Natural Dyes, Our Global Heritage of Colors

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Natural dyes and colorants in the world today: a crossroads between vanishing ancient knowledge and new applications

The whole spectrum of colours can be obtained from a multitude of plants, animals and fungi, to dye clothes, textiles and artefacts, and to colour our skin, our hair and the food we eat. The discovery and use of natural dyes and pigments contributed to the maintenance of the age-old bond between humankind and nature and could now help to revive and enhance it. Natural dyes and colorants are an essential part of the world’s ecological and cultural heritage; their selection and uses to create colours are common to all civilizations. During the past century, archaeological discoveries have largely contributed to show that, since the dawn of humankind, the quest for sources of dyes and pigments went abreast with the selection for food and medicinal plants and animals. Throughout history, natural colorants have played a major part in economic and cultural exchanges between nations.

A major break occurred in this long history during the 19th century: with the development of organic chemistry in Europe, industrialized countries generally adopted synthetic dyes and pigments extracted from fossil resources, coal-tar and oil. Cheap and easy to apply, they caused a cultural revolution. Mass synthetic colouring of everyday plastics, textiles, paints, cosmetics and food has now led people all over the world to take colours for granted. In the new era of synthetic colorants, research into natural dyes largely changed focus, shifting from economic issues to historical, archaeological and heritage aspects, until, recently, the situation changed with the global growing awareness of the threats on environment and of the need for a sustainable “green economy”.

Fast vanishing traditional knowledge

In other parts of the world, certain people long retained extensive and unique know-how about the colouring properties of indigenous plant and animal species. This traditional knowledge is intimately connected with each culture: its art, symbols and religious beliefs, and its medicine (most dye plants and animals are also medicinal). Today, however, such knowledge is rapidly disappearing with the encroachment of western life styles into the remotest parts of the globe and the loss of the last generation of “living treasures” among traditional dyers. Many unique sources and processes must urgently be recorded before it is too late.

New applications and developments: a threat for natural environments?

Today, while scientists are debating how long some fossil resources can remain economically viable, everyone acknowledges that they are finite. The search for alternatives to fossil-based raw materials and energy is reviving the age-old quest of humankind for natural resources, with needs of unprecedented magnitude, at global scale. Natural resources evidently involving natural organic dyes and pigments - the industrial potential is now becoming again a major economic and cultural issue. The sudden revival of interest in natural dyes and colorants for economic purposes, not only for textile dyeing but notably also for use in cosmetics, hair dye and food colourings, could be observed in recent international congresses, such as “Naturally… International Symposium/Workshop on Natural Dyes”, organised by UNESCO and the Crafts Council of India in Hyderabad (India) in November 2006, which was attended by some 700 participants from 60 countries, including traditional dyers/craftspeople, scientists, textile artists, professionals from different branches of industry, government representatives. The global dimension and quick progress of research and development in the field was again demonstrated during the two subsequent International Symposia and Exhibitions on Natural Dyes (ISEND), organised in 2008 and 2009 by Pr. Kim, Ji-Hee, the Museum of

1 Cardon 2007.
2 Cf. Roquero 2006, concerning cultures of Latin America.
Natural Dye Arts and the City of Daegu, in Daegu, Republic of Korea. The next ISEND gathering will take place in France, in La Rochelle, 24 to 30 April 2011.3

This renewed economic interest raises a number of crucial issues: sustainable development of the production and uses of natural colorants cannot be disconnected from such problems as the responsible management of wild natural resources; the adoption of ethical research methods respecting the rights of indigenous people regarding natural resources; the generalized use of environmentally friendly production technologies. If all environmental implications are not properly addressed for lack of sharing and discussing of relevant knowledge, a consumer-driven, sudden development of the uses of natural dyes on a massive industrial scale might paradoxically lead, among other consequences, to catastrophic plundering of the last stations of some threatened dye sources in some countries and finally to the extinction of the resource. To meet the challenge of scaling production up to industrial requirements, all possibilities for advances excluding the collection of uncommon wild plants should be investigated. It is highly important to organise regular international meetings of the different groups of specialists in research and development involving the production and uses of natural colorants: to exchange information on all that is happening in this field; to share views on the most appropriate policies to heighten the awareness of the wonderful qualities of natural dyes and colorants among general public; to find solutions to protect these “new” commercial products against falsification and fraudulent imitations based on synthetic colorants. The aim of the organisers of ISEND 2011 Europe is to provide such an opportunity to discuss the recent evolution of the production and uses of natural dyes and colorants in the world.

Parallel research approaches must be intensified to gather together relevant knowledge which may orient further developments: characterizing the chemical composition of traditional dye sources still incompletely studied will allow more precise identification of the colorants present in ancient textiles, thereby enriching our common global heritage. Such identifications will bring new light into the history of contacts and influences between ancient civilizations. The results may also suggest new applications for these traditional dyes, or complementary uses, if interesting biological activities of the colorants studied are confirmed or discovered. Vast research campaigns of prospection and evaluation of the colouring potentials of plants from different natural environments could certainly also reveal a wealth of “new” colorants, not traditionally used. Among such “new” colorants could prominently figure plant waste products. Lastly, improving the technologies of production and extraction will facilitate increased uses of natural colorants in a wide range of applications.

Although this paper cannot pretend to offer a complete, detailed overview of the current cultural and economic importance of natural dyes and colorants in the world to-day, it may serve to highlight some promising development trends in this field, both in historical research and in economic development.

I. Advances and challenges in research into the History and Archaeology of Natural Dyes and dyeing techniques

Following the development of organic chemistry and synthetic colorants during the 19th century, research into natural dyes lost its economic goals, switching to historical, archaeological and heritage conservation issues. Over the last century, this historical approach has become a fruitful field of interdisciplinary international collaborations between historians, archaeologists, anthropologists, ethnomonutonists, ethnozoologists and chemists: no less than 29 annual meetings of the international group of Researchers into Dyes in History and Archaeology (DHA) have been held since 19864; 21 volumes of the Journal DHA have been published, including thematic bibliographies5. Milestone books have successively offered an interdisciplinary, global approach to this field of research6.

3 All information on ISEND 2011 Europe can be found on the website of the event, http://www.isend2011.com/.
4 Website of the group: www.chriscooksey.demon.co.uk/.
The contribution of dye analyses of groups of archaeological or ethnological textiles using improved sample preparation and compound identification techniques

By combining information from written sources and from new data provided by recent archaeological excavations, with the results of dye analyses of ancient textiles, new insights have been gained into historical themes such as the relationships between different cultures and their natural environment, early developments in the cultivation and breeding of selected colouring plant and animal species, international trade routes, ancient empiric knowledge of dyeing chemistry, intercultural technological influences in dyeing processes; etc.

Before developing some examples of recent results, the complexity of dye analyses of ancient textiles must be stressed. Natural dyes, like all natural products, have a very complex composition; therefore, they need sophisticated analytical methods for their identification. The combination of colorants, and the proportions in which they are present in each plant or animal dye source, form a kind of “fingerprint”. Data bases collecting detailed chemical profiles of securely identified dye sources from different parts of the world must be built up, in order to allow comparisons with the composition of the unknown dyes present in ancient textiles. A satisfactory match between the results of the dye analysis of an ancient textile and one of the dye samples made with known dye sources, is the key to a fairly secure identification of the biological source(s) used by the ancient dyer of the textile.

For the past twenty years High Performance Liquid Chromatography (HPLC) completed by Diode Array Detector (DAD) in the UV-visible range and/or Mass Spectrometry (MS) has been the preferred method. It has proved an accurate and sensitive combination of techniques allowing very fine dye analysis, through the separation of all compounds present and their characterization. The methods for extraction, separation and detection are constantly evolving, however. Over the last ten years, emphasis has been given to lowering detection limits and developing “soft” methods of extraction of the colorants from the dyed textile fibres to be analyzed, leading to improved recognition of the molecular structures composing the dye. A new, particularly difficult approach, aims at tracing the original colorants used in archaeological samples presenting severely aged dyes, by studying dye degradation products.

Case study: recent identifications of true purple and red insect dyes in archaeological textiles from Roman Egypt

Recent research conducted by the author and colleagues provides an illustration of the method described and of the historical implications of the results obtained. It involves the study of dyes present on archaeological textiles discovered in great numbers, in the course of excavations of series of quarry-sites and praesidia (small Roman fortresses) of the 1st-3rd centuries CE, in the Eastern Desert of Egypt. In those, among the sites, where rubbish heaps have been preserved in good conditions, great numbers of ostraca (inscribed pieces of broken pottery), have been discovered. The meticulous study of the stratigraphy of the deposits by the archaeologists of the team and the discovery of dated ostraca and inscribed stones provides fairly secure and precise dating for most textile fragments. A series of 66 dye analyses recently concerned 63 different textiles having a purple ground, or tapestry decorations in a range of purple shades. True purple from Muricid molluscs was identified in 10 textiles, i.e. 15 % of the selected group. One of them, - a beautiful shaded band ranging from black and dark purple to bright violet on a mauve ground - includes yarns of two different colours that are only due to purple dyes, which brings the number of identifications of true purple to 11 (Fig. 1). These results were obtained by following an optimised analytical procedure that had been previously developed in an international research programme on indigoid dyes in Muricidae.

[10] Excavations have been going on since 1995, under the direction of Dr. Hélène Cuvigny, CNRS/Institute of Research into the History of Texts, Paris, with logistic help from the French Institute of Oriental Archaeology in Cairo and funding from the French Ministry of Foreign Affairs.
[11] For textiles including decorations in different shades of purple, analyses were performed for each different shade, in order to try and relate dye composition and resulting shade.
species. This allowed fine separation, and quantification of the proportions of all indigoids in the dyes. The presence of 6-monobromooindigo in significant amounts in all samples dyed with true purple would suggest that one of the three main purple-producing Mediterranean species of Muricidae was used, namely the banded dye-murex, *Hexaplex trunculus* (Linnaeus, 1758). This would situate the centre(s) of production in the Mediterranean, rather than on the coastline of the Red Sea, where the banded dye-murex is not known to live.

**Figure 1.** Fragment of shawl (pallium) or hanging D99.2511.44 (discarded in 96 CE) found in the rubbish heap of Didymoi, a Roman fort in the Eastern desert of Egypt. The dark purple and bright violet shades are dyed with true purple (Photo D. Cardon).

In some samples, true purple was found to have been combined with red colorants. Two of the sources of red dyes used in these cases are insect dyes: firstly, the kermes insect – the *kokkos* of the Greek, *coccus* of the Latin-speaking people in antiquity – which was identified by the high proportion of kermesic acid and lower proportion of flavokermesic acid in the dye, combined with indigoids characteristic of true mollusc purples (Fig. 2); the other insect dye combined with true purple

**Figure 2.** Fragment of tunic with contrasting band (clavus) D98.14101.3 (discarded in 125-140 CE) found in the rubbish heap of Didymoi. The purple colour of the clavus is a combination of true purple and kermes (Photo D. Cardon).

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12 Program PHC “Polonium” n° 13848QC supported by the French and Polish Ministries of Research. The research consortium was constituted of Witold Nowik, in charge of the Analytical Department, Research Laboratory of Historical Monuments, Champs-sur-Marne (France), Dominique Cardon for CIHAM/UMR 5648, CNRS, Lyons (France), and Pr. Marek Trojanowicz, Katarzyna Kusyk and Renata Marcinowska, Department of Chemistry, University of Warsaw (Poland).
contained a high proportion of carminic acid and lower proportions of kermesic acid and other compounds characteristic of *Porphyrophora* insects – one species of which has been discovered in several places in Egypt\(^ {13}\) (Fig. 3). The use of a red dyestuff called *krimnos* (same etymology as “carmine” and “crimson”) - most probably a *Porphyrophora* species - is presented as an alternative to kermes in a recipe to imitate true purple, in the Papyrus of Stockholm, whose recipes mostly date back to Bolos of Mendes, a Greek-Egyptian philosopher who lived between 200 and 100 BC\(^ {14}\). The choice of these two insect dyes in these archaeological textiles confirms that insect reds were the next prestigious dye sources after true purple, with which they shared a strong symbolic value, probably related to the sacrifice of the thousands of animals needed for colouring textiles and other art objects\(^ {15}\). This study is changing our understanding of the social diffusion of true purple in Roman Egypt, by showing that, among the proud wearers of true purple, could figure some of the low-rank officers, soldiers, and some of their civilian companions, who together composed the population of these small sites, far away in the desert\(^ {16}\).

**Figure 3.** Side of cloak hood, with vertical band in tapestry. Dios. 5637.1 (discarded during the second century CE) found in the rubbish heap of Dios, a Roman fort in the Eastern desert of Egypt. The purplish, discoloured shade of the band is a combination of true purple and a *Porphyrophora* species (Photo D. Cardon).

Strikingly, a similar prestige appears to have been attached to red insect dyes by several ancient people of Central Asia. This is becoming more and more evident from current studies of fully dressed mummies of men, women and children, as well as loose textiles, discovered in ancient dwellings and burial sites of the mid-2nd millennium BC to the 3rd century CE, in the Taklamakan Desert in Xinjiang, China\(^ {17}\). In several exceedingly fine or/and ornate textiles, crimson red to fuschia pink shades have been analyzed as mostly composed of carminic acid, present in various proportions, together with other compounds usually also found in dyes from *Porphyrophora* species. However, none of the analytical results corresponding to these archaeological textiles exactly matches the chemical profiles obtained from Polish cochineal (*P. polonica*), Armenian cochineal (*P. hamelii*), or any of the other

\(^{13}\) Cardon 2007, pp. 655-6.  
\(^{14}\) Halleux 1981, p. 137.  
\(^{15}\) Cardon 2007, pp. 551, 609-19.  
\(^{16}\) Cardon et al. 2010.  
\(^{17}\) Excavations conducted by the Franco-Chinese Archaeological Mission in Xinjiang, under the direction of Dr. Abduressul Idriss, Institute of Archaeology of Xinjiang, and Dr. Corinne Debaine-Francfort, CNRS, UMR 7041 “Archaeology and Sciences of Antiquity », Laboratory « Central Asia», University of Nanterre, France.
species of *Porphyrophora* studied so far (Fig. 4)\(^{18}\). Moreover, these results confirm other studies of archaeological textiles discovered in sites ranging from Siberia to the Mediterranean and dated from the Bronze Age to the Middle Ages, which detect dyes rich in carminic acid but with very diverse combinations and proportions of other anthraquinone compounds, that do not correspond exactly either to the chemical composition of the two best known *Porphyrophora* spp.\(^{19}\).

![Adult females of the sophora carmine scale insect, *Porphyrophora sophorae* (Arnchagelskaja, 1935) coming up to the surface of the ground at mating season, in the Moyunkum desert, Kazakhstan. (Photo Roman Jashenko).](image)

**Figure 4.** Adult females of the sophora carmine scale insect, *Porphyrophora sophorae* (Arnchagelskaja, 1935) coming up to the surface of the ground at mating season, in the Moyunkum desert, Kazakhstan. (Photo Roman Jashenko).

This example serves to show that making further progress in the field of dye analyses of historical and archaeological textiles urgently requires enlarging the collections of reference samples of dye sources from many parts of the world. Other indispensable tasks are to go on completing the documentation on the history of dyes and dyeing processes of many parts of the world; and improving chemical analytical techniques, with the aim of maximizing the level of detection of colorants while minimizing the dimensions of samples or – even better - developing non destructive methods of dye analyses that can compare with the precision of the HPLC-DAD-MS system.

**II. Recent economic developments in the production and applications of natural colorants: case studies from the European Union**

In this second part, present current developments in the large scale production and uses of natural colorants in Europe are merely presented as examples allowing a thorough examination of the conditions required for advances in the field, or of the remaining obstacles. The author living and working in Europe, it was easier for her to get fairly complete information from the economic actors in

\(^{18}\) Cardon 2001; Cardon 2007, pp. 635-656.

this new field of production because she knows most of them. But it should be understood that similar, very interesting developments, are taking place in many countries in all other parts of the world.

II.1. Revival of dye plant production

For natural dyes to be used at large scale in industrial processes, the supply needs to be secure and the quality needs to be guaranteed\textsuperscript{20}.

In Europe, two complementary ways of securing a constant supply in terms of both quantity and quality have been studied and are now being applied at large scale.

II.1.1. Optimized cultivation of dye plants

- Crops that historically were of major importance in Europe are reappearing at large scale, quite often in the very regions where they were most developed since the Middle Ages (examples of the firms Rubia Pigmenta Naturalia\textsuperscript{21} in the southern part of the Netherlands for madder, consortium Bleu de Lectoure/ CAPA/CATAR\textsuperscript{22} in the region of Toulouse, in the south of France, for woad)
- New crops concern a number of wild plant species, selected for their dye-content and potential for large-scale production (examples of the firms Couleurs de Plantes\textsuperscript{23} in France (Fig. 5), CON-"Colors of Nature - Farben der Natur" GmbH\textsuperscript{24} in Austria, both with a wide range of dye plants including weld (\textit{Reseda luteola} L.), dyer’s broom (\textit{Genista tinctoria} L.), dyer’s chamomile (\textit{Anthemis tinctoria} L.), saw-wort (\textit{Serratula tinctoria} L.), golden rod (\textit{Solidago virgaurea} L.), coreopsis (\textit{Coreopsis} spp.), etc.)

II.1.2. Use of colorants from side- and by-products of the industrial transformation of a variety of plants

Examples of food and wine processing, timber industries (firms La Gardonnenque in the south of France producing tons of anthocyanic colorant from locally obtained grape pomace; CON-Colors of Nature in Austria using colorants from the local timber exploitation and from food processing (onion skins, walnut husks).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{dyer_broom_field.jpg}
\caption{Mechanical harvesting of a field of dyer’s broom in the west of France for Couleurs de Plantes. (PhotoCouleurs de Plantes.)}
\end{figure}

\textsuperscript{21} www.rubiapigmentanaturalia.nl.
\textsuperscript{22} www.bleu-de-lectoure.com.
\textsuperscript{23} www.couleurs-de-plantes.com.
\textsuperscript{24} www.colorsofnature.at."
II.2. Plant processing and dye extraction

Two main ways of processing dye plants and securing a constant quality have been devised in order to allow applications at large scale.

II.2.1. Extraction of plant material for the production of concentrated liquid or powdered colorant (examples of the firms Rubia Pigmenta Naturalia in the Netherlands, producing colorant from madder; examples in France: consortium Bleu de Lectoure/CAPA/CATAR, producing indigo from woad, cooperative La Gardonnenque producing the liquid colorant enocyanin from grape pomace, firm Couleurs de Plantes producing powder or liquid colorants from a wide range of dye plants).

II.2.2. Processing of dried ground plant material, blending for homogeneous quality, and packaging into bags (like tea bags), ready for both extraction and dyeing as a continuous, energy-saving process. This is the solution advocated by a group of Austrian researchers and adopted by CON-Colors of Nature in Austria.

II.3. Present applications of plant dyes at industrial scale in Europe

II.3.1. Textile Applications

II.3.1.1. Use of liquid or powder colorant extract from dye plants with similar processes as for synthetic dyes.

This is the solution adopted by Rubia Pigmenta Naturalia in the Netherlands, Couleurs de Plantes in France. These firms have developed standardised processes for the use of their extracts and sell these together with precise descriptions of dyeing formulas and procedures. They also often develop optimised processes for special applications, in collaboration with the textile firms that wish to use their products.

Bleu de Lectoure has an active policy of collaboration with local textile industries that has resulted in the development of processes for application of woad indigo pigment to:

- cone-dyeing of hemp yarn and cotton yarn for weaving of jeans cloth;
- fleece-dyeing of lambswool and yack hair for spinning into yarns for knitwear.

II.3.1.2. Combined dyestuff extraction and subsequent dyeing

In Austria, several industry-oriented studies worked on dye plants, aiming to establish the fundamentals of dye plant use in the textile industry with optimized solutions in terms of resource use, energy and water consumption, and water pollution. As a result, an optimized dyeing process is proposed, which differs from solutions adopted by other groups in Europe. The “Austrian” approach is based on the production of dye plant powder bags, with water being used to extract the dyestuff and to prepare the dye bath at the same time. For environmental reasons, the use of mordant is limited to alum and iron mordants.

The advantage of this process, for the Austrian group of researchers, is that it saves energy compared to the dyeing process with liquid natural colorant products. Moreover, the residues can be returned to agriculture for composting, or used in biogas production.

II.3.2. Other Applications

Some applications of a whole range of natural dyes to high quality paper from linen cloth, produced in historical paper mills, are quite successful but remain as a niche market.

Application of natural colorants is fast growing, at large scale, in the food industry and also in cosmetics.

For cosmetics, two strategies are represented among European firms.

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- In some cases, such as Bleu de Lectoure, the heritage value of a dye of historical importance, in this case woad, is declined along the whole line of products. Taking advantage of the qualities of woad seed oil, the firm has collaborated with partners specialised in cosmetics to produce and sell a whole range of creams, soaps, lotions, “Graine de Pastel”.

- Other producers of plant colorants and pigments, such as Couleurs de Plantes, offer a range of extracts, of different colours, and collaborate with firms that have their own line of cosmetics to adapt natural dyes to make-up or hair dyes applications. Examples: a line of make up by Yves Saint-Laurent, using plant colorant extracts from Couleurs de Plantes; for hair dyes, the launching of the line “Henne Color Premium” by the firm NJD or the line “Palette By Nature”, by the firm Act by Nature in USA.

### III. The problem of certification and label: the example of G.O.T.S.

The demand for greener, cleaner, ethically produced cotton, and other natural fibres, continues to grow. There are many national and international standards: some are laws, but most are developed and operated by a variety of associations and organizations. The G.O.T.S. (Global Organic Textile Standard) was created by an international group involved in organic textile and environment preservation in order to create a globally acceptable standard. Among them were Soil Association (SA, UK), Internationaler Verband der Naturtextilwirtschaft (IVN, Germany), Japan Organic Cotton Association (JOMA, Japan) and Organic Trade Organisation (OTA, USA). The aim of these standards is to define requirements to ensure organic status of textiles, from harvesting of the raw materials, through environmentally and socially responsible manufacturing up to labelling in order to provide a credible assurance to the end consumer. These standards for organic textiles cover the production, processing, manufacturing, packaging, labelling, exportation, importation and distribution of all natural fibers. Both Rubia Pigmenta Naturalia and Couleurs de Plantes have applied for certification of their products by G.O.T.S.: Rubia Red is certified and has a REACH pre-registered submission number; Couleurs de Plantes had 12 colorant extracts and 7 mordants/adjuvants G.O.T.S. certified. Until recently, however, G.O.T.S was not totally adapted to the specific problems of protection and certification of natural dyes. In the words of Christian Pladerer, of CON-“Colors of Nature - Farben der Natur”: “in order to make it possible for customers to differentiate plant-dyed textiles from those which are coloured with synthetic colorants, creating an own-label for plant dyes is recommended. As a preliminary stage, it is necessary to introduce the “plant-dyed” specification to establish a corresponding market gap.”

### Conclusion

It appears that presently, in Europe as in other parts of the world, the first technological steps have been made to lift natural dyes, pigments and colorants to a more industrial scale. Further developments, both in terms of quantities produced, and in terms of standards of quality (technical, esthetical, environmental, social, ethical) will depend on the growing demand from consumers-citizens. A promising sign is the recent interest for natural dyes shown by trend leaders such as Li Edelkoort, founder of Trend Union, who recently organised a seminar at her office in Paris during which particular focus was given to natural colorants. The last issue of Bloom, a magazine published by Trend Union, is entirely dedicated to natural dyes. It looks as if the very long love story between humankind and the colours abundantly offered by nature is entering a new, fascinating era.

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28 info@trendunion.com.
29 info@bloom-magazine.com.
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Acknowledgements

My heartfelt thanks go to The Reed Foundation, Elena Phipps and the other members of the board of Textile Society of America who kindly invited me to share my passion for the colours given by nature with such a nice group of fellow textiles lovers.