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To cite this version:

Yanis Caro, Thomas Petit, Isabelle Grondin, Mireille Fouillaud, Laurent Dufossé. HYDROXYANTHRACQUINONE DYES FROM PLANTS. Symposium on natural colorants “Plants, Ecology and Colours”, May 2017, Antananarivo, Madagascar. 2017. hal-01518543

HAL Id: hal-01518543
https://hal.archives-ouvertes.fr/hal-01518543
Submitted on 4 May 2017

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HYDROXYTHRAQUINONE DYES FROM PLANTS

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Introduction

In the plant kingdom, numerous pigments have already been identified, but only a minority of them is allowed by legal regulations for textile dyeing, food coloring or cosmetic and pharmaceuticals' manufacturing. Anthraquinones, produced as secondary metabolites in plants, constitute a large structural variety of compounds among the quinone family. Anthraquinones are structurally built from an anthracene ring with a keto group on position 9,10 as basic core and different functional groups such as -OH, -COOH, etc. may substitute at various positions. Anthraquinones and their derivatives occur either in a free form (aglycone) or as glycosides. Hydroxyanthraquinone dyes usually refer to hydroxylated 9,10-anthracenedione (from mono-, di-, tri-, up to octa-). They absorb visible light and are coloured (red, orange and yellow). This work gives an overview on hydroxyanthraquinone dyes described for the first time.

1) Plant sources of hydroxyanthraquinone dyes

About 700 natural hydroxyanthraquinone pigments have already been identified from insects, lichens, filamentous fungi, or plants, and only few of them (e.g. carminic acid, Arpitk red 1), and alizarin from madder color) are already manufactured as natural colorants in textile, food, cosmetic or pharmaceutical industries. For example, fifteen hydroxyanthraquinone derivatives from madder roots (Rubia tinctorum L., which contains 2-3.5 % pigments of dry weight) (CI Natural Red 8) play an important role in textile dyeing, printing, and cosmetics; but not in food in Europe or USA, even if it seems to have / had some uses in food in Japan (confectionery, boiled fish, soft drinks). Alizarin (Pigment Red 83, CI Mordant Red 11) is the main hydroxyanthraquinone dye in madder color. It is naturally bound to the disaccharide primroseov to build up the pigment ruberythric acid (yellow) in Rubiacene. Purpurin (CI Natural Red 16) is a minor component in the madder color, but is the main dye in addition with munjistin (orange-red crystals) in Indian madder (Rubia cordifolia). The color shades of madder color vary from scarlet, pink (high content of pseudopurpurin and/or purpurin, called pink madder or rose madder), carmine red (high content of alizarin), to red with a blush tint (alizarin lakes). Also oxidative coupling of two single hydroxyanthraquinones to form dimers (dianthrones) was found in plants, like the pharmacologically used pigment hypericin from Hypericum species which is a dianthrone built up from two pigment emodin (yellow). Several other plant species, although producing hydroxyanthraquinone dyes are not considered viable contributors to the natural red dye market. This is the case of Anchusa tinctoria, Carthamus tinctoria, Lithospermum spp. and Gallium spp. Other plant species well-known as laxatives can produce hydroxyanthraquinone dyes like physcin, and they include senna pods (Cassia angustifolia), cascara sagrada (Rhamnus purshiana), fragula (Rhamnus frangula), rubarb root (Rheum palmatum), yellow dock (Rumex crispus) and aloe (Aloe vera).

2) Negative effects of hydroxyanthraquinone dyes

As hydroxyanthraquinone dyes are not yet widely applied, research work need to extend the knowledge concerning their potential roles on human health. Their positive and/or negative effects due to the 9,10-anthracenedione structure and its substituents are still not clearly understood and their potential role or effect on human health is currently being discussed by scientists.

For example, the roots of the European madder are rich in the highly colored, naturally occurring, glycosidic anthraquinoid compounds ruberythric acid, and lucidin-primroseov. An intrinsic problem is the simultaneous hydrolysis of the glycoside lucidin-primroseov to the unwanted lucidin and rubiadin aglycones. Indeed, several toxicological studies have concluded that rubiadin, lucidin, and more generally madder color, can induce carcinogenicity in rat kidney and liver, and they should be dealt carefully as a significant carcinogen against human (no data available for humans). Aloan from Aloe spp. also presents negative effects on human diet.

3) Positive effects: Antitumor Activity and Cytotoxicity

Other well-known hydroxyanthraquinone dyes of natural origin and used as natural colorants (like carminic acid) are neither toxic nor known to be carcinogenic. Furthermore, numerous pharmacological studies have proved that some hydroxyanthraquinone dyes have biological positive effects. Examples including emodin, aloe-emodin, rhein, physcin, purpurin, dammacanthal, which can inhibit the growth and proliferation of various cancer cells, such as lung adenocarcinoma, myelogenous leukemia, neuroblastoma, hepatocellular carcinoma, bladder cancer, and others through cell death and survival's modulation.

Fig.1: Main hydroxyanthraquinone natural dyes from plants

Fig.2: Mixogen lucidin and rubiadin pigments from madder color

Conclusion

Finally, all these findings clearly indicate that hydroxyanthraquinone dyes of natural origin, such as from higher plants, might be considered as potent sources of novel anticancer drugs and, at least, promising anti-leukemic agents, anti-invasive agents for human pancreatic and gastric cancers chemotherapy, and antitumor agents for hepatocellular carcinoma, bladder cancer, and others. However, the cytotoxicity caused by quinones in general is very complex and seems to occur through several mechanisms. Thus, due to differences in structures and characteristics among hydroxyanthraquinone dyes, and to the dose-dependent responses observed, the molecular mechanism of the toxicity of each pigment remains to be fully elucidated.

References

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Abstract

In the plant kingdom, numerous pigments have already been identified, but only a minority of them is allowed by legal regulations for textile dyeing, food coloring or cosmetic and pharmaceuticals manufacturing. Anthraquinones, produced as secondary metabolites in plants, constitute a large structural variety of compounds among the quinone family. Derivatives that contain hydroxyl groups, namely hydroxyanthraquinones, are colored. They have attracted the attention of many researchers due to their large spectrum of possible applications especially in the fields of dyeing. These dyes produce a wide range of nuances in shades (red, orange and yellow). Fifteen anthraquinones’ derivatives from madder color roots (*Rubia tinctorium* L.) play an important role in dyeing (CI Natural Red 8). Purpurin (CI Natural Red 16) is a minor component in the madder color, but is the main dye in addition with munjistin in Indian madder (*Rubia cordifolia*). Alizarin (Pigment Red 83, CI Mordant Red 11) is the main red dye in madder color. Several other species, although producing hydroxyanthraquinones dyes, are not considered viable contributors to the natural red dye market. This is the case of *Anchusa tinctoria*, *Lithospermum spp.*, *Carthamus tinctoria* or *Galium* species.

Some hydroxyanthraquinone dyes, either extracted from insects (carminic acid), microbes (Arpink red*™*) or plants (alizarin from European madder roots), are already manufactured and marketed as natural colorants in textile, food, cosmetic or pharmaceutical industries. As these dyes are not yet widely applied, research work need to extend the knowledge concerning their potential roles on human health. Their positive and/or negative effects due to the 9,10-anthracenedione structure and its substituents are still not clearly understood and their potential role or effect on human health is currently being discussed by scientists. For example, rubiadin, lucidin, and more generally madder color, can induce carcinogenicity and should be dealt carefully as a significant carcinogen. In contrast, numerous pharmacological studies have proved that some hydroxyanthraquinones have positive effects. Examples including emodin, rhein, physcion, damnocanthal, purpurin, which can inhibit proliferation of various cancer cells. This work gives an overview on hydroxyanthraquinone dyes described in plants.

Keywords: natural colorants; pigments; dyeing plants; anthraquinones; madder

References: