayer acts as a reflector. In the species *Viburnum tinus*, in which lipid multilayer structures were originally identified,[9] the globules are arranged in layers with a relatively consistent spacing [Figs. 3(a), 3(e), and 3(f)]. The layers are well modeled as a multilayer with the introduction of significant disorder that widens the reflectance peak over a wider wavelength range, reduces its intensity with respect to the number of layers, and increases the angular range over which the light is reflected. This disorder is introduced in the material by the globular nature of the layers and by the imperfect uniformity of the spacing of layers and their orientation with respect to incoming light.

This same architecture has evolved multiple times in different species.[48,71] This is unusual because large quantities of similarly sized lipid globules are rarely found within the cell wall itself.[72,73] In each of these species, the architecture of the cell wall and globular multilayers is slightly different, producing similar overall blue colors but with different perceptual characteristics (e.g., metallic vs plastic-like). This biological diversity demonstrates that small modifications to this basic photonic architecture can produce a variety of hues and optical effects. To our knowledge to date, this lipid-based multilayer reflector is restricted to fruits and has not been identified in any other plant organ.

Without using electron microscopy methods to directly image the fruit cell wall, the unequivocal identification of lipidic multilayer structures is more complicated than with helicoidal cellulose. Differences between the color of pigments released from the plant material and the color it appears suggest structural color. Differences in the appearance of coloration in reflectance and transmission also suggest structural color. However, to confirm the presence of architectures of the right lengthscale to produce structural color and to characterize the structure itself, staining with osmium tetroxide and TEM imaging of cross sections are necessary. Further chemical analyses can then be applied to identify the materials composing the structure.[74] This combination of optical characterization and electron microscopy, alongside modeling of the observed structures, can be used to understand whether the observed structures are the source of structural color.

These structural colors arising from lipids embedded in the cell wall are produced by 3D architectures, with limited iridescence on the macroscale. The hierarchical architecture of these structural colors, wherein multilayers occur within the larger structure of the cell itself, allow for the production of variably saturated colors and reflectances (appearing as "shine") with the same basic structure and materials. Its biological morphogenesis remains an open question, along with how it might be reproduced artificially. Artificial materials have not yet been engineered exploring this architecture

either using the same biomaterials or through replacement with other materials in the two phases.

Epicuticular wax scattering

In what is likely the most common (but underreported) form of structural color in fruits, epicuticular waxes (waxes on the surface of the plant) can scatter light to reflect color (Fig. 4). In conjunction with underlying absorbing pigments (which are generally necessary in structural color to make the reflected light visible against background scattering), this scattering effect can produce vivid coloration[17] [Figs. 4(a)–4(d)]. In this case, a layer of wax particles [Figs. 4(e) and 4(f)] external to the cuticle reflects light before it enters the plant tissue. The wax layer is formed from a coating of wax crystals that self-assemble on the surface of the cuticle.[75] Epicuticular plant waxes are a diverse set of molecules and chemical mixtures, encompassing n-alkenes, n-alcohols, and long-chain fatty acids, and the chemical composition of epicuticular waxes can vary dramatically species-to-species. The range of crystal shapes produced is also highly varied, which provides opportunities for tunable coloration depending on the crystal shape, density, and chemical composition.

Unlike helicoidal cellulose and lipid layers, thin, disordered layers of epicuticular waxes are infiltrated with air. Light is scattered by the highly disordered ultra-thin particle layer, although without a *periodic* structure producing coherent interference. This produces greater scattering intensity at shorter wavelengths, or a UV-blue biased optical profile [Fig. 4(g)]. Unusually, it means that the reflectance profile of these fruits has no peak in the visible (or UV) portion of the spectrum (the maximum visible intensity is defined by human or avian visual receptors). Despite this, they are chromatically distinctive to both humans and birds with additional UV receptors.[17] Other wax structures are known to produce white or glaucous reflectance,[76] but on UV-blue bloom fruits, the structure produces chromatic coloration, due to the steepness of the reflectance spectrum profile of the light scattered from their surfaces and the dark pigmentation inside the outermost cells, which absorbs the scattered light that passes through the wax layer. Epicuticular waxes have evolved to produce UV-blue color on fruits at least seven times,[17] although it is clear that similar wax structures contribute to the optical appearance of many more fruits,[77] as well as leaves and stems.[78] Although bloom most often leads to UV-blue reflectance, other geometries of epicuticular waxes can produce different colors. For example, the gold sheen on *Tradescantia* leaves[79] is produced through thin film interference on oriented wax crystals.

Epicuticular wax is found on almost all the above-ground surfaces of land plants[80] and has highly variable chemistries as well as hydrophobic and hydrophilic properties.[81] This diversity of chemistries and properties means that epicuticular waxes can serve a variety of functions in different species. For instance, they contribute to pest and infection defense[82,83] as well as water management.[84] Epicuticular waxes are also biocompatible and good stable stores of carbon.[85] These properties make them potentially useful in coatings and sprays in food and crop husbandry, on outdoor surfaces, as well as in coatings for medical devices and body-interfacing materials.[86] For identification, epicuticular wax is in general easily removed from the surface through either mechanical abrasion or dissolution in organic solvents. The color can also be eliminated through the application of refractive-index matching oil to the surface. The wax
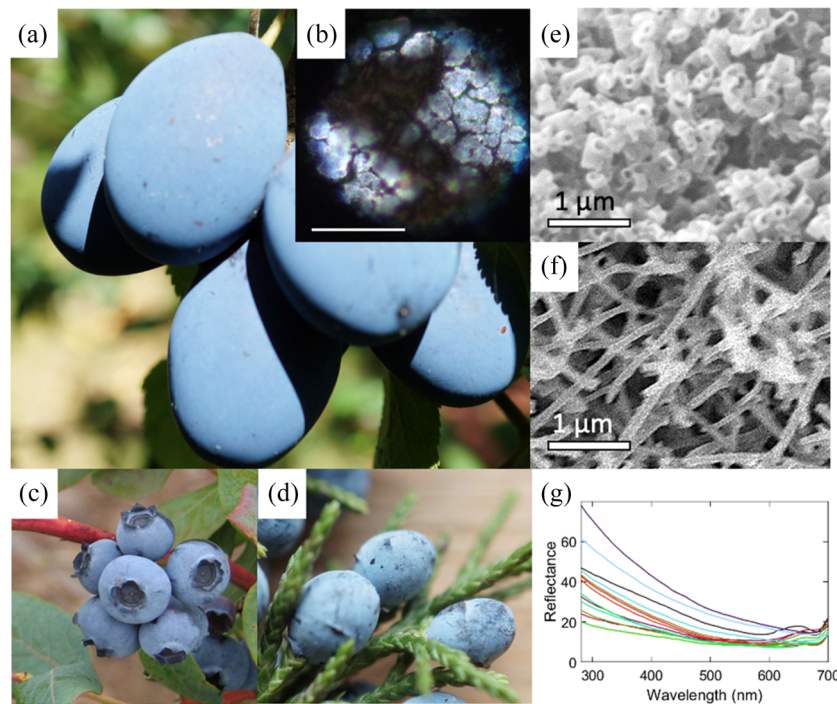
FIG. 4. Epicuticular waxes are a common but underappreciated mechanism of altering plant, and especially fruit, colors. (a) Damson fruit (*Prunus domestica*) with high density epicuticular waxes appears blue. (b) Blueberry wax in reflectance light microscope (scale bar 200 μm). (c) Blueberries (*Vaccinium* sp.) and (d) juniper berries (*Juniperus communis*) also produce epicuticular waxes. (e) and (f) SEM images of epicuticular waxes from plum (*Prunus domestica*) and juniper berries. (g) Reflectance spectra from different subspecies of wild and domesticated plums (*P. spinosa*/*P. domestica*) with epicuticular waxes, showing increasing reflectance into the UV (below 400 nm) region of the visible spectrum. Images in panels (c) and (e)–(g) reproduced with permission from Middleton *et al.*, Sci. Adv. **10**(6), eadk4219 (2024). Copyright 2024 AAAS.

itself can be tested for pigmentation through dissolving and measuring with a spectrophotometer. The spectral profile in blue-scattering wax coatings is UV-blue biased with, in general, no spectral peak, therefore also generally reflecting strongly in the UV—although molecular UV-absorption in some cases reduces this effect.[17]

The crystals are self-assembled from the extrusion of the wax compounds onto the surface, making epicuticular waxes a promising opportunity for artificial replication thanks to their self-assembly to form complex morphologies. Some morphologies of wax have already been replicated artificially,[17,87,88] although in other waxes, it remains an open question how the varied mixture of compounds contributes to the repeated crystallization of nanostructures of similar shape and size.

Other plant structural colors

Although we have focused here on fruits, other plant organs also produce structural colors (Fig. 5). In flowers, the most common mechanism is diffraction gratings (surface corrugation on the photonic scale) including a high degree of disorder, which produces an iridescent blue/UV signal, which is salient to bee pollinators[10,89] [Fig. 5(a)]. In the California poppy (*Eschscholtzia californica*), conical protrusions from the surface cells focus light on pigments in the cytoplasm, thus enhancing the orange appearance of the petals.[90]

In buttercups (*Ranunculus* sp.), a double planar interface leads to high specular reflectance and the characteristic intensity of the yellow color [Fig. 5(c); Ref. 91]. None of these phenomena have yet been identified in any plant organ aside from flowers.

Leaves produce helicoidal cellulose stacks similar to those found in some fruits[57–60] [Fig. 5(d)]. However, some species produce a type of structural color uniquely known in leaves, reflectance from modified chloroplast-like organelles[40,92–94] [Fig. 5(e)]. The functional significance of leaf coloration and reflectance is much more complicated to determine than in fruits or flowers, where color serves as a signal to pollinators or seed dispersers.[28] Leaf surfaces fulfill a range of roles, primarily harvesting solar energy through photosynthesis but also serving other functions such as protecting against herbivory.[95] Most of the structurally colored leaves reported thus far occur in understory rainforest environments with low intensity illumination,[96] which suggests that there may be a common environmental factor selecting for the evolution of structural color in leaves.[97] However, the exact link remains speculative.

One significant question that remains open is why almost all the structural colors found in plants are blue, rather than other colors. Theoretically, any wavelength of visible light could be produced by nanostructures, yet the overwhelming tendency among plants is to create only blue to UV hues, with few exceptions.[33] One possibility is that blue pigments are more energetically expensive to produce or
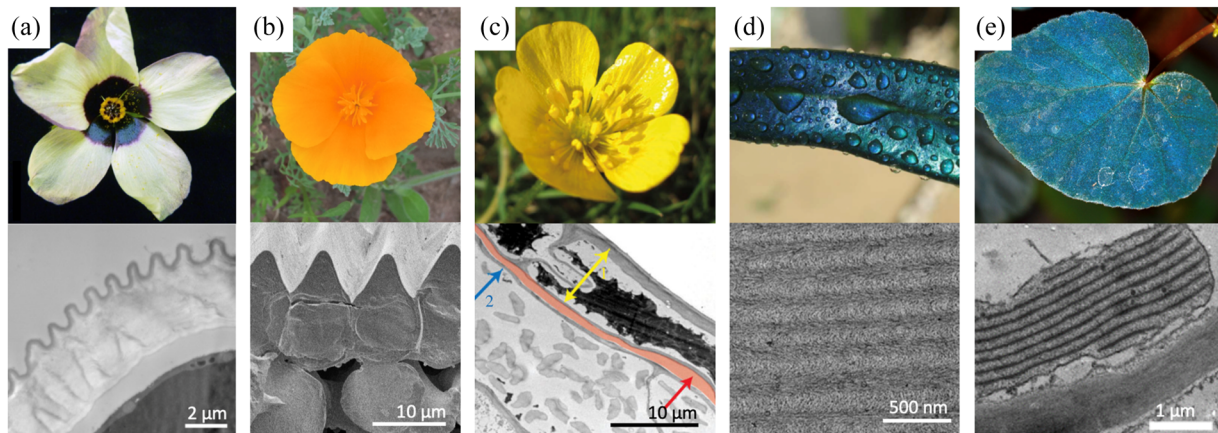
FIG. 5. Other plant structural colors and optical effects. (a) Diffraction gratings occur in flowers, such as those of *Hibiscus trionum*.[10] (b) Conical protrusions of cellulose and cuticle in *Eschscholtzia californica* (California poppy) focus light on the lower wall of the cells, resulting in enhanced color and a silky appearance.[90] (c) A double planar interface produces high specular reflectance in buttercups *Ranunculus repens*.[91] (d) Helicoidal cellulose, as seen in *Pollia* and *Margaritaria* species, also occurs in leaves, such of those of *Microsorum thailandicum*.[57] (e) Iridoplasts, modified chloroplasts, which reflect blue light and can change orientation in response to high or low light levels, occur in some *Begonia* species.[92] Images in panels (a)–(c) and (e) reproduced with permission from original sources. Photo credit: (d) Lundquist.

difficult to evolve than pigments producing other colors, resulting in greater opportunity for blue structural colors to persist.[97] Furthermore, plants have pigments capable of producing green, red, yellow, and orange hues (chlorophyll, anthocyanins, flavonols, and carotenoids, along betalains in some groups of plants).[98] The prevalence of these pigment-based methods of producing most other colors may render structural color an unnecessary and expensive method of producing colors that are already easy to evolve using materials plants already possess. Reasoning from the perspective of physical optics suggests that the addition of disorder tends to add a blue contribution to the spectrum, meaning that disordered photonics can produce "pure" blue, but only mixed colors at longer wavelengths.[15] Both perspectives are reasonable and may contribute to the prevalence of blue structural colors over other structural colors. However, structures producing other hues are found in the animal kingdom,[26,99] so it is somewhat surprising that so few have been identified in plants. The lack of non-blue structural colors in plants may also partly result from limited research, rather than their true lack in nature.

Engineering structural color

The most common, plant-derived biomaterial used in engineering applications is cellulose and its derivatives.[100] In the reproduction of cellulose nanocrystal helicoids, like those found in the outermost cells of *Pollia* and *Margaritaria* fruits, cellulose nanocrystals are suspended and then allowed to assemble to the low-energy packing state, which produces a left-handed helix.[19] Although CNCs have also been coated onto a substrate using non-entropic assembly, through spin-coating,[101] the majority of applications have made use of the self-assembling properties of cellulose nanocrystals, with tunable pitch lengths using charge properties of the crystals. However, the use of CNCs has been extended further, into inkjet printing,[102] microfluidic encapsulation,[103] infiltration and embedding in other materials,[104] and others.[105] An important benefit of the CNC

material is its innate assembling properties, meaning that it permits a bottom-up and therefore scalable approach.

In contrast, there has been very little exploration of the potential of reproducing the other fruit coloration strategies. Recrystallization of waxes for coloration and other effects[17] has been suggested, and carnauba waxes are already used as a biodegradable and non-toxic coating in food packaging,[106] although the latter does not utilize waxes for color production. The lipid globules encapsulated in cell wall structures have had less attention, in part because their discovery is still quite recent, but also because a widely known self-assembling analog to these materials remains to be identified.

In order to use the photonic architectures found in fruits as engineered materials, they need to be reproduced with either top-down or bottom-up approaches or a combination of both. Engineering approaches do not need to mimic the biological method to constructing photonic materials, but understanding how plants achieve the construction of such complex structures may stimulate new engineering methods and ideas to produce similar structures on a large scale. The synthesis of helicoidal cellulose in plant cell walls is believed to occur by active biocontrol, not by passive self-assembly.[43] Microtubules are thought to guide the placement of cellulose microfibrils, in what is effectively a vast parallelization of a top-down approach to laying down cellulose into a helicoidal arrangement.[66] This parallelization means that the system as a whole is functionally "self-assembling" from the perspective of the plant, despite requiring some cellular machinery. This combination of both top-down (through guided deposition of cellulose) and bottom-up (through the self-assembly of CNCs) is particularly exciting for the current state of the art in material engineering in part because it means that abiotic controls (thermal, chemical, or through photonic activation) can alter the color produced by the structure without needing to change the system.[107] Many such self-assembling biological molecules work alongside active biological control to build up complex architectures. By incorporating these self-ordering natural materials for photonic engineering within scalable (and top-down)

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processes, we have the potential to access new realms of nano-engineering.

The range of structural color produced synthetically is now wide and continues to grow. Yet, many of these materials and methods for creating them have not made it into everyday use. The transfer of technologies based on structural colors does carry some constraints that differ from those of other plant products, such as pigments. Some structurally colored materials require such different handling to pigments that they cannot simply substitute pigments in current manufacturing processes, and instead require rethinking the manufacturing process in order to accommodate the properties of the structurally colored materials. Other structural colors have restricted ranges of use (due to temperature- or mechanical-robustness). A common issue for engineered structural color is that they exhibit iridescence, which makes them unsuitable for use as ordinary colorants. Structural colors found in fruits could be part of a solution to this problem, as the effects we describe in this paper are in general non-iridescent.

Many plant biomaterials have benefits with regard to biocompatibility and sustainability. Plants produce materials of incredible strength, durability, flexibility, and adaptability to extreme environments. There have been valuable advances in developing structural color from animal biomaterials such as chitin/chitosan, keratin, melanin, and silk.[108] As we have seen from animal-derived products, the potential for biomaterials is great; we believe that the future of plant science will continue to provide significant lessons and opportunities for engineers and physicists of all kinds. In particular, those pursuing the development of producing durable, hardwearing, self-replicating, responsive, and multifunctional materials have much to learn from plant optical biomaterials.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

R. Middleton: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal); Writing – review & editing (equal). **M. Sinnott-Armstrong**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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