PERSPECTIVE

Colonizing Taxa (Weeds) as Sources of Natural Pigments and Dyes

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Abstract

There is a growing global demand in the dyes and pigments industry for naturally-occurring pigments as substitutes for chemically synthesized pigments. This is because of increasing concern about potential adverse health effects for those involved in dye and pigment production and concerns about environmental pollution that can result from dye industries, discharging excessive and unused dyes into waterways. Naturally occurring, principal plant pigments: anthocyanins, betalains and carotenoids are much favoured over chemical dyes and pigments because of their safety to humans. Once optimized, the extraction, processing and production of plant dyes are also relatively benign from an environmental perspective.

The story of human civilizations is intimately linked with colour and the use of natural plant pigments from several well-known sources. This paper provides a brief review of this historical link of plant pigments, from ancient civilizations to the present. It also provides an overview of the chemistry of the most commonly used plant-based pigments (anthocyanins, flavones and flavonoids).

With examples of potentially the most useful taxa, we also explore the opportunities for colonizing taxa (weeds) to be utilized as sources of natural dyes and pigments, which can substantially supplement or substitute the synthetic dyes and pigments, currently available. There are many species to select from although only a few appear to be presently yielding commercially exploitable natural plant pigments. The global attention continues to be on the well-known species, already cultivated or harvested from the wild, while the research on newer sources is sparse and uncoordinated, except in a few countries and regions with traditional, long histories of natural pigment use.

Some natural dyeing technologies have been developed by artisans and practical-minded, lifestyle enthusiasts. In searching for eco-friendly technologies to support the livelihoods of people more broadly, dyes and pigment-based industries appear quite significant. There are technological constraints to overcome but these are no more challenging that any others we face. The global outlook for an expansion of the sources of dyes from plants is favourable and the potential contribution from colonizing plants as new sources is also quite significant. Our review finds that the research related to pigments from natural sources (i.e. applied chemistry, biochemistry, pharmacology and industrial applications) is quite intense in many countries, particularly in the last two decades.

Keywords: weeds, plant dyes, pigments, chemical dyes, anthocyanins, carotenoids, betalains, food colourants, indigo, woad, textile dyes

Introduction

Throughout history, natural dyes have been associated with humans. The ancient Mayans, Incas, Aztecs, Chinese, Indians, Greeks, and Persians used natural plant pigments extensively to colour their garments and other woven materials, such as rugs, and yarn (Francis, 1992; Green, 1995; Roquero, 2008; Franco-Maass et al., 2019).

In the year of 1856, Sir William Henry Perkin introduced the first synthetic organic dye - mauveine, synthesized from aniline. A new era of the chemically-synthesized dye industry thus began with the commercialization of mauveine. In subsequent years, as chemistry developed, a large number of synthetic dyes have been made, using relatively simple chemical conversions. A very large number of chemically-synthesized pigments have been commercialized, since the early late-19th and throughout the 20th Century (Green, 1995).

Synthetic dyes are popular because they are cheaper to produce and are brighter in colour than natural pigments and can produce a large array of colour variations. The introduction of synthetic dyes in the dye industry greatly affected the commercial production of natural dyes from plant sources. Throughout the 20th Century, the use of natural dyes declined in various dye-using industries, which preferred the more reliable and less expensive synthetic dyes (Green, 1995).

Unfortunately, synthetic dyes have negative side effects for humans and the environment, including health and safety risks for the people involved in the industries such as cancer, caused by toxic mordants (e.g. ferrous sulphate) (MacFoy, 2004). Significant environmental pollution of waterways has also resulted from the dye extraction and production processes, involving mordants and other chemicals (Mahanta and Tiwari 2005; Sutradhar et al.; 2015; Teron and Borthakur, 2012).

As a counter to the use of synthetic dyes, there has been a growing interest over the past few decades in natural plant pigments and dyes. Although not always cost-effective, natural plant pigments are considered environmentally safer, as they are less toxic to humans and other animals and are biodegradable. As consumer demand grows strongly for natural products, dyes of natural origin are becoming increasingly popular, especially in developing countries and there is also an increasing global demand for such products (Green, 1995).

Obtaining natural plant dyes have traditionally been mostly a cottage industry. However, there are clear signs that plant harvesting, dye extractions and processing are fast becoming profitable, medium-scale industries in some countries that can increasingly contribute to the livelihoods of rural folk, adding to household incomes.

Although plants exhibit a wide range of colours, not all of these pigments can be used as dyes. Some do not dissolve in water, some cannot be adsorbed onto plant fibres, whereas others fade when washed or exposed to air or sunlight. In a recent review of plant dyes, Siva (2007) commented: "*It remains a mystery, why plants reward us with vibrant dyes*".

Research on plant pigments dates back at least a century or more, which has resulted in a vast repository of knowledge of their chemistry, biochemistry and other aspects (Mansour, 2018; Delgado-Vargas et al., 2000). Nevertheless, research on the source plants has been sporadic and limited in different countries and societies.

Our objective in this paper is to draw on such available information and assess the potential for colonizing taxa (weeds) to be sources of natural plant pigments, which could be developed further. We also provide a brief historical overview of plant dyes, contextual discussions and perspectives to illustrate the opportunities for promoting colonizing taxa as sources of natural plant pigments.

A brief history of plant- and insect-based dyes

Obtaining colourful plant dyes was an ancient tradition in the pre-Columbian civilizations in Mesoamerica and South America for millennia. Ethnographic studies of ancient records of the Olmec, Mayan, Aztec and Inca civilizations in Mesoamerica indicate the dyeing of textiles dating back several millennia (Baryanyovits, 1978; Roquero, 2008; Franco-Maass et al., 2019).

The earliest written record of the use of natural dyes was found in China dated 2600 BC. Dyeing was known as early as 2500 BC in the Indus Valley period in sub-continental India, and in the Greek, Persian and Roman civilizations, leading to Middle Ages in Europe (500-1500 BC) (Green, 1995; Han, 2015; Han and Quye, 2018; Li et al., 2019).

One of the earliest indications of textile dyeing comes from a 5000-year-old piece of cloth coloured red with madder (*Rubia cordifolia* L., Family Rubiaceae) found in the Indus Valley Civilization sites at *Mohenjo-Daro*, in Pakistan (Siva, 2007). Madder continues to be a pre-eminent global dye plant. It is a climber, which grows abundantly in the forests of Pakistan, India, China, Korea, and Japan. The roots yield alizarin and several analogues (anthraquinonoids), which are pigments that have been used to dye silk and wool red since ancient times (Siva, 2007; Sabatini et al., 2020).

Cochineal – an ancient dye

Cochineal dye, or carmine ("Spanish Red") dye[1] is an ancient insect-based dye that dates back to ancient Aztec, Maya and Inca civilizations in Central and South America. Archaeological evidence indicates that it may well be the earliest recorded natural dyes used by humans (Baryanyovits, 1978; Antunéz De Mayolo, 1989; Lambare et al.,, 2011; Diaz-Cayeros and Jha, 2014; Armitage et al., 2015). It is certainly one of the best-known dyes used by human societies.

Dactylopius coccus Costa, 1835 (syn. *Coccus cacti* L., 1758) is a scale insect from which the crimson-coloured carmine dye is derived. This tropical South American insect lives on many different kinds of *Opuntia* cacti, feeding on the plant (Figures 1, 2 and 3). Its most preferred cacti species is prickly pear (*Opuntia ficus-indica* (L.) Mill.), which has been introduced across the globe. This species is now prevalent in Africa and the Indian sub-continent (Brutsch and Zimmerman, 1993).

Figure 1. Cochineal beetles feeding on *Opuntia* spp.

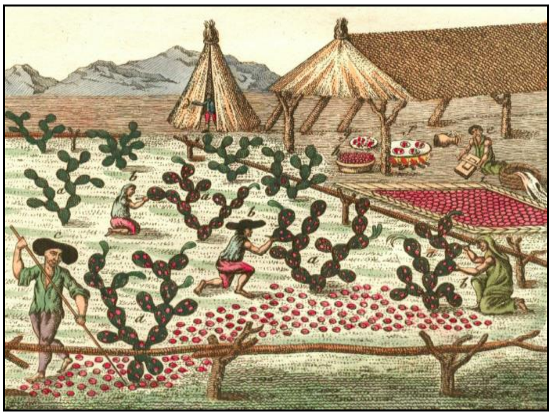


Figure 2. A pictorial depiction of Cochineal beetles feeding on cacti, harvested in Central America

[1] The word cochineal is derived from the French "cochenille", derived from Spanish "cochinilla", in turn derived from Latin "coccinus" meaning "scarlet-coloured".

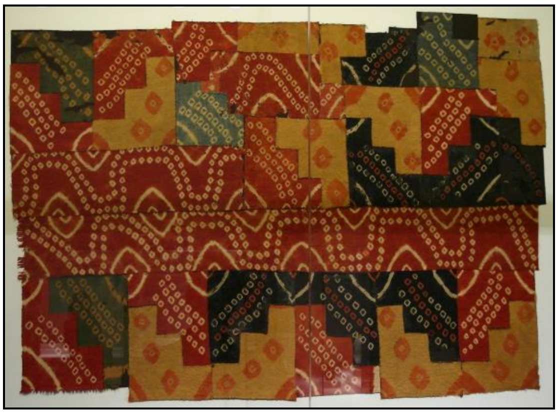


Figure 3. A pre-Colombian textile dyed with cochineal (dated to 800-1300 AD)

The cacti and the cochineal insects were also introduced to Australia by Captain Arthur Phillips, in 1788, as the continent was first colonized. However, the insect failed to establish. The cacti, on the other hand, ravaged many parts of Australia, before it was brought under control using a biological control agent – the cacti moth [*Cactoblastis cactorum* Berg, 1885] (Donelly, 2016; NMA, 2022).

Cochineal insects are a highly sought-after commodity even now. The harvested insects are sun-dried, crushed, and dunked in acidic alcohol to make an extract of carminic acid or carmine (Figure 4), depending on the processing. Extracts from about 80-100,000 insects are needed to produce one kg of carmine dye, which is most commonly traded as a powder with a carminic acid content of 40 to 60%. Liquid aqueous alkaline forms and their spray-dried derivatives are also available. The primary uses of carmine are as a colourant in the food, pharmaceuticals and cosmetics industries (Baryanyovits, 1978; Green, 1995).

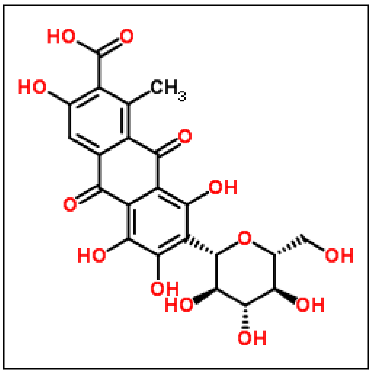


Figure 4. Structure of Carmine ($C_{22}H_{20}O_{13}$)

Peru continues to be the largest producer of cochineal, followed by Mexico, Chile, Argentina and the Canary Islands (Green, 1995). The global demand for carmine is still quite high. The carmine-red industry was worth US $ 33.9 million in 2017 and is expected to grow at a rate of 6.7% per year to about US $ 57.5 million by 2025. Most of this demand is from the food colourant industry (Allied Market Research, 2022a).

The interest in cochineal and carmine dyes as economically-viable industries for poverty alleviation has been awakened in the past decade or so throughout Latin American countries, especially Mexico, where, during the 16th and 17th Centuries, it was the third-most valued commodity, after gold and silver (Diaz-Cayeros and Jha, 2014).

However, cochineal dye and carmine red, used in foodstuff has also led to an increased incidence of severe allergies in humans, noted in the past two decades. These have led to calls for health risk assessments and strict regulations of natural plant pigments, increasingly used globally as food colourants (Voltolini et al., 2014).

Indigo – the King of Dyes

Indigo, a blue pigment obtained from inkweed (*Indigofera tinctoria* L.) and several other weedy *Indigofera* species, is considered the '*King of Dyes*' (Sabatini et al., 2020). In modern times, many other plant species have also been found to contain indigo pigment molecules. Indigo is arguably the world's oldest-known natural blue dye, in almost all cultures. It later became world-famous because of the blue-dyed *denim* fabric (McKinley, 2011).

Indigo's history is also steeped in past civilizations, the Middle Ages (500-1500 AD) and the colonial era (about 1490s to about 1960s). The oldest known indigo-dyed fabric, dated to 6,000 years ago, was found in Peru (Splitstoser, 2016). Its uses continue unabated in fabric colouring in modern-day Americas, the Middle East (Iran, Turkey, Iraq), South Asia (India, Pakistan, Bangladesh) and South-East Asia, especially China (van Schendel, 2008). Historically, indigo-yielding plant species were important cash crops from Central Asia to the southern United States and Central America. Indigo-dyed textiles were widely traded along the legendary *Silk Road* that linked China to Europe (Li et al, 2019; Zhang et al., 2019).

Indigotin, the blue dye (Figure 5), is produced from a glycoside in the leaves. Indican, its source glycoside ($C_{14}H_{17}NO_6$), is a colourless water-soluble derivative of the amino acid tryptophan. Indican readily hydrolyzes to release β-D-glucose and indoxyl. Exposure to air oxidizes indoxyl to the insoluble blue pigment indigotin. Indican is obtained from the processing of the plant's leaves, which contain as much as 0.2–0.8% of this compound.

The leaves are soaked in water and fermented to convert the glycoside to indigotin by natural enzymes in the plant (viz. β-d-glucosidase and β-glucuronidase). Indigotin precipitates from the fermented leaf solution when mixed with a strong base, such as sodium hydroxide, pressed into cakes, dried, and powdered. The powder is then mixed with various other substances to produce different shades of blue and purple.

Many Asian and South-East Asian countries have used indigo as a dye, particularly for silk, for several millennia. Indigo dye was also known to ancient civilizations in Mesopotamia, Egypt, Persia, Greece, Italy, Mesoamerica, Andean countries (Peru, Chile) and West Africa (McKinley, 2011; Mansour, 2018; Li et al., 2019; Sabatini et al., 2020).

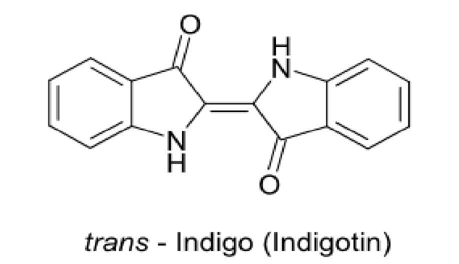


Figure 5. *trans* Indigo (Indigotin) ([2(2′) *E*]-[2,2′-Biindolylidene]-3,3′(1*H*,1′*H*)-dione)

Indigo was also cultivated in India, which was the earliest major global centre for its production. Ancient civilizations valued indigo more than gold as a luxury product. In India, indigo use can possibly date back to 4000 years. During the Middle Ages, indigo moved with other trade goods through the well-established trade routes in Asia. Venetian dyers called it the '*Endigo fino le Bagad*'("*fine Baghdad indigo*"). Baghdad was a major trade centre in Western Asia, *en route* from India to Europe. The indigo sold in Baghdad originated in India. Marco Polo (1254-1324) reported in the 13th Century that the indigo he saw in India was unlike the Venetian indigo (Rembert, 1979; van Schendel, 2008).

By the 16th Century, the Portuguese had established a sea route around Africa (Vasco de Gama, in 1498) to India. By 1516, they were importing indigo into Europe. The Portuguese then introduced small-leaved indigo (*Indigofera suffruticosa* Mill.; Family: Fabaceae), into Asia, especially India. Until that time, true indigo (*Indigofera tinctoria* L.), a native of tropical and temperate Asia and Africa, was the indigo of commerce (Rembert, (1979; van Schendel, 2008). *Indigofera tinctoria* continues to be a high-value rotational, legume crop in India (Figure 6).

In the colonial era in Asia, indigo was a vital commodity imported from the East to the West, firstly by the *Dutch East Indies Company* (1602-1799) and, later, by the *East India Company* (1600-1873) and the *British Raj*. In a single year (1838), the British exported six million pounds of indigo from India, worth two million sterling pounds in the London markets (Nadri, 2015).

Indigo is also closely linked with America's history and especially, slavery. Enslaved Africans carried the knowledge of indigo cultivation from

Africa to the USA. In the 1700s, the profits from indigo outpaced those of sugar and cotton. During the American Revolution (1765-1791), the dollar had no strength, and indigo cakes were used as currency. The original American flag was also made from indigo textiles (Nadri, 2015).

Figure 6. *Indigofera tinctoria* (Fabaceae)

Nowadays, India dominates global indigo production. Indigo is called “blue gold” or “*Neel Amma*” (an endearing term meaning ‘*Blue-Mother*’) by local communities in many parts of India (Figure 7a, 7b). The thriving export market is quite small and priced at about Indian Rupees 3000 (US $ 41 per kg), which cannot compete with synthetic indigo dye, priced around US $ 9 per kg. Nevertheless, cultivating Indigo, dye extraction, and colouring fabrics collectively provide significant rural employment. The natural dye yields about Indian Rs. 20,000 per acre per year. However, the dye production processes expose workers to the dye and other chemicals with unknown effects (see Figure 8) (McKinley, 2011; Gilon, 2020).

As colonizing taxa, *Indigofera* species grow fast in the warm and wet tropics, and even in some parts of warm-temperate countries, such as Korea, Japan and Australia. Its cultivation needs little fertilization, and plants can be harvested after three months of growth. As an example of the potential to utilize weeds for human development, it remains a significant but much under-utilized species.

In the USA, indigo cultivation has now become a niche market, practised by artisans and weavers, interested in natural dyes. An influential not-for-profit organization - *The International Center for Indigo Culture* (ICIC), based in South Carolina, explores the plant’s rich past and promising future. The ICIC provides training on cultivating indigo, dye production and generating profits as a livelihood enterprise (Miller, 2019).

Other sources of Indigo

Records indicate that the ancient Chinese obtained indigo from not just Indigofera tinctoria but also from the Chinese rain bell [*Strobilanthes cusia* (Nees) Kunz.; Family Acanthaceae] and millgar (*Wrightia laevis* Hook.f.; Family Apocynaceae) (Zhang et al., 2019). Both are well-known ornamental flowers.

A third well-known indigo source is Woad (*Isatis tinctoria* L.; Family: Brassicaceae) a common weed of disturbed habitat, native to Central Asia and Southern Europe (Figure 9). Woad has been used as a source of indigo since ancient times (Speranza et al., 2020). Archaeologists have discovered textile remains, dyed in blue, obtained from woad, and well preserved from the Neolithic, Bronze, and Iron Ages (Mouri et al., 2014).

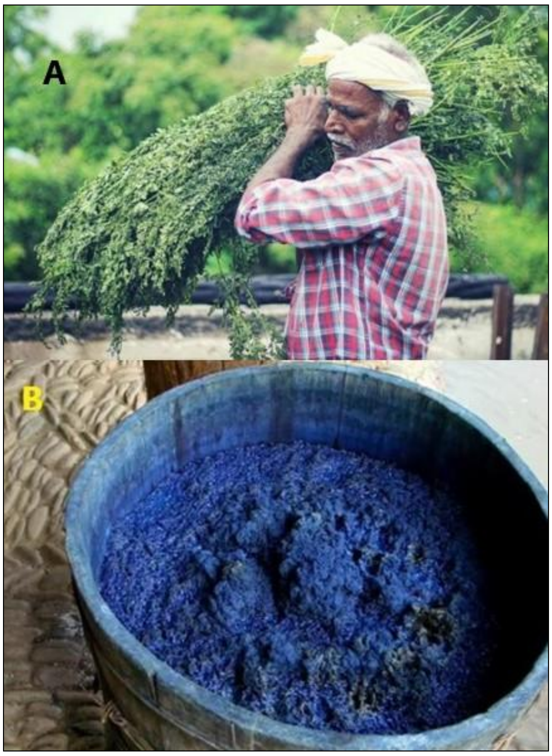


Figure 7. (a) A worker in India’s Indigo industry carrying Indigofera plants for processing; (b) A vat of Indigo after pigment extraction and precipitation.

Figure 8. Indigo cakes are cut into blocks before drying and packaging (source: Gilon, 2020)

The ancient Egyptians also used *Isatis tinctoria* as an indigo source to dye colourful wrappings of mummies and other decorative artworks. Historical accounts on the use of indigo obtained from woad in Europe date back to Roman times. Historical sources report that Celtic and Germanic people used woad to paint their bodies and hair for prophylactic or ritual purposes. *Pliny the Elder* (23-79 AD), in his 12-volume encyclopaedic *Naturalis Historia*, reported the custom of female Britons covering their bodies with indigo blue for religious ceremonies. Julius Caesar (100-44 BC) reported in his book *De Bello Gallico* that the Celtic populations used woad indigo to colour themselves (tattoos) to generate a fearsome appearance. The Romans called these people '*Picti*', which means "*painted people*", suggesting that the woad dye may have been used both for textile and body art (Zech-Matterne and Leconte, 2010).

Records indicate that woad was widely cultivated in Europe (Germany, France, England and Italy), and extensively used as indigo dye and medicinal plant during the 12th to 17th Century.

Figure 9. Woad (*Isatis tinctoria*)

In the early 17thCentury, *Isatis tinctoria* was intentionally taken from Europe into North America by early colonists as a textile dye crop. However, in the late 17th Century, the use of woad as a dye declined in Europe due to the import of indigo blue from *Indigofera tinctoria*, cultivated in India, and other *Indigofera* species, grown in the Caribbean and the American colonies. In the 19th Century, the production of synthetic blue dyes then led to a complete abandonment of woad as a dye source.

Nevertheless, *Isatis tinctoria* is well recognized as an important source of two indolic alkaloids - indigo (blue coloured) and indirubin (red coloured), both of which are extensively used to dye textiles, cosmetics, foods, and pharmaceutical preparations. As a ruderal weed, woad is now widespread all over Western and Southern Europe, the Mediterranean region and Western Asia, and has extended its distribution northwards into Southern Russia.

There is currently a significant research interest in Europe to cultivate and develop woad as a commercial source of indigo dye. The species appears to be well suited to mountainous areas and could be successfully reintroduced as a crop in areas with climatic conditions (CORDIS, 1997; Guarino et al., 2000; Spataro and Negri, 2008).

Anthocyanins

All plants possess chlorophyll, the ubiquitous, green, photosynthetic pigment. In addition, flowering plants (Angiosperms), as well as evolutionarily more primitive liverworts and mosses, also possess, a wide range of other pigment molecules, which occur in different plant parts. These are primarily flavones and flavonoids and their coloured derivative compounds and are called "anthocyanins", derived from two Greek words: *anthos*, which means flower, and *kyanos*, which means dark blue (Blank, 1947 [2]; Clevenger, 1964a, b; Harborne and Williams, 2000; Pina, et al., 2021; Cruz et al., 2022).

Anthocyanins are water-soluble and mostly occur in plant cell vacuoles. Along with their flavonol and flavone co-pigments and metal ions, influenced by vacuolar pH, anthocyanins produce an infinite array of flower colours, which range from orange to blue (Harborne and Williams, 2000; Delgado-Vargas et al., 2000; Tanaka et al., 2005). These pigments are usually associated with floral tissues and fruits of flowering plants but are present in leaves and other tissues as well (Yoshida et al., 2009). Other flavonoids and flavones are essentially colourless and yet they provide the whiteness in flowers and also act as co-pigments to anthocyanins (Yoshida et al., 2009; Pina et al., 2021; Cruz et al., 2022).

Anthocyanins are responsible for the diverse pigmentation from orange to red, purple and blue in flowers and fruits, such as blackberry (*Rubus fruiticosus* L. agg.; *Rubus laciniatus* Willd. and other *Rubus* spp.), red raspberry (*Rubus idaeus* L.), black raspberry (*Rubus occidentalis* L.) blueberry (*Vaccinium corymbosum* L.), cherry (*Prunus avium* L.), black currant (*Ribes nigrum* L.). apple (*Malus domestica* Borkh.), plum (*Prunus domestica* L.), blood orange [*Citrus* x *sinensis* (L.) Osbeck], elderberry (*Sambucus nigra* L.) and grapes (*Vitis vinifera* L.) (Clifford, 2000; Horbowiczi et al., 2008).

[2] F. Blank's 1947 article refers to the fundamental work of Paul Karrer and Richard Willstätter on anthocyanins in the late-early-20th Century. Most of the original work on anthocyanins was published in *Justus Liebigs Annalen der Chemie* (often cited as just *Liebigs Annalen*), which is one of the oldest in Organic Chemistry journals. It was first established in 1832 (**https://en.wikipedia.org/wiki/Liebigs_Annalen**).

The same pigments are involved in different colours of vegetables, such as red onion (*Allium cepa* L.), radish [*Raphanis raphanistrum* ssp. *sativus* (L.) Domin], red cabbage (*Brassica oleracea* L., red lettuce cultivars (*Lactuca sativa* L.), eggplant (*Solanum melongena* L.), red-skinned potato (*Solanum tuberosum* L.) and purple or red sweet potato cultivars [*Ipomoea batatas* (L.) Lam.]. Often, these compounds also occur in leaves, stems, seeds, and other tissues (Horbowiczi et al., 2008).

Thus far, 19 anthocyanidins have been isolated, characterized and identified for their characteristic colour (Table 1). These 19 anthocyanidins are responsible for the production of an infinite array of colours in flowering plants when they combine with sugars (glycosides) and metals. Chemically all anthocyanidins are highly oxidized 2-phenyl benzopyrylium cation (Blank, 1947). This 2-phenyl benzopyrylium cation (flavylium cation) is also called the chromenylium cation (Figure 10). The positive charge on the oxygen atom renders the formation of a long conjugated double bond chain, which is important for colour formation (Blank, 1947).

The substitutions in the A, B and C rings lead to colour variations. For instance, pelargonidin, the commonest of the anthocyanidins, which range in colour from orange to pink contains four hydroxyl substitutions, two in A and one each in B and C. The addition of one more hydroxyl group to pelargonidin at the 4'-position in the B ring shifts the colour from red to magenta and the compound is cyanidin (see Table 1). One more addition of a hydroxyl group to cyanidin at the 5'-position (a total of six OH groups) gives rise to the formation of delphinidin pigment with a blue to purple-black colour.

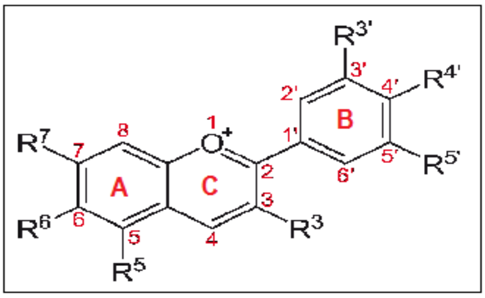
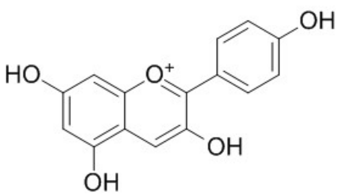
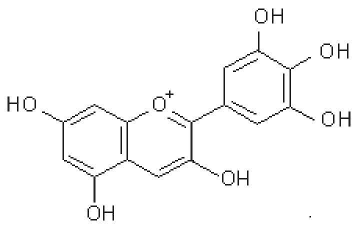
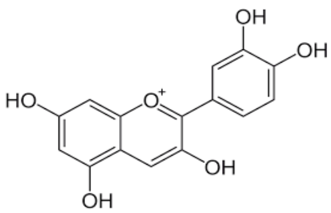
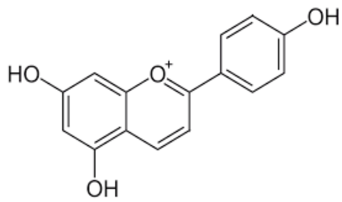
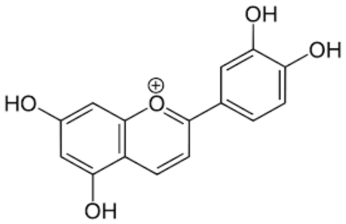
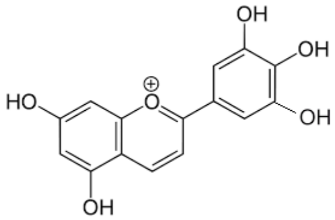
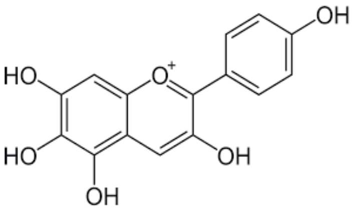
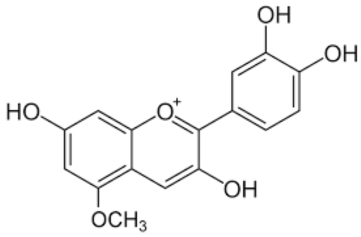
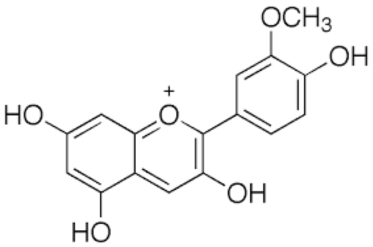
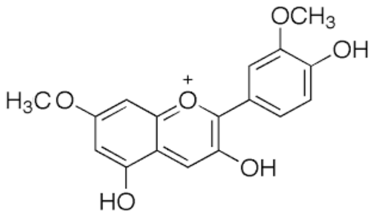
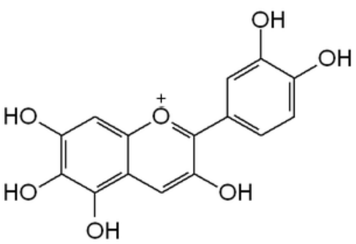
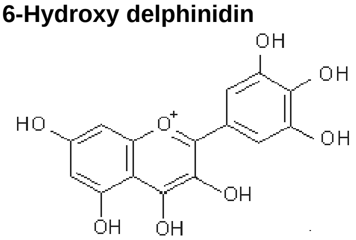


Figure 10. The flavylium cation: a benzo-pyrylium cation with a phenyl group substitution in position 2

Table 1. Different anthocyanidins with their chemical structures, names, colours, and plant sources

Pelargonidin  Name: 3,5,7,4'- tetrahydroxyl flavylium Colour: Orange Source: Horseshoe Geranium (*Pelargonium zonale* (L.) L'Hér.) [Geraniaceae]; morning-glory (*Ipomoea* L. spp.) [Convolvulaceae]; purpletop (*Verbena* L. spp.) [Verbenaceae] Reference: Willstatter and Bolton, 1915; Toki, et al. 1995; Saito et al., 1996; Freyre and Griesbach, 2004; Diretto et al., 2019	**Delphinidin**  Name: 3,5,7,3',4',5'-Hexahydroxyflavylium Colour: Blue-red Source: Field larkspur (*Delphinium consolida* L.) [Ranunculaceae] Reference: Willstatter and Bolton, 1915
Cyanidin  Name: 3,5,7,3',4'-pentahydroxyflavylium Colour: Orange-red Sources: cornflower (*Centaurea cyanus* L.) [Asteraceae], cotton-rose mallow (*Hibiscus mutabilis* L.) [Malvaceae], knotweeds (*Polygonum* L. spp.) [Polygonaceae] Reference: Willstatter and Everest, 1913; Freyre and Griesbach, 2004	**Apigeninidin**  Name: 5,7,4'-trihydroxyflavylium Colour: Orange Sources: Cardinal flower *Rechsteineria cardinalis* (Lehm.) Kuntz. [Gesneriaceae]; *Adiantum* L. spp. [Adiantaceae], and *Dryopteris* Adans. spp. [Aspleniaceae]; sorghum (*Sorghum bicolor* L.) [Poaceae] Reference: Robinson and Robinson, 1932

Luteolinidin  Name: 5,7,3',4'-Tetrahydroxyflavylium Colour: Orange Sources: *Rechsteineria cardinalis* (Lehm.) Kuntze [Gesneriaceae], *Bryum cryophilum* Martensson [Bryaceae], *Adiantum* L. spp. [Adiantaceae], and *Dryopteris* Adans. spp. [Aspleniaceae], *Sorghum bicolor* L.[Poaceae], *Azolla* Lam. spp. [Salviniaceae] Reference: Crowden and Jarman, 1974	**Tricetinidin**  Name: 5,7,3',4',5'-Pentahydroxyflavylium Colour: Red Source: *Camellia sinensis* L. [Theaceae] Reference: Roberts and Williams,1958
Aurantinidin  Name: 3,5,6,7,4'-Penta-hydroxyflavylium Colour: Orange-red Source: *Impatiens aurantiaca* Teijsm. ex Koord. [Balsaminaceae] Reference: Clevenger, 1964b	**5-Methyl cyanidin**  Name: 3,7,3',4'-Tetrahydroxy-5-methoxyflavylium Colour: Orange Source: *Egeria densa* Planch. [Hydrocharitaceae] Reference: Momose et al., 1977
Peonidin  Name: 3,5,7,4'-Tetrahydroxy-3'-methoxyflavylium Colour: Orange-red Source: *Paeonia* spp. [Paeoniaceae] Reference: Willstatter and Nolan, 1915; Willstatter and Bolton, 1915; Freyre and Griesbach, 2004	**Rosinidin**  Name: 3,5,4'-Trihydroxy-7,3'-dimethoxyflavylium Colour: Red Source: *Primula rosea* Royle [Primulaceae] Reference: Harborne and Sherratt
6-Hydroxy cyanidin  Name: 3,5,6,7,3',4'-Hexahydroxy-flavylium Colour: Red Source: *Alstroemeria* Dumort. spp. [Alstroemeriaceae] Reference: Saito et al., 1985	**6-Hydroxy delphinidin**  Name: 3,5,6,7,3',4',5'-Heptahydroxy-flavylium Colour: Blue-red Source: *Alstroemeria* Dumort. spp. [Alstroemeriaceae] Reference: Saito et al., 1988

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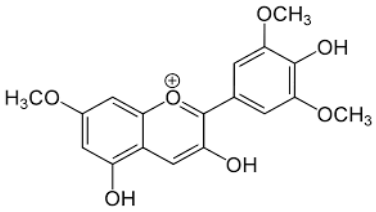
Hirsutidin



Name: 3,5,4'-Trihydroxy-7,3',5'-trimethoxy-flavylium
Colour: Blue-red
Source: *Primula hirsuta* All. [Primulaceae]
Reference: Karrer and Widmer, 1927; Carew and Krueger, 1976

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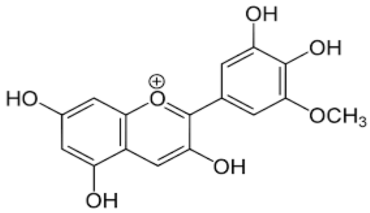
Petunidin



Name: 3,5, 7,3',4'-Pentahydroxy-5'-methoxy-flavylium
Colour: Blue-red
Sources: *Petunia hybrida* Vilm.[Solanaceae], *Passiflora quadrangularis* L. [Passifloraceae], *Gladiolus atroviolaceus* Boiss. [Iridaceae], *Cactus opunita* L. [Cactaceae]
References: Willstatter and Zollinger, 1917; Willstatter and Burdick, 1917; Carew and Krueger, 1976

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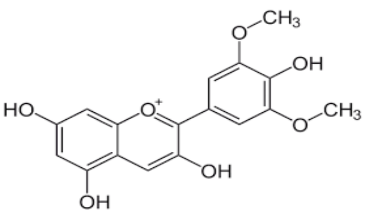
Malvidin



Name: 3,5,7,4'-Pentahydroxy-3',5'-dimethoxy-flavylium
Colour: Blue-red
Source: *Malva sylvestris* L. [Malvaceae]
Reference: Willstatter and Burdick, 1917; Carew and Krueger, 1976; Freyre and Griesbach, 2004

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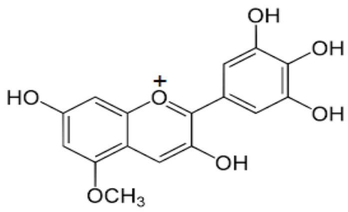
Pulchellidin



Name: 3,7,3',4',5'-Pentahydroxy-5-methoxy-flavylium
Colour: Blue-red
Source: *Plumbago capensis* Thunb. [Plumbaginaceae]
Reference: Harborne, 1962

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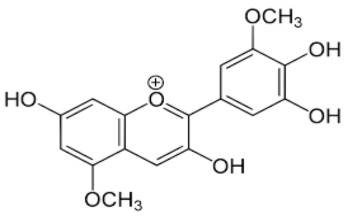
Europinidin



Name: 3,7,4'-Trihydroxy-5, 3', 5'-trimethoxyflavylium
Colour: Blue-red
Source: *Plumbago capensis* Thunb [Plumbaginaceae]
Reference: Harborne, 1966

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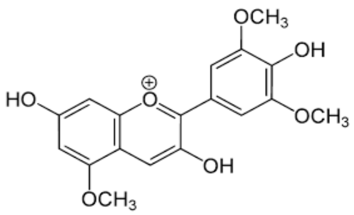
Capensinidin



Name: 3,7,3',4'-Tetrahydroxy-5,5'-dimethoxy flavylium
Colour: Blue-red
Source: *Plumbago capensis* Thunb [Plumbaginaceae]
Reference: Harborne, 1962

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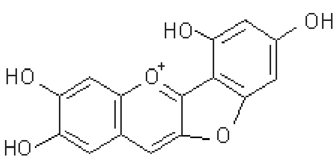
Riccionidin A and B



Riccionidin B is the dimmer of Riccionidin A
Name: [1] Benzofuro [3,2-b] chromen-5-ium-2,3,6,8-tetrol
Color: Yellow
Source: *Ricciocarpos natans* (L.) Corda [Ricciaceae], *Marchantia polymorpha* L. [Marchantiaceae], *Riccia duplex* Lorb. & K. Müller [Ricciaceae]
Reference: Kunz, 1994; Cruz et al., 2022

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The three non-methylated anthocyanidins: cyanidin, delphinidin and pelargonidin (Table 1) are the most widespread pigments in nature. Most species contain a limited number of anthocyanidins, but some have a mixture of several compounds. Sunlight is essential for the production of anthocyanidins, but they are unstable to light as well. Within plant tissues, conjugation with sugars, in the form of glycosides, imparts both photo-stability and water solubility to anthocyanins (Blank, 1947; Cruz et al., 2022).

Glucose is the most common six-carbon sugar present in anthocyanidins. Besides, other six-carbon sugars (rhamnose, xylose and galactose) and a five-carbon sugar - arabinose are also commonly associated with the pigments. Often, the sugars are further acylated with organic acids, such as acetic, malonic, malic, caffeic, ferulic and sinapic acids. Glycosylation of anthocyanidins commonly takes place in the 3 or 5 positions, but rarely at position 7 (Seitz and Hinderer, 1988) (see Figure 11).

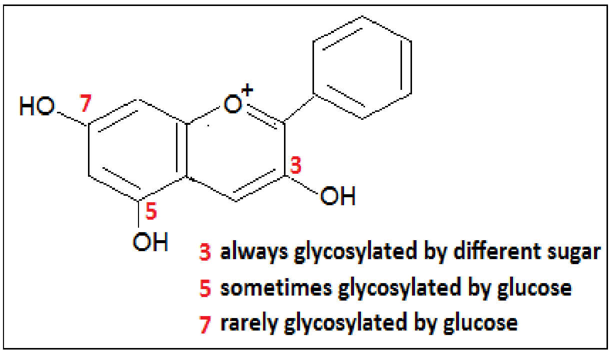

Figure 11. Glycosylation in the basic anthocyanidin structure

Apart from glycosylation, the colour stability of anthocyanins depends also on a combination of other factors, such as the pigment concentration, pH, temperature, and presence of complexing agents, such as phenols, flavonols, alkaloids and metals The molecular co-pigmentation of anthocyanins with such compounds is the main colour-stabilizing mechanism in plants (Mazza and Brouillard, 1987; 1990).

A co-pigment alone is colourless, but when added to an anthocyanidin, it can greatly enhance colour. A co-pigment may be one of the flavonoids, alkaloids, metals, and or a different anthocyanin. Co-pigments can associate with the comparatively electron-poor flavylium ion. This association provides protection from the nucleophilic addition of water to the flavylium ion (Mazza and Brouillard, 1987; 1990.

Interactions with water convert the flavylium ion into the colourless pseudo base, which consequently results in the loss of colour. The complexation of a co-pigment with an anthocyanin causes an increase in colour intensity (hyperchromic effect), and a shift of the wavelength of maximum absorbance (bathochromic shift) (Mazza and Miniat, 1993). The ionization at the ring oxygen (i.e. flavylium ion), the association with sugar at different hydroxyl groups, and the co-pigmentation – all are strongly governed by the pH of vacuole sap in flower petals (Pina et al., 2021; Cruz et al., 2022).

Yoshida and co-workers (1995) inserted a pH-sensitive glass capillary electrode into a flower petal cell of the morning glory (*Ipomoea tricolor* Cav.) Cultivar 'heavenly-blue'. Rich in bluish anthocyanin, the flower usually changes colour from a purplish-red to a sky-blue as it opens. The researchers found that as a flower opens, its vacuolar sap becomes more alkaline, causing the pigment molecules to change colour to blue around pH 7.7. The colour red is retained in the petals (and buds) when the vacuolar pH of floral tissues is below 7.0 (around 6.6-6.9). Such changes in the cyanidine molecule are what make autumn leaves of many plants, as well as roses (*Rosa* L. spp.), strawberries and cranberry (*Vaccinium oxycoccos* L.) juice red. It also makes blueberry, some grapes, blackberry, and red cabbage change colour from blue to purple.

Anthocyanins are widely ingested by humans, through the consumption of variously-coloured fruits, vegetables and red wines. Depending on the nutritional habits, the daily intake of anthocyanins for individuals has been estimated from several milligrams to hundreds of milligrams per person (Bridle and Timberlake, 1997; Clifford, 2000; Delgado-Vargas et al., 2000; Cruz et al., 2022).

Anthocyanins occurring in fruits, and vegetables are protective against a variety of diseases, particularly cardiovascular disease and some cancers (Clifford, 2000; Delgado-Vargas et al., 2000; Horbowiczi et al., 2008). Glycosides of cyanidin have been demonstrated to have anti-oxidant and radical-scavenging effects, which may protect cells from oxidative damage and reduce the risk of cardiovascular diseases and cancer (Tulio et al., 2008, Fimognari et al., 2005, Chen et al., 2006). Cyanidins may also inhibit the development of obesity and diabetes as well as contain inflammatory mechanisms (Sasaki et al., 2007).

Some anthocyanins have been implicated in the defence mechanisms of plants (phytoalexins) against fungal diseases. For instance, Nicholson et al. (1987) found Apigeninidin and Luteolinidin (Table 1) produced by sorghum [*Sorghum bicolor* (L.) Moench] cultivars as a response to fungal infections.

Betalains

Plants in a large number of Families, classified under the Order Caryophyllales contain a group of unique nitrogen-containing pigments, known as betalains (Robinson, 1963). Like anthocyanins, betalains are also water-soluble and found in cell vacuoles, but betalains and anthocyanins have never been found in the same plant together (Stafford, 1994). Betalains are not related chemically to anthocyanins. Betalains are glycosides of aromatic indole derivatives (Delgado-Vargas et al., 2000).

The core moiety of all betalains is the betalamic acid [4-(2-oxoethylidene)-1,2,3,4-tetrahydropyridine-2,6-dicarboxylic acid] (Figure 12). The betacyanins and betaxanthins, chemically two different categories of betalains, are formed from betalamic acids by their condensation with different groups. Betalamic acid condenses with cyclo-DOPA or its glucosyl derivates to form violet-coloured betacyanins. Betaxanthins are formed by the condensation of the acid with amino acids or their derivates (Slimen et al., 2017).

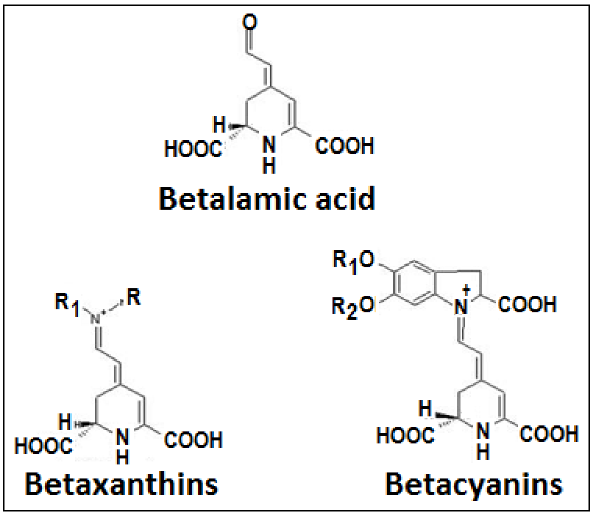

Figure 12. Structures of betalamic acid, betacyanins and betaxanthins

Betacyanins are of four different structural types - betanin, gompherin (from *Gomphrena* L. spp.), amaranthin (from *Amaranthus* L. spp. and related genera) and bougainvillein (from *Bougainvillea* Comm. ex Juss. spp.). Red beet (*Beta vulgaris* L.) is the major source of betanidin and its glucosylated form betanin. Among betaxanthins, indicaxanthin, the yellow pigment of cacti (*Opuntia* L. spp.) and vulgaxanthin of red beet are the most commonly studied betacyanins (Slimen et al., 2017).

Betacyanins are among the earliest plant pigments that have been extensively used in the food industry worldwide. They can also act as dietary cationized antioxidants with potential human health benefits (Francis, 1992; 1999; von Elbe and Goldman, 2000). Similar to anthocyanin and carotenoid pigments (see below), there is presently a globally-visible food and nutrition industry interest in betalains for their potential health benefits (Prior, 2003 Mortensen, 2006).

For example, yellow betaxanthins, in various vegetable and fruit extracts, in addition to their role as natural food colourants, could be used to provide “essential dietary amino acids” via incorporation into foodstuffs. The shelf-life of betalains is relatively short and they are also affected by higher temperatures. But they can be used in foods, such as gelatine desserts, confectioneries, poultry, flavoured milk products, ice cream, yoghurt, and meat products (sausages and hams), which are kept in cold or frozen (Delgado-Vargas et al., 2000; Kanner et al., 2001; Prior, 2003).

Carotenes and Carotenoids

Carotenoids are the widest distributed group of pigments. They occur in all photosynthetic plants and algae, also in non-photosynthetic organisms: fungi, bacteria and animals. Carotenoids are responsible for many of the brilliant red, orange, and yellow colours of fruits, vegetables, fungi, flowers, and also of birds, insects, crustaceans and fish. They do not reside in the cell vacuole but in cellular organelles (plastids), either in green chloroplasts or in non-green chromoplasts (Delgado-Vargas et al., 2000).

Carotenoids are essentially hydrophobic lipids, which are soluble in other lipids and solvents. They can be divided into carotenes containing only carbon and hydrogen, and xanthophylls made up of carbon, hydrogen and oxygen. Carotenoids owe their name to carrots (*Daucus carota* L.), and xanthophyll is derived from the Greek words for yellow and leaf (Mortensen, 2006).

The primary carotenoids in plants are β-carotene, violaxanthin, and neoxanthin. Secondary carotenoids are localized in fruits and flowers (i.e. α-carotene, β-cryptoxanthin, zeaxanthin, capsanthin, antheraxanthin). More than 700 such carotenoid pigments have been discovered (Delgado-Vargas et al., 2000). Many are used as natural food colourants (Mortensen, 2006; Mansour, 2018).

All carotenoids can be considered as lycopene derivatives ($C_{40}H_{56}$) and have eight isoprene units (C_5H_6) as shown in Figure 13. Some carotenoid structures are presented in Figure 14.

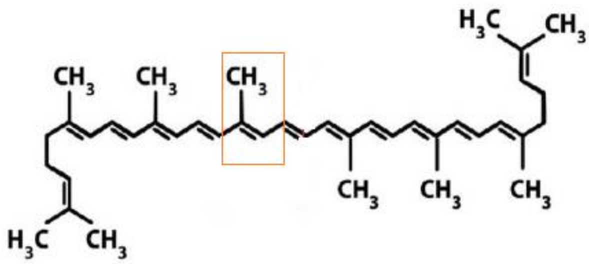

Figure 13. Lycopene and Isoprene Units (box in red). Lycopene is the precursor of β-carotene. The ‘polyene’ structure makes them highly reactive

Carotenoids are accumulated in chloroplasts of all green plants as a mixture of α- and β-carotene, β-cryptoxanthin, lutein, zeaxanthin, violaxanthin, and neoxanthin. These hydrophobic molecules exist as free complexes formed by a non-covalent bonding with proteins. In green leaves, carotenoids have two well-known functions: (1) accessory pigments in light-harvesting, and (2) function as photo-protectors against oxidative damage to chlorophyll (Delgado-

Vargas et al., 2000). Their composition depends on the plant's growth stage and development.

Lycopene is responsible for the red pigment in tomato (*Solanum lycopersicum* L.); α- and β-carotenes are responsible for the orange colour in carrots. Capsanthin and capsorubin are the main orange-red carotenoids found in chillies, paprika or bell peppers (various cultivars of *Capsicum annum* L.). Carotenoids can range in colour from bright red and yellow to various shades of orange (Delgado-Vargas et al., 2000).

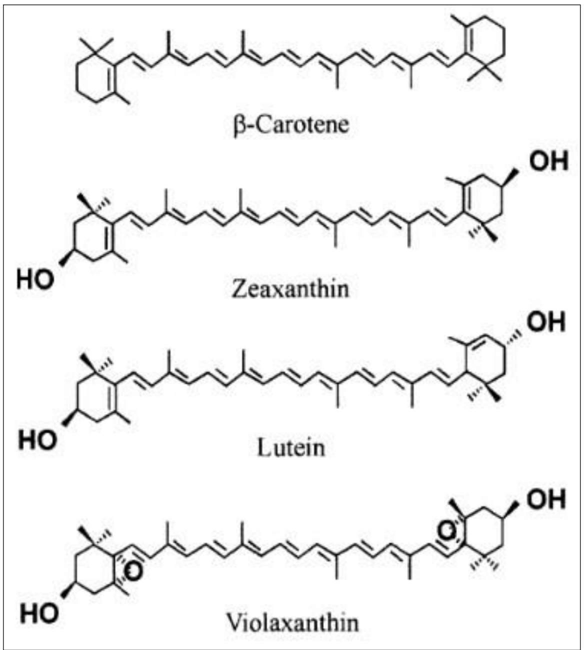

Figure 14. Some examples of Carotenoids

The roles carotenoids play in plant cells are largely determined by their associated proteins. The pigment molecules are non-covalently bonded to proteins and are abundant in cell membranes.

Similar to anthocyanins, carotenoids provide colours to flowers, seeds and fruit, which attracts pollinators and other animals that disperse pollen, seeds, or fungal spores. Many carotenoids are strongly free-radical oxygen-scavenging, which results in the well-known anti-oxidant and protective activities and benefits to human health. Also, a synergistic effect between β-carotene and vitamins E and C has been observed in cellular protection (Delgado-Vargas et al., 2000; Mortensen, 2006).

Carotenoids have been used as food colours for centuries. Beneficial properties of the pigments, such as β-carotene being a precursor of Vitamin A and well-established anti-oxidant activities have led to the wide application of carotenoids in the food industry. There are various commercial preparations in oily or aqueous media, including emulsions, colloidal suspensions, and complexes with proteins. These preparations have found applications as the pigment in margarine, butter, fruit juices and beverages, canned soups, dairy and related products, desserts and mixes, preserves and syrups, sugar and flour confectionery, salad dressings, meat, pasta and egg products (Delgado-Vargas et al., 2000; Mortensen, 2006; Mansour, 2018). The main carotenoids in marigolds (*Tagetes* L. spp.) are lutein and zeaxanthin (Figure 14), which are widely used as food colourants (Delgado-Vargas et al., 2000).

Weeds as sources of Natural Pigments

Many colonizing taxa, which are considered ‘weeds’, are being increasingly recognized as potential sources of anthocyanins, betalains, carotenoids and other natural plant pigments. Among weedy species, it is common to find a large variation in the external colours in flowers and leaves, which indicate the presence of a wide range of pigments. Table 2 provides a non-exhaustive list of such taxa that have already been utilized for the extraction of natural plant pigments for various industries. The literature examined reveals that most are severely under-utilized or at various stages of research and development as potential sources.

Presently, these pigments and dyes are promoted and utilized mostly as components of the lifestyle change and sustainable living culture movements, as demonstrated with indigo (Miller, 2019). Many natural dye industries remain as cottage industries in developing countries, where up-scaling to industrial-scale utilization from these sources is yet to happen.

In compiling the Table, our focus was only on colonizing taxa because they are easy to cultivate in small holdings in any country, or easy to harvest in the wild for commercial purposes. In our review, we encountered many other weedy species, which have been casually mentioned as being pigment sources used in different countries, but we excluded those for which significant published citations could not be found. The literature reveals that the dye extraction processes are much varied, and the colour outcomes depend heavily on the main dyeing conditions (such as dye bath pH, dyeing time, dyeing temperature, mordant and salt addition) and on the material dyed (yarn, cordage, wool, silk, cotton or other fabric).

As reviewed by Green (1995), many other horticultural species, introduced widely across the tropical belt, have the potential to be exploited as sources of natural dyes. Such species are also under-utilized in most countries and need to be assessed more broadly as commercial sources, which may provide livelihood options for communities. Examples are roots of Indian madder (*Rubia cordifolia* L.), the world-famous “Turkish Red” from the roots of rose madder (*Rubia tinctorum* L.), the root bark of Indian mulberry (*Morinda tinctoria* Roxb.); seeds of annatto (*Bixa orellana* L.), leaves of henna (*Lawsonia inermis* L.), red sandalwood (*Pterocarpus santalinus* L.), barks and roots of Indian mulberry (*Morinda citrifolia* L.), rhizomes of turmeric (*Curcuma domestica* Val. (Mayolo and Ketchum, 1989; Green, 1995; Özgökce and Yilmaz, 2003; MacFoy, 2004; Guerrera, 2006; Adeel et al., 2012).

Table 2. A Selection of Weeds as potential sources of natural dyes and pigments *

Species/Common Name	Nature of Dye/Pigment and Comments	References
Acacia catechu Willd. ('cutch')	An indigenous tree in India. Heartwood is extracted for dyes ('black catechu'), composed of tannic acid, catechin, quercetin and gum as minor components. It is a popular brown dye and preservative for canvas, fishing nets and similar items and also as a tanning agent for leather, particularly in India.	Jain, 1980; Green, 1995; Yadav et al., 2014
Acacia nilotica (L.) Willd. ex Del (pricky acacia)	Pods are the source of a black/brown dye used in ink manufacture.	Green, 1995; Yadav et al., 2014
Amaranthus retroflexus L. (amaranth); *A. spinosus* L.; other amaranths	Amaranth dye (Hopi Red Dye) - Pink-red azo dye (azorubine) from flowers and leaves (primarily, trisodium salt of 3-hydroxy-4-(4-sulfonato-1-naphthylazo)-2,7-naphthalene disulfonate). Alum and vinegar are common mordants to create different colours; used in dyeing wool, silk and yarn. The natural red-violet amaranth dyes have been used for millennia. Synthetic azo dyes, based on the template are registered as a food additive and textile colourant.	Piatelli et al., 1964; MacFoy, 2004; Cai, Sun and Corke, 2001; 2005; Stintzing et al., 2004
Ambrosia peruviana Willd.(Peruvian ragweed)	Stems and leaves yield a green dye.	Antunéz De Mayolo, 1989
Argemone mexicana L. (Mexican prickly poppy)	Stems yield a latex, which is a yellow dye.	Antunéz De Mayolo, 1989
Artemisia princeps Pamp. (mugwort); *A. annua* L.	Leaves and stems yield a blue dye.	Lee and Kwon, 2015
Anagallis arvensis L. (scarlet pimpernel), *A. monelli* L.	Flavonols, quercetin and kaempferol and 3- and 3,5-glycosides of malvidin, delphinidin and pelargonidin occur in different coloured forms in *Anagallis* spp. (Primulaceae)	Harborne,1968; Freyre and Griesbach, 2004
Baccharis genistelloides (Lam.) Pers., *B. latifolia* (Ruiz. & Pav.) Pers. (groundsel bush)	Leaves yield a yellow or green dye. Widely used for millennia by Andean Peruvian weavers. Often mixed with others to get different pigments.	Antunéz De Mayolo, 1989
Bidens pilosa L. (cobbler's pegs)	Flowers and stems yield a yellow-orange or green pigment. Peruvians use urine, black soot, and lemon juice (as mordants) to create different colours.	Antunéz De Mayolo, 1989
Boerhavia erecta L. (erect spiderling)	The major betacyanins in leaves were betanin, isobetanin and, neobetanin	Stintzing et al., 2004
Carthamus tinctorius L. (safflower)	Red and Yellow dyes from components, such as carthamin and precarthamin. Extracted using an acidified aqueous solution, the pigment is produced as a dried powder. Widely used in dyeing wool and silk fabrics and as a food colourant.	Green, 1995; Cardon, 2007; Han and Quye, 2014; Han, 2015
Centaurea segetum Hill (corn-flower)	The blue colour of cornflower arises from a complex of six molecules each of anthocyanin and flavone, with one ferric iron, one magnesium and two calcium ions.	Shiono et al., 2005; Lockowandt et al., 2019
Chromolaena odorata (L.) R.M. King & H. Rob. (Siam weed)	The entire plant yields a green dye. Used on silk.	Junsongduang, et al. 2017
Cuscuta jalapensis Schltdl. (dodder)	The entire plant yields a yellow dye.	Franco-Maass et al., 2019
Cymbopogon citratus (DC.) Stapf (lemon grass)	Leaves produce a green-golden dye. Used on silk.	Junsongduang et al., 2017
Dahlia coccinea Cav.; other *Dahlia* spp. (dahlia)	Orange and yellow dyes from flowers; cultivated in Mesoamerican countries and dyes are available in markets. Anthocyanin contents in flowers (strongly purple) can be as high as 257 mg/100 g Fresh weight.	Franco-Maass et al., 2019; Espejel et al., 2019.

Table 2 (cont.). A Selection of Weeds as potential sources of natural dyes and pigments *

Species/Common Name	Nature of Dye/Pigment and Comments	References
Eichhornia crassipes (Mart.) Solm. (water hyacinth)	Anthocyanins in the labellum of the flower are mainly malvidin and cyanidin. The carotenes present are α- and β-carotenes.	Shibata et al., 1965; Krishna Veni et al., 1981
Foeniculum vulgare Mill. (fennel)	Flowers and plant parts yield a bright yellow and deep green dye depending on the mordant used. Alum is commonly used to obtain brown, bronze or yellow dyes for cotton clothing.	Haddar et al., 2014
Galium aparine L. (cleavers); *Galium verum* L. (yellow bedstraw); *Galium corymbosum* Ruiz & Pav., *Galium hypocarpium*(L.) End. ex Griseb. [3]	The most common dye used by the Inca in the South American Andean civilizations (Peru). Red or purple dye from roots; Made into various other colours with weak acids. Yellow, orange and carmine dyes from roots. Anthraquinone pigments.	Antunéz De Mayolo, 1989; Özgökce and Yilmaz, 2003; Roquero, 2008; Armitage et al., 2015; Sabatini et al., 2020
Gardenia jasminoides Ellis (cape jasmine)	An indigenous species of China and Japan. Widely grown ornamental. Fruits are dried and extracted in aqueous alcohol to obtain a 'crocin extract', a stable yellow, used widely as a food colourant.	Green, 1995
Hedera helix L. (English ivy)	Green dye from leaves	Guarerra, 2006; Maxia et al., 2013
Helianthus annus L. (sunflowers)	Flowers yield medium-yellow and green dyes; sold in regional markets in South American countries.	Franco-Maass et al., 2019
Hypericum perforatum, L. *Hypericum laricifolium* Juss.(St. John's wort)	Flowers and leaves yield a yellow-brown dye, which can produce a range of colours from yellow, green, maroon and red. Yarn can be coloured brown by boiling in water with dried biomass for 2 h.	Antunéz De Mayolo, 1989; Özgökce and Yilmaz, 2003
Impatiens balsamina L. (Indian balsam)	The main pigment is the anthocyanin - pelargonidin; Brown and orange dye from flowers; the mordants used are alum and tin. Used on Wool and silk fabrics.	Clevenger, 1964b; Yadav et al., 2014; Singh, 2017
Indigofera tinctoria L.; *Indigofera suffruticosa* Mill.; *Indigofera hirsuta* L.; *Indigofera aspalathoides* DC. (indigo)	One of the best-known global dye plants. Now cultivated in many tropical countries. Blue-black or purple dye (Indigotin) is obtained from stems and leaves. The best grades yield 70–90% indigotin in dried leaves. Used on both silk and cotton.	Antunéz De Mayolo, 1989; MacFoy, 2004; Yadav et al., 2014; Sabatini et al., 2020
Ipomoea tricolor Cav. cv. *'heavenly-blue'; Ipomoea* spp. (morning-glory)	Petals of the blue morning glory contain only one tricaffeoylated anthocyanin, the "heavenly-blue anthocyanin" is peonidin.	Yoshida et al., 1995; Saito et al. 1996
Jatropha gossypifolia L. (Bellyache bush); *J. curcas* L.; *J. suffruticosa* Mill. (jatropha)	Leaves produce an indigo-blue, brown or green dye. Used on cotton fabrics.	MacFoy, 2004
Lantana camara L.; *Lantana horrida* Kunth. (lantana, verbena)	Green dye from very mature fruit **. Freshly opened lantana flowers are yellow (rich in β-carotene) and undergo post-anthesis chromatic alteration to orange, scarlet and magenta due to the synthesis of delphinidin monoglucoside.	Mathur and Ram, 1986; Franco-Maass et al., 2019
Leucaena leucocephala (Lam.) de Witt (lead tree)	Seed, pods and bark yield a yellow or pink dye, based on mordants; used in both silk and cotton.	MacFoy, 2004; Junsongduang et al., 2017
Ligustrum vulgare L. (privet)	A blue dye is obtained from fruits.	Yadav et al., 2014
Mentha longifolia (L.) Hudson (horse mint); *M. pulegium* L. (penny royal)	Wool and yarn, treated with alum, are boiled in water with dried Mint gives a grey colour. Ferrous sulphate as mordant gives brown colours. Pigmented flavonoids are implicated.	Özgökce and Yilmaz, 2003

[3] The updated Kew Plant List (http://www.theplantlist.org/tpl1.1/record/kew-86137) accepted names are: *Galium corymbosum*Ruiz & Pav. (syn. *Relbunium ciliatum*), *Galium hypocarpium*(L.) End. Ex Griseb. (syn. *Relbunium hypocarpum*). Many studies on the pigments used by the ancient Aztec, Maya, and Inca refer to these species with the synonyms (*Relbunium* spp. or *Rubia* spp.) (Roquero, 2008)

Table 2 (cont.). A Selection of Weeds as potential sources of natural dyes and pigments *

Species/Common Name	Nature of Dye/Pigment and Comments	References
Papaver rhoeas L. (poppy)	Petals yield a red or violet dye, used as a colouring in syrups.	Guarerra, 2006; Maxia et al., 2013
Phytolacca americana L. (pokeweed)	Berries yields an ivory dye used on silk.	Park and Jung, 2014
Populus alba L.(poplar)	Leaves are a source of green pigment.	Maxia et al., 2013
Persicaria tinctoria (Aiton) H. Gross (syn. *Polygonum tinctorium* Aiton) (Japanese indigo)	The source of world-famous Japanese blue-dye 'aizome' from leaves. Uses date back to the 6th Century AD. "Sukumu" is the name given to Japanese Indigo leaves that have been fermented and prepared for traditional Japanese indigo dyeing. The pigments are due to Indole alkaloids, which include indigo, indirubin, isatin and others (tryptanthrin and kaempferol).	Heo et al., 2013; Park et al., 2014; Qi-yue et al., 2020; Tu et al., 2021; Lopez et al., 2021
Rubus adenotrichus Schltdl.; *R. ulmifolius* Schott. (blackberry)	Fruits yield purple, violet and rose pigments. Roots yield a yellow dye. Extensively used for dyeing cloth.	Guarerra, 2006; Maxia et al., 2013
Rumex acetosa L.; *R. tuberosus* L. (docks)	Roots yield a pink dye. Leaves yield a green pigment. Wool and yarn, treated with alum, are boiled in water with dried Docks biomass gives a beige colour.	Özgökce and Yilmaz, 2003
Salvia multicaulis Vahl.; *S. nemorosa* L. (Balkan Sage)	Wool and yarn, treated with alum, are boiled in water with dried Salvia biomass. The process results in grey colours. Luteolin, 3′,4′,5,7-tetrahydroxy flavone - a common, yellow-pigmented flavonoid is implicated.	Özgökce and Yilmaz, 2003
Senecio salignus DC. (ragwort)	Dark yellow dye from flowers.	Franco-Maass et al., 2019
Solidago canadensis L. (goldenrod)	Yellow dye from flowers. Solidago flowers are monochromatically yellow due to carotenoid accumulation.	Horvath et al., 2010
Tagetus erecta L. (Mexican marigold); *T. lucida* (terragon), *T. patula* L. (French marigold); *T, terniflora* (Andean marigold)	Bronze, brown and yellow dyes are obtained from flowers. Various colours can be produced with extracts using different mordants (Alum, copper sulphate, stannous chloride and ferrous sulphate). Yellow dye from flowers. Lutein (a xanthophyll pigment) is usually present as esters of palmitic or myristic acids. A golden yellow dye is used to colour animal-based textiles (wool, silk) without a mordant, but a mordant is needed for cotton and synthetic textiles	Green, 1995; Yadav et al., 2014; Singh, 2017; Franco-Maass et al., 2019
Tamarix aphylla (L.) Karsk. (athel tree)	Cotton fabric was dyed green. Flavone derivatives - luteolin and apigenin, and flavonoids - quercetin and kaempferol derivatives are implicated.	Baaka et al., 2016
Tradescantia spathacea Sw. (boat lily)	Leaves produce a pink dye. Used on silk.	Junsongduang et al., 2017
Tridax procumbens L.	Dried leaves are extracted for flavonoids (apigenin and quercetin), which form the basis of dyes. Natural mordants can be used to produce highly colour-fast dyes for silks.	Sudhakar, 2020
Urtica dioica L. (stinging nettle)	Yellow and orange dye from leaves for dyeing cloth.	Guarerra, 2006; Yadav et al., 2014; Singh, 2017

* **Note:** Many of the above examples are presented as "eco-friendly" 'green' technologies that can be further developed. While some articles clearly articulate which chemical compounds are implicated, some are vague on the most likely pigments involved and their chemistry.

Apart from producing colours to attract flower visitations by pollinators and other animals, the main plant pigments - anthocyanins, betalains and carotenoids - display a range of biological activities, including antioxidant, anti-inflammatory, anti-microbial and anti-tumour activities; improvement of vision and neuroprotective effects (Prior, 2003).

Although in *vitro* studies have adequately demonstrated such biological activities, data and information on the absorption and metabolism of these natural plant pigments in humans are poorly understood (Steinmetz and Potter, 1996; Hertog et al., 1993; Delgado-Vargas et al., 2000; Prior, 2003; Cai et al., 2003; Mortensen, 2006; Mansour, 2018).

The stability of pigments in foods is affected by factors, such as pH, temperature, light, oxygen, and activity in water. The effects of these parameters on the stability of the pigments of amaranthus have been standardized (von Elbe and Goldman, 2000).

Much research work on pigments has been carried out on flowers and foliage of ornamental plants (Yoshida et al., 1995; 2009). However, detailed research reports are hardly available on weedy taxa and their colourants, except for a few notable species (see Table 2), highlighted below.

Pigments in some notable global weeds

Amaranthins from *Amaranthus* spp.

The well-established reports on the colours of amaranthus (*Amaranthus* L. spp.) show the scope for the utilization of weeds to obtain natural colours (Figure 15). Most amaranths are cosmopolitan, annual weeds, which produce abundant and colourful inflorescences and millions of seeds per plant. Historically, water-soluble extracts of amaranth inflorescences have been used for colouring drinks, foods, and other products in Mexico, Bolivia and Ecuador. In India and Mexico, women used amaranth juices as facial rouge.

Figure 15. Red and Orange-Yellow Amaranth inflorescences harvested for pigments (A) A field in India and (B) A field in Guatemala

A total of 16 betacyanins and three betaxanthins have been identified from various amaranths. The typical pigment of amaranth, known as 'amaranthin' (Figure 16), is a betacyanin (Mabry and Dreiding, 1968; Lehman, 1990; Cai et al., 2001; 2005), the structure of which was elucidated as 5-O-[2-O-(β-D-glyco-pyranosyluronic acid)-β-D-glyco-pyranoside] (Piatelli et al., 1964).

For its high value as food additives, amaranths have been rapidly developed as a new crop in the world. Amaranthin, as a natural colourant has been used in many types of foods across the world (von Elbe and Goldman, 2000).

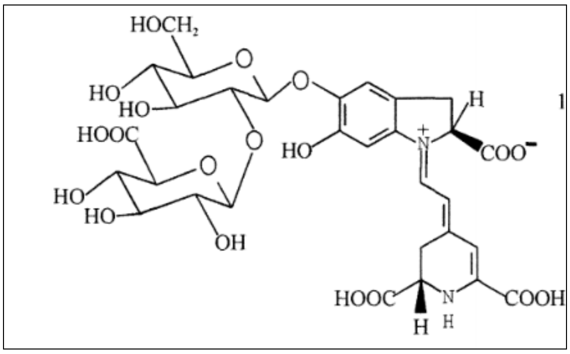

Figure 16. Amaranthin [$C_{30}H_{34}N_2O_{19}$] – a betalain (source: Cai et al., 2001)

Lantana

The genus *Lantana* comprises over 150 species, some of which are popular ornamental plants. Others, such as *Lantana camara* L. are globally recognized colonizers of disturbed habitats, including bushlands and forests. It has also been implicated in toxicity to livestock (Ghisalberti, 2000).

The colour of lantana flowers varies from yellow to orange to red with different shades of pink, in-between colours, and even white (Figure 17 a, b). Some varieties of lantana contain flowers with one colour inside the tube and another on the outer edges of the petals. Generally, the colour inside the tube is yellow, which attracts thrips for pollination (Mathur and Ram, 1986).

Carotenoids (dominated by β-carotene) are the pigments responsible for the yellow colour of freshly-opened lantana flowers. After the completion of pollination (post-anthesis), chromatic alterations occur with anthocyanin production, changing the flower colours from yellow to orange, scarlet red and magenta due to the synthesis of delphinidin monoglucoside (Mathur and Ram, 1986).

Water Hyacinth

Water hyacinth [*Eichornia crassipes* (Mart.) *Solms*], the free-floating aquatic is perhaps the most significant and predominant aquatic weed of global concern. Its attractive pale-purple or lilac flowers (Figure 17c) have been the cause of its introduction, globally, as an ornamental plant. The colour of the water hyacinth flower has long been attributed to only one anthocyanin: delphinidin 3-diglucoside (Shibata et al., 1965).

However, Krishna Veni et al. (1981) found a different set of anthocyanins in the labellum of the hyacinth. The labellum of the flower when young contains both chlorophyll and carotenoids at its centre. As it reaches maturity, chlorophyll declines with a concomitant synthesis of more carotenoids at the centre and anthocyanins in the regions around it. The carotenes are identified as α- and β-carotenes and the anthocyanins as malvidin and cyanidin (Krishna Veni et al., 1981).

Morning-glories (*Ipomoea* L. spp.)

Many morning glory species are globally-popular ornamentals; they are also cosmopolitan, agricultural and environmental weeds. They grow abundantly in disturbed habitats in the tropics and warm temperate regions of the world (Miller et al., 1999). The colour of the flower varies from species to species. In general, the flowers of most species are either white, pink, or blue, while in *Ipomoea coccinea* L., the flowers are red (Figure 17d, e).

Floral colour in *Ipomoea* species is determined by the type of anthocyanin pigment produced. So far, 44 anthocyanidin glycosides of pelargonidin, cyanidin, and peonidin have been isolated from their cyanic flowers (Saito et al., 1996; Toki et al., 2001a, b, 2004; Diretto et al., 2019).

Asian pigeonwings (*Clitoria ternatea* L.)

Asian pigeonwing (or butterfly-pea) is regarded as an environmental weed in some tropical regions because it can infest forest areas. However, it is a globally-popular, pretty home garden plant that can be used for dyes (Junsongduang et al., 2017).

The intense blue colour of the *Clitoria* flower is due to six major anthocyanins - ternatins (A1, A2, B1, B2, D1 and D2) [Terahara et al. 1990]. These have been characterized as malonylated delphinidin 3,3’,5’-triglucosides having 3’,5’-side chains with alternating D-glucose and p-coumaric acid (Francis, 1999). There are many different shades of blue, ranging from lighter to deep and purplish-blue (Figure 17f).

Figure 17. (a) Red and yellow and (b) pink and yellow Lantana flowers, (c) Lilac-coloured Water hyacinth flowers, (d) Common, blue Morning-glory flowers, (e) Red-flowered *Ipomoea coccinea*, (f) Blue-coloured *Clitoria ternatea* flowers

Natural Pigments - Future Outlook and Prognosis

Up to now, natural plant dyes have been much neglected as renewable resources, although there is an increasing demand for ‘environmentally-friendly’ colourants for textiles produced from natural fibres (wool, silk, cotton, linen etc.) and natural dyes for various other industries.

Apart from the examples discussed in our review, many other weeds have colourful flowers and foliage, which are yet to be fully investigated for their pigment compositions, biological properties and potential applications (Özgökce and Yilmaz, 2003; Maxia et al., 2013; Singh, 2017; Sudhakar, 2020). They open up exciting areas of research for scientists interested in sustainable technologies (Mahanta and Tiwari, 2005; Teron et al., 2012; Yadav et al., 2014; Siva, 2017; Mansour, 2018).

Indigo, in India, characterizes the demand and future outlook for natural pigments from weedy taxa. Records indicate that in 1896-97, indigo was grown in 1.6 million ha of land and the British India Company exported 19,000 tons of indigo to the Middle East and Europe. Production in India virtually ceased in the 1920s (Nadri, 2015). Eighty years later, in the new millennium, India was importing about 52 tons (half of the annual demand in India), mainly from China. The decline in production was a direct outcome of synthetic indigo, made in Germany, being cheaper. However, the industry has been resurrected as a small, but sustainable industry in several States, providing an income of Indian Rs, 15-20,000 per acre (Gilon, 2020).

Traditionally, the extraction of natural indigo involves a highly labour-oriented process, making it uneconomical. However, with technology-based solutions and mechanization of the extraction process, the costs of production have declined, making it fairly competitive in niche markets looking for natural pigments. The global demand for synthetic indigo is about 16,000 tons per year, with which the natural dye has to compete. Although estimates are hard to get, there is an increasing demand for natural indigo, as an "eco-friendly" product, especially valued in the highly lucrative denim, viscose and kimono fabric clothing industries.

Apart from textiles, indigo as a colourant is in high demand for ink, paper and other industries in all regions of the world. Both synthetic and natural indigo are in high demand and are valued at US $ 1.12 billion in 2020, expected to grow at about 5% per year to about US $1.64 billion by 2028 (Allied Market Research, 2022b).

Use in Textiles

Dye plants were an essential part of textile dyeing in ancient times, such as the use of indigo, which is accurately dated back in China to about 4000 years ago (Li et al. 2019). In Asia, the oldest piece of cloth coloured red with madder was dated back to 5000 years before now, in the Indus Valley Civilization sites (Siva, 2007). Tracing the botanical provenance of dye plants, recorded in historical documents and artefacts ensures correct knowledge of raw materials that had been used for dyeing for millennia. This is important to recreate and preserve historical dyeing practices (Han and Quye, 2018).

As analytical techniques improve, the knowledge about the chemistry of pigment molecules has greatly expanded (see Yoshida et al.,2009 and Delgado-Vargas et al., 2000), along with the understanding of the genetic basis of colours. Applications of this knowledge to the array of colours and associated pigments present in flowery weeds appear to present commercial opportunities that have been thus far underexploited for societal benefits. Given that the demand for natural dyes of plant origin is increasing in many countries, particularly in the textile industry, more attention needs to be focused on these sources.

Natural dyes are particularly useful for the dying of natural fibres, such as cotton, silk and wool. However, recently, it has been demonstrated that synthetic fibres can also be dyed with natural dyes, such as the yellow pigments (curcumin) obtained from turmeric rhizomes. Such possibilities will most likely, expand the future applications of natural pigments, which deliver rare and important colours, in synthetic textiles (Adeel et al., 2012). There is also a growing demand for non-toxic methods of textile colouration to meet 'health-sensitive' applications, such as children's garments, as well as intimate clothing and for those suffering from certain types of allergies (Sudhakar, 2020).

As shown in the examples, many weedy plants are good sources of pigments, although sufficient research has not yet been done in a coordinated way to exploit them. Natural pigments will continue to compete with the cheaper synthetic dyes, despite the proof that the chemical production, as well as the various uses of synthetic dyes, can pollute the environment. Synthetic dye production is dependent on heavy metal-based mordants, such as potassium aluminium sulphate [$K(Al)(SO_2)_4$], ferrous sulphate ($FeSO_4$. xH_2O), stannous chloride ($SnCl_2$), copper sulphate ($CuSO_4$), and potassium dichromate ($K_2Cr_2O_7$) (Siva, 2017).

The continuous availability of natural pigments from plant sources, however, is a significant challenge in competing with synthetic pigments. The evidence from many countries is that lack of attention to the source species has caused their decline in abundance, particularly related to unsustainable land-use practices, such as 'slash and burn' agriculture (MacFoy, 2014).

Colourants in Food

Since the 1960s, there has been a clear preference for natural pigments as colourants in various food, such as gelatine, yoghurt, ice cream and various other confectionaries. Compared with synthetic colourants, natural pigments are non-toxic and possibly more nutritious and healthier. Although the evidence of nutraceutical values has been hard to find (Clifford, 2000), food scientists consider this consumer trend to increase in the future. Stability under various environmental conditions, shelf-life and continuous availability are challenges that natural pigments face in competing with synthetic pigments (Delgado-Vargas et al., 2000).

Many anthocyanins, including the glycosides of cyanidins (Tulio et al., 2008; Fimognari et al., 2005; Chen et al., 2006), carotenoids, such as β-carotene and lutein (Delgado-Vargas et al., 2000; Prior, 2003; Mortensen, 2006), the red betalains from amaranths (Slimen et al., 2017), are proven free radical scavenging anti-oxidants. Expanded future research may indicate various weedy species as sources of such invaluable molecules of pharmacological value.

When developed further, natural pigments of weed species appear to have considerable utilization potential as simple food colourants, with the added benefits of being nutraceuticals. Research is indicative of the considerable potential in using the natural colourants in flowers (carotenoids, flavones, flavonoids and phenolic acids, in particular) for purported health benefits (Pires et al., 2018; Lockowandt, et al. (2019). Success in these applications will depend on more extensive chemical and biological research on plant pigments, especially, the floral sources, backed by commercial interests in the food and pharmaceutical industries.

Medicinal uses

Natural colourants from plants with anti-microbial properties have been widely used as both herbal medicines and dyes for at least 4000 years. This field is undergoing a resurgence. For instance, in recent times, indigo and indirubin are drawing considerable research attention, especially in China. For instance, "*Indigo Naturalis*" ("Qing-Dai") - a dried powder or paste processed from the stems and leaves of *Baphicacanthus cusia* (Nees) Bremek. (Family Acanthaceae), *Polygonum tinctorium* Ait. (Family Polygonaceae) and *Isatis indigotica* Fort. has long been well-recognized in Chinese Traditional Medicine.

A recent article from Qi-Yue and co-workers (2020), titled "*From Natural Dye to Herbal Medicine*", showed that the ancient dye indigo has a wide spectrum of pharmacological properties and can be used to treat ailments, such as leukaemia, psoriasis, and ulcerative colitis. There is also considerable evidence of anti-inflammatory, anti-oxidant, anti-bacterial, anti-viral and immune-modulatory activities in the pigment molecules, which present broad application prospects (Qi-yue et al., 2020).

Our review finds that when compared with indigo, obtained either from *Indigofera* spp., *Isatis tinctorium* and other sources, such as *Polygonum tinctorium*, very few other weedy species have been adequately studied for potential exploitation. Apart from indigo, data on the commercial value of various natural pigments to either textile industries or food and cosmetic industries are also non-existent, which is a severe limitation for developing these resources.

The production of "*Ayurvastra*" (also, called '*Herbal Textiles*') [4], is the art of colouring fabric with mixtures of medicinal herbs in India (Mader, 2011). It is an emerging area in which proponents (Baid, 2009; Singh, 2016) claim that medical benefits of natural pigments can be obtained through dyeing cotton, silk, wool and other fibres, which can be woven into fabrics. The claim is that contact with skin is therapeutically beneficial, inducing sleep and calmness. The clothes can also help alleviate allergies and breathing problems and are suitable for children and sensitive adults (Baid, 2009; Singh, 2016).

In the most recent review, Mishra and Gautam (2020) expressed the view that "*the blends of herbs and textiles have tremendous scope in the world textile market and may become a major textile product in the future…to achieve health in an eco-friendly manner*". The inventions, however, do not make clear which chemical constituents in the plant extracts might be biologically active, imparting the claimed health benefits. Proving 'causes and effects', using scientifically valid research, is much needed in this emerging field, to verify the claims.

Advantages and limitations

As shown recently by the review of "*Chemistry behind the Colour*" of flavylium-ion based (anthocyanidins) (Cruz et al., 2022), research is quite intense on many groups of natural pigments and using them as templates to produce synthetic derivatives. As this chemistry knowledge expands on pigment molecules, their applications in various industries (dyes for textile and other fibres; food and cosmetics colourants) as well as pharmaceutical applications, will increase. More and more sustainable plant sources are likely to be sought.

Natural plant pigments are, without a doubt, much less toxic to humans than synthetic dyes. However, in textile dyeing with natural pigments colour-fastness in fabrics has been quite challenging. However, when optimized and carried out well, the pigment extraction and production, as well as the actual dyeing processes can be less polluting, and much less health hazardous to the workers involved than in the production and use of synthetic chemicals. Therefore, natural pigment extraction, production processes and uses can be considered "eco-friendly".

Nowadays, there is also a significant interest in reducing the amounts of metallic mordants and

[4] "Ayurvastra" is a combination of the Sanskrit words *Ayur*—which means life or longevity—and *Vastra* or *Vastram*—which means clothing.

increasing natural mordants in dye production. Tannins, obtained from the barks and wood of various plants dominate the natural mordants (Siva, 2007). In addition, aqueous extracts of seeds of Indian gooseberry (*Phyllanthus emblica* L.), black myrobalan (*Terminalia chebula* Retz.) and tamarind (*Tamarindus indica* L.) have proven to be effective mordants in textile dyeing (Sudhakar, 2020).

In natural dyeing industries, the materials used are largely recyclable, which adds to the sustainability of those technologies. Added to these advantages are the subtlety, softness and uniquely harmonizing colours of natural pigments, which appeal to human consciousness (Siva, 2007; Singh, 2017; Junsongduang, et al., 2017). Although natural dyes have such advantages, tedious extraction of pigments from the raw material, low colour value and the longer time it takes to produce a commercial product, combine to make the cost of natural dyes considerably higher than synthetic dyes.

As light-absorbing molecules, some of the natural dyes are also unstable and short-lived and need a mordant to "fix" and enhance their colour-fastness properties. Also, there are problems like difficulty in the collection of plants, lack of standardization, lack of availability of precise technical knowledge of extracting and dyeing techniques and species availability in different regions of the world (Siva, 2007; Singh, 2017; Junsongduang et al., 2017).

Disappearing Knowledge

Knowledge of dyeing plants and their extensive use pervaded continents worldwide for millennia. This know-how was crucial for the cultural development and stability of various ancient civilizations, which were largely geographically limited in spread across the globe. Different cultures have used a variety of species (both plant and animal origin) to extract pigments and this knowledge gradually spread across continents. The close association of ancient human societies with the earliest recorded dyes - cochineal, indigo and woad – demonstrate this amply.

However, traditional knowledge of plants used for textile dyeing, steeped in human history, is disappearing because of inadequate documentation and records. There is not much information available on global or regional databases of either dye-yielding plants or their extraction, applications, mordant types, advantages and disadvantages (Siva, 2007; Yadav et al., 2014). Other factors that have caused a decline in the use of natural dyes are modernization, including new fabrics and urban lifestyles and the competition with synthetic colours.

Indigenous knowledge is rapidly being lost as increasingly less of it is being passed on to succeeding generations (MacFoy, 2004). Among other reasons why the knowledge of species used for dyeing is disappearing is fast are civil and ethnic conflicts, which prevent people from settled life, and the financial uncertainties faced by current societies (Mati and De Boer, 2010).

Textile dyeing with local plants, however, is experiencing a revival connected to ecotourism and global interest in sustainable natural products (Diaz-Cayeros and Jha, 2014). The re-awakening is visible in many countries, with intensive research and reviews of plant sources, such as India (Siva, 2007; Teron and Borthakur, 2012; Singh, 2017), China (Han and Quye, 2014; Li et al., 2019) and Thailand (Junsongduang, et al. 2017) in the Asian-Pacific region. Similar information reviews from Turkey (Özgökce and Yilmaz, 2003) and the Mediterranean (Guarino, 2000; Guerrera, 2006) discuss the challenges in preserving knowledge that appears to be fading through generations.

In the Americas also, e.g. Mexico (Franco-Mass et al., 2019), and Latin America (Roquero, 2008; Lambare et al., 2011), research on ancient colourful dyes is quite intense, based on novel analytical techniques to determine the pigment sources (Sabatini et al., 2020). Broadly, the various research groups agree that to exploit the full potential of natural plant pigments, it is important to preserve the local knowledge related to textile dyeing techniques and processes (Guerrera, 2006; Teron and Borthakur, 2012; Sutradhar et al., 2015).).

As Guerrera (2006) noted: "*One hopes that the research carried out into old dyeing uses can contribute to preserving traditional knowledge for possible future artisan activities that may be sources of some income in local enterprises*. *Preserving the memory of the techniques used in the past is likely to enable people to obtain once again today the original shades and the soft tonalities of colour that for many centuries characterized carpets and cloths dyed with traditional plant substances".*

Franco-Maass et al. (2019) recently agreed that: "*The commercialization of artisanal textiles can also help to preserve individual and social memories of traditional dyeing and enrich existing knowledge and techniques. Therefore, the use and extraction of natural dyes should be encouraged and preserved*".

Conclusions

Our article is a condensed overview of natural pigments occurring in plants, for which the accumulated organic chemistry, biochemistry and other related literature is vast. Readers are referred to various key references provided for more comprehensive information on the topics covered.

There can be no doubt that synthetic colourants have advantages over the natural ones, based on the higher pigmenting power, stability, storage, facility in the processing, and they are cheaper to make and are available in unlimited quantities (Delgado-Vargas et al., 2000; Mortensen, 2006; Mansour, 2018). However, as reviewed herein, since the interest in natural plant pigments, has been well-awakened now, they will remain a topic of significant commercial interest, which bodes well for research into new sources, especially from colonizing taxa, and their chemistries. The knowledge of ancient dyeing plant sources (genera, species and families) is crucial to future research in this regard.

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[5] Willstatter's articles, marked with a hash (#) are quoted in Blank, 1947.