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► **To cite this version:**

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

HAL Id: hal-01518543

<https://hal.science/hal-01518543>

Submitted on 4 May 2017

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HYDROXYANTHRAQUINONE 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, -CH₃, -COOH, etc. may substitute at various positions. Anthraquinones and their derivatives occur either in a free form (aglycone) or as glycosides. **Hydroxyanthraquinone dyes** usually refers 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 in plants.

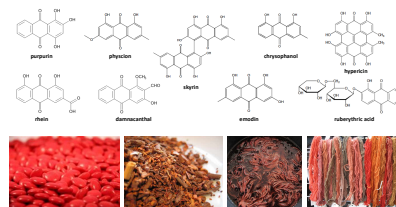


Fig.1: Main hydroxyanthraquinone natural dyes from plants

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 (f.i. carminic acid, Arpink red™, and alizarin from madder color) are already manufactured as **natural colorants** in textile, food, cosmetic or pharmaceuticals industries. For example, fifteen hydroxyanthraquinones' 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 primeverose to build up the pigment **ruberythric acid** (yellow) in *Rubiaceae*. **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 bluish tint (alizarin lakes). Also oxidative coupling of two single hydroxyanthraquinones to form dimers (dianthrone) was found in plants, like the pharmaceutically used pigment **hypericin** from *Hypericum* species which is a dianthrone built up from two pigment **emodin** (yellow). Several other plant species, although producing hydroxyanthraquinones dyes are not considered viable contributors to the natural red dye market. This is the case of *Anchusa tinctoria*, *Carthamus tinctoria*, *Lithospermum spp.* and *Galium spp.* Other plant species well-known as laxatives can produce hydroxyanthraquinone dyes like **physcion**, and they include senna pods (*Cassia angustifolia*), cascara sagrada (*Rhamnus purshiana*), frangula (*Rhamnus frangula*), rhubarb root (*Rheum palmatum*), yellow dock (*Rumex crispus*) and aloes (*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-primeveroside. An intrinsic problem is the simultaneous hydrolysis of the glycoside lucidin-primeveroside 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). Aloin from *Aloe spp.* also presents negative effects on human diet.

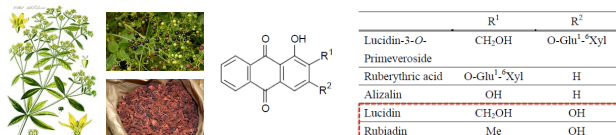


Fig.2: Mutagen lucidin and rubiadin pigments from madder color

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-dependant responses observed, the molecular mechanism of the toxicity of each pigment remains to be fully elucidated.

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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, alo-emodin, rhein, physcion, purpurin, damnacanthol**, 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.

Pigment	Biological positive effects
Emodin	can reduce toxicity and enhance efficacy in combination chemotherapy with standard drugs (arsenic trioxide and docosahexaenoic acid, or gemcitabine) against tumor cells.
Rhein	used in clinical studies on animal disease models or functional cells exerted multiple functions including anti-carcinogenesis, antioxidant, anti-inflammation and immunosuppression.
Physcion	has anti-tumour and anti-fungal properties. Recent research suggests that it effectively inhibited a part of the pentose-phosphate pathway responsible for constructing the cellular building blocks necessary for rapid growth of cancer cells. The inhibition of cancer cell proliferation and tumour growth in nude mice xenografts takes place without obvious toxicity. It should be useful in treating leukemia and it also inhibits the growth of lung head and neck tumors.
Purpurin	has antigenotoxic effect against a range of environmental carcinogens in <i>Drosophila melanogaster</i> . The pigment also clearly inhibited the formation of hepatic DNA adducts in mice exposed to carcinogens.
Damnacanthol	presents in Noni plants, targets several tyrosine kinases and has antitumoral effects.

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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 hydroxy-anthraquinones, 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 hydroxyanthraquinone 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 pharmaceuticals 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, damnacanthal, 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

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