Handbook of Natural Colorants

Edited by

THOMAS BECHTOLD

and

RITA MUSSAK

Leopold-Franzens University, Austria

WILEY

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Handbook of Natural Colorants

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Series Preface

Renewable resources, their use and modification are involved in a multitude of important processes with a major influence on our everyday lives. Applications can be found in the energy sector, chemistry, pharmacy, the textile industry, paints and coatings, to name but a few.

The area interconnects several scientific disciplines (agriculture, biochemistry, chemistry, technology, environmental sciences, forestry, . . .), which makes it very difficult to have an expert view on the complicated interaction. Therefore, the idea to create a series of scientific books, focusing on specific topics concerning renewable resources, has been very opportune and can help to clarify some of the underlying connections in this area.

In a very fast changing world, trends are not only characteristic for fashion and political standpoints but science is also not free from hypes and buzzwords. The use of renewable resources is again more important nowadays; however, it is not part of a hype or a fashion. As the lively discussions among scientists continue about how many years we will still be able to use fossil fuels, opinions ranging from 50 years to 500 years, they do agree that the reserve is limited and that it is essential not only to search for new energy carriers but also for new material sources.

In this respect, renewable resources are a crucial area in the search for alternatives for fossil-based raw materials and energy. In the field of the energy supply, biomass and renewable-based resources will be part of the solution alongside other alternatives such as solar energy, wind energy, hydraulic power, hydrogen technology and nuclear energy.

In the field of material sciences, the impact of renewable resources will probably be even bigger. Integral utilization of crops and the use of waste streams in certain industries will grow in importance, leading to a more sustainable way of producing materials.

Although our society was much more (almost exclusively) based on renewable resources centuries ago, this disappeared in the Western world in the 19th century. Now it is time to focus again on this field of research. However, it should not mean a 'retour à la nature', but it should be a multidisciplinary effort on a highly technological level to perform research towards new opportunities, to develop new crops and products from renewable resources. This will be essential to guarantee a level of comfort for a growing number of people living on our planet. It is 'the' challenge for the coming generations of scientists to develop more sustainable ways to create prosperity and to fight poverty and hunger in the world. A global approach is certainly favoured.

This challenge can only be dealt with if scientists are attracted to this area and are recognized for their efforts in this interdisciplinary field. It is therefore also essential that consumers recognize the fate of renewable resources in a number of products.

Furthermore, scientists do need to communicate and discuss the relevance of their work. The use and modification of renewable resources may not follow the path of the genetic engineering concept in view of consumer acceptance in Europe. Related to this aspect, the series will certainly help to increase the visibility of the importance of renewable resources.

Being convinced of the value of the renewables approach for the industrial world, as well as for developing countries, I was myself delighted to collaborate on this series of books focusing on different aspects of renewable resources. I hope that readers become aware of the complexity, the interaction and interconnections, and the challenges of this field and that they will help to communicate on the importance of renewable resources.

I certainly want to thank the people of John Wiley & Sons, Ltd from the Chichester office, especially David Hughes, Jenny Cossham and Lyn Roberts, in seeing the need for such a series of books on renewable resources, for initiating and supporting it and for helping to carry the project to the end.

Last, but not least, I want to thank my family, especially my wife Hilde and children Paulien and Pieter-Jan for their patience and for giving me the time to work on the series when other activities seemed to be more inviting.

Christian V. Stevens
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June 2005

Preface

Looking out of the window on a bright and colourful autumn day we can recognize that nature provides us with a firework of yellow, red and green colours, inspiring mankind to bring more colour into the products of daily life. However, we have known for a long time that access to the colours of nature is coupled with laborious procedures and a high number of restrictions.

The invention of synthetic organic chemistry and the desire for more bright and stable colorants can be seen as one of the strong driving forces in the historical development of natural sciences. In the 20th century synthetic colorants dominated almost every field of possible application, such as mass coloration of plastics, textiles, paints, cosmetics and food.

For almost 100 years research on natural colorants was continued by only a few groups who were enthusiastic enough to persist against the straightforward arguments for the use of synthetic dyes, relying on cost, performance, colour strength and brilliance, which can easily be achieved using artificial dyes.

During the last decade more and more new aspects were integrated into the assessment of any chemical product used. Interestingly, every new argument that had to be considered also added to the argument strengthening the position of natural colorants. Increased awareness of product safety and higher attention to the possible adverse impact of a chemical product on human health brought changes in the regulations for the use of colorants in food and cosmetics.

Concentration on renewable resources, sustainability and replacement of oil-based products are driving forces to reassess the potential of natural resources including natural colorants, at least for application in very specific fields. Growing consumer interest in purchasing 'green' products, which exhibit an improved environmental profile, can be seen as the breakthrough force for reintroducing natural colorants into the modern markets.

During our own scientific work on natural dyes for textiles and hair dyeing we learned that knowledge about natural colorants and their possible application, at present, is quite fragmented. There are collections of knowledge about natural colorants like Schweppe's *Handbuch der Naturfarbstoffe*, that summarizes properties and sources of natural dyes from a chemical and more historical aspect. However, for the demands of the future development of natural colorants into applications of the present, there is no useful source of information available that could help to give an overview of the state of the research and knowledge in the field of natural colorants.

The search for scientists working on natural colorants who were able and willing to write a contribution for this book was the major challenge in editing this book. The interdisciplinary range of content that should be covered by the different authors made our work particularly difficult, but is understandingly one of the key aspects of this book. The introduction of natural colorants into modern products is an interdisciplinary task that has to consider farming, dyestuff extraction, analysis, properties and application at the same time. Success will only be achieved if integrative concepts are presented that consider all stages of production at the same time.

The organization of the different chapters follows this order. In the first chapters a short review about plant sources and applications of natural colorants in historical times is given. Aspects of farming crops and product processing are then summarized for the different chemical classes of dyes. In the more application-oriented chapters the use of natural colorants in, for example, food, wood, textile and hair dyeing is presented. Sustainability and consumer aspects are discussed in the final chapters of the book.

We would like to thank all authors for their contributions. Their expertise in their particular field, covering a whole array of specialized knowledge, makes the book a unique source of information, which summarizes the present knowledge about natural colorants in depth.

We are aware that every collection of information will be incomplete and further aspects could have been introduced and considered in more detail. However, we are convinced that the book as it stands will be a useful instrument to overview the fragmented situation of natural colorants and will support a rapid and efficient entry of new researchers into this emerging field of sustainable chemistry. From this point of view we are also convinced that the book will strengthen the position of natural colorants in the future, by facilitating access to information and thereby indirectly helping the revival of natural colorants to gain momentum.

Thomas Bechtold and Rita A. M. Mussak
Dornbirn/Linz
2008

Part I
Historical Aspects

1

History of Natural Dyes in the Ancient Mediterranean World

Maria J. Melo

The colours used on textiles and artifacts, their social significance and the scope of their trade, are part and parcel of a people's overall history.

Jenny Balfour-Paul, in *Indigo*, British Museum Press, 2000

1.1 Introduction

1.1.1 Ancient Mediterranean World

The build-up of *Mare Nostrum* probably began much earlier than the 6th–5th millennium BC and there is material evidence pointing to such activity as early as the 12th–11th millennium BC [1]. *Mare Nostrum*, the Roman name for the Mediterranean Sea, was to become the home for a global market that expanded beyond its natural borders in the 1st millennium BC. The Phoenicians, the Etruscans, the Greeks and finally the Romans shaped *Mare Nostrum*, a geographic as well as a cultural domain. It was also home for the first global dye, Tyrian purple, which was traded by the ingenious and industrious Phoenicians. The purple of Tyre was famous, as were the textiles dyed and produced by the Phoenicians. It is said that the Greeks named the Phoenicians after *Phoinikes*, the ancient Greek word for 'red colour', probably as a result of their famous purple trade.

By the time of the founding of the Mediterranean civilizations, what we would consider the classical palette for natural dyes had already been established, and the most valued colours were indigo for the blues, anthraquinone-based chromophores for the reds and 6,6′-dibromoindigo for purple. These colours were traded all over the Mediterranean,

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regardless of distance to be travelled or the price to be paid. The natural sources for yellows were much more diverse, so yellows could generally be obtained locally. For dyeing, with the exception of some browns, all other colours and shades, including green and orange, could be obtained with these blue, red, purple and yellow dyes. This classical palette was preserved over centuries, if not millennia. The first adjustment resulted from the loss of Tyrian purple following the fall of Constantinople and the subsequent collapse of the Roman social and commercial web. This was followed by a new entry, cochineal red, brought by the Spanish from the New World [2]. However, even with the introduction of cochineal the chemical nature of the classical pallete was maintained, as carminic acid is still a substituted 1,2-dihydroxy anthraquinone. This classical palette was only challenged by the audacity of chemists, who created new molecules, and colours never seen before, from the mid-19th century on [3].

1.1.2 Dyes from Antiquity

Natural dyes, discovered through the ingenuity and persistence of our ancestors, can resist brightly for centuries or millennia and may be found hidden in such diverse places as the roots of a plant, a parasitic insect and the secretions of a sea snail. By contrast, the bright colours that we see in the green of a valley, the red of a poppy, the purple of mauve or the blue of cornflower are less stable. Natural dyes were used to colour a fibre or to paint. It is useful to distinguish between dyes and pigments based on their solubility in the media used to apply the colour; dyes are generally organic compounds that are soluble in a solvent, whereas pigments, used in painting, are usually inorganic compounds or minerals that are insoluble in the paint medium (oil, water, etc.) and are dispersed in the matrix. A lake pigment is a pigment formed by precipitation, namely by complexation with a metal ion, forming a dye on the surface of an inorganic substance.

Dyeing, in red, blue, purple or yellow, is a complex task that requires skill and knowledge [4]; this is true now and has been for several millennia. Colour is obtained by applying a chemical compound called a chromophore or chromogen, something that brings or creates colour. When used as a textile dye, the chromophore must also be captured as strongly as possible into the fibres; i.e. it must be resistant to washing. Dyes can bind to the surface of the fibre or be trapped within them. They are often bound to the textile with the aid of metallic ions known as mordants, which can also play an important role in the final colour obtained. Alum, as a source of the aluminium ion, is an important historical mordant and was widely used in the past. Other important mordants used in the past were iron, copper and tin ions [4,5]. Dyes, like indigo, which are trapped in the fibres due to an oxidation–reduction reaction, without the aid of a mordant, are known as vat dyes.

Natural dyes, as lake pigments, have been widely applied in painting. For example, anthraquinones and their hydroxy derivatives have been used as red dyes and pigment lakes from prehistoric times, and we can find written accounts of the use of anthraquinone reds and purples as dyes in ancient Egypt [5, 6]; anthraquinone lakes (e.g. madder red) were also very popular with Impressionist painters, including Vincent van Gogh. Lake pigments can be prepared by precipitating the dye extract with aluminium or other inorganic salts, such as alum [7]. Pure dyes such as indigo were also used as painting materials, e.g. in medieval illuminations (Figure 1.1).

Figure 1.1 *Medieval Portuguese illumination, dating from a 12–13th century, Lorvão 15, fl. 50 kept at Torre do Tombo (Lisbon). Dark blues were painted with indigo, whereas for the backgound the inorganic and precious pigment lapis-lazuli was used (See Colour Plate 1)*

These *eternal* colours will be described in more detail in the following sections, after a brief account of the analytical techniques used to reveal the secrets of these ancient materials. The natural colorants will be organized according to the colour: first the anthraquinone reds, followed by the blues and purple, where indigo and its bromo derivatives play a major role. Yellows will close this historic overview.

1.1.3 Unveiling the Secrets of Ancient Dyes with Modern Science

Identifying the dyes and dye sources used in the past has only been possible with the development, in the past two decades or so, of sensitive new microanalytical techniques [8,9]. Chromophores are extracted, then separated chromatographically and characterized by UV-Vis spectrophotometry or mass spectrometry; whenever possible comparison with authentic references is performed. Currently, the use of HPLC-DAD (high-performance liquid chromatography with diode array detection) enables dyestuff characterization from as little as 0.1 mg of thread. For unknown components, or those not characterized before, analysis by HPLC-MS (HPLC with mass spectrometric detection) may provide further information. Recently developed mild extraction methods allow more detailed chemical information to be obtained on the historical natural dyes, and as a consequence it is sometimes possible to identify the natural sources [10, 11].

Mordant analysis can also provide relevant information about the dyeing method or process used. The metal ions can be quantified by inductively coupled plasma separation with atomic emission spectrometric (ICP-AES) or mass spectrometric detection (ICP-MS) of samples (*ca*. 0.25 mg textile strands) previously digested with nitric acid solutions [12, 13]. Before the sample analysis, calibration curves must be constructed using standards. Concentration linearity in the range of ppb to ppm (or higher) can be achieved.

1.2 Ancient Reds

1.2.1 Anthraquinone Reds

The most stable reds used in antiquity are based on the 1,2-dihydroxy anthraquinone chromophore (Figure 1.2), also known as alizarin. Dyes containing anthraquinone and its derivatives are among the most resistant to light-induced fading [5]. These

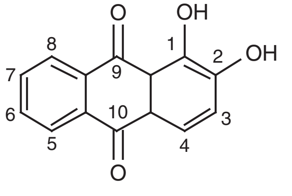

Figure 1.2 *Alizarin; 1,2-dihydroxy anthraquinone*

dyes were obtained from parasitic insects, such as the famous *Kermes vermilio*, or from the roots of plants belonging to the Rubiaceae or madder family, and were among the reds that dominated the dye markets of Europe [2, 14]. Alizarin and purpurin are the main chromophores in *Rubia tinctorum*, the most important species of the family Rubiaceae. In Persia and India, other red dyes – of animal origin – were also used. These dyes were imported, or sometimes found locally, and were considered luxury goods. Well-known examples are the reds based on the laccaic acids, kermesic acid and carminic acid (Table 1.1), from the parasite insects, lac, kermes and cochineal, respectively [2]. The female lac insect secretes a red resin, stick-lac, from which are obtained both the lac dye and the shellac resin. Common or Indian lac, *Kerria lacca* (= *Laccifer lacca*, *Carteria lacca*, *Tachardia lacca* and *Lakshadia lacca*) and *Kerria chinensis* are examples of species that have been widely exploited [5]. In both cochineal (*Dactylopius coccus*) and kermes (*Kermes vermilio*)