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Investigation on the dyeing power of some organic natural compounds for a green approach to hair dyeing

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ABSTRACT

Organic compounds present in plants have been used in various experimental conditions for dyeing tests aimed to develop safe and environmentally friendly temporary and semipermanent hair dyes. Yak hairs were used as a model for the colorimetric evaluation of red, yellow, blue, and brown shades conferred to hair by selected natural compounds. Two different sources for red, yellow, blue and brown shades were tested. Anthocyanins from mulberry fruits and alizarin emerged as promising candidates for red shades, anthocyanin-blue and curcumin for blue and yellow, respectively, and p-benzoquinone and juglone for browns. The influence of pH, dye concentration, soaking time, and medium in which the dyes have been dissolved or dispersed has been studied.

1. Introduction

The production and the use of compounds both safe and environmentally friendly are receiving growing attention in many areas, and a renaissance of the interest toward the natural pool as valuable source of available and renewable row materials is occurring. Since ancient times plants have been used for dyeing purposes and even now they play a key role in food, inks, textile, and cosmetic fields [1]. In this context, the interest in developing efficient and not-toxic formulations for hair dyes never weakened.

Hair color formulations can be classified [2] as temporary, semipermanent and permanent (the two formers are based into a non-oxidation mechanism, whereas the last is based mainly on oxidation reactions) depending on their persistence on the hair. Temporary dyes are compounds of low molecular mass which does not penetrate into the cortex and are deposited on the surface of the hair. They allow to obtain a slight change or a higher gloss of hair color that lasts until the first wash. Semipermanent dyes are able to produce changes in the shade of the natural hair color that can be fade slowly and progressively, and permanent dyes confer a permanent change to hair color. Semi-permanent hair dyes include organic compounds with low molecular weight that allow them not only to pass through the hair cuticle but also to diffuse throughout the cortex, providing a longer-lasting coloration, able to intensify natural hues and to cover the first white hair. They are usually called 'direct' dyestuffs because are ready for use and their employ is growing owing to the vast availability of formulations and the easiness of application which permits also household uses.

The mostly used temporary and semi-permanent hair dyes are of synthetic origin and can be classified in numerous ways, one of these is the classification as azo compounds, anthraquinones, triphenylmethanes, nitrophenylenediamines, nitroaminophenols and aminoanthraquinones [3]. These coloring agents permit to achieve a wide range of color, with shades strongly dependent on the nature of the moiety bound to the aromatic ring (e.g. presence of acid or basic groups) and on the pH of application. When they are non-ionic and contain no water solubilizing groups, they are called 'disperse dyes' [4a]. Their sparing solubility in water can be increased by adding to the dye bath an organic solvent (2–3%) partially soluble in water or a surface-active agent. This latter usually improves the dyestuff solubility increasing its uptake by the hair and simplifying its diffusion through the hair cuticle by swelling the same [4b,c].

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Table 1
Dyeing tests on yak hair using anthocyanins from mulberries fruits.

Entry	pH	Time (h)	% (w/V)	Medium	L^*	a^*	b^*	ΔE
Yak[a]	–	–	–	–	69.7 ± 0.4	1.2 ± 0.2	12.5 ± 0.5	–
1[b]	2.7	12	0.1	Water	48.8 ± 0.6	13.8 ± 0.6	−2.5 ± 0.1	28.6 ± 0.7
2[b]	2.7	12	0.1	A[c]	34.6 ± 0.9	17.1 ± 0.7	−4.3 ± 0.1	42.1 ± 0.9
3[d]	2.7	12	0.1	A[c]	51 ± 2	7.8 ± 0.8	−3.2 ± 0.1	25 ± 2

[a] Starting yak hair parameters.
[b] Data from extract-1 (see Section 2.4).
[c] Water/2-propanol/benzyl alcohol (75/20/5).
[d] Data from isolated pigment.

Besides synthetically-derived dyes there are direct dyes available in nature and known since ancient times when they were used not only as skin and hair dyes, but mainly as textile dyes [5]. Among them, henna leaf and walnut husk were the most efficient natural hair dyes and at present henna (*Lawsonia inermis* L.) is still the most commonly used natural plant for this purpose.

In principle, a wide range of vegetables might be used as starting material for "green" hair dye compositions but the exploitation of natural pigments for hair dyeing is more complicated than that on the textiles that can use longer exposition times, higher temperatures and presence of mordants [2b,c]. This is due to many factors such as the poor stability of the dyes in solution, their tendency to undergo oxidation and browning phenomena, the pH-dependent color shift and the degradation by UV light [2a]. In addition, usually plants contain low concentration of pigments that are often impure and poorly soluble [2e]. Notwithstanding, in the light of several studies about the toxicity of synthetic permanent and semipermanent hair dyes [6] the interest toward natural dyes has recently increased (even if this not admit to assume that 'natural' means safe) and grown in popularity thus increasing their importance in the market of natural products.

Due to these reasons, searches aimed to the replacement of synthetic hair dyes with natural colorants have recently intensified but only in a few cases the results have been reported in terms of CIE (International Commission of Illumination) dyeing parameters [7]. This prompted us to turn our previous interest [8] on hair dyes toward some vegetal sources in order to explore their potentialities as hair colorants. Herein we report the results obtained on white yak hair, used through this work as test fiber.

2. Materials and methods

2.1. Materials

Benzyl alcohol, 2-propanol, ethanol, methanol, HCl 37%, *n*-hexane, light petroleum, diethyl ether, ethyl acetate, dichloromethane, citric acid, 2-amino-2-methyl-propanol, iron (II) oxalate, p-benzoquinone, 5-hydroxy-1,4-naphtoquinone (juglone), 1,2-Dihydroxyanthraquinone (alizarin), 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-1-benzopyran-4-one, 3,3′,4′,5,6-pentahydroxyflavone (quercetin), and guaiazulene were purchased from Sigma–Aldrich (Milan, Italy). 1,7-Bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (curcumin) was purchased from Fluka. The shampoo used for washing dyed yak hair was from Marie Danielle Linea Hotel, Milan, Italy (pH 5.5, composition: aqua, sodium laureth sulfate, cocamide Dea, disodium laureth sulfosuccinatelauramidopropyl betaine, sodium chloride, *Triticum vulgare* gluten, parfum, propylene glycol, methylisothiazolinone, benzyl alcohol, phenoxyethanol, methylparaben, ethylparaben, propylparaben, butylparaben, citric acid, CI42051/19140). Paper used to filter was from Bibby Sterilin Italia cod 250-60. Blue chamomile oil was a gift of Dr. Lorenzo Micele.

White Yak hair samples, used as substrate for dyeing experiments, were purchased from Socap (Napoli, Italy).

The ^1H spectra were recorded at 600 MHz on a Varian Inova 600 Instrument. Chemical shifts were measured in δ (ppm) and referenced to the solvent (3.6 ppm for ^1H NMR in CD_3OD). *J* values are given in Hz. GC–MS analyses were performed on a gas chromatograph Agilent 6890 equipped with a (5%-phenyl)-methylpolysiloxane column (30 m length, 0.250 mm i.d., 0.25 μm thickness), interfaced to a quadrupole mass detector Agilent 5973 N. Flash chromatography (FC) was performed on silica gel (0.040–0.063 mm). Extraction of anthocyanins fraction from mulberry's fruits was carried out using Waters Sep-Pak Vac 12 mL C18 – 2 g cartridges. pH Values are determined using an AMEL Instruments Mod. 2335 pHMETER with combined electrode Hamilton 3 M KCl.

2.2. Dyeing procedure

The dyeing experiments were carried out, as specified in related Tables, using different baths, prepared as follows.

Water bath: in this case dyeing experiments was made dissolving or dispersing different amount (% w/V are given in Tables 1–6) of dye in 10 mL of water. For each dye bath the pH was adjusted to the required value using a 1 M aqueous solution of citric acid in water or 2-amino-2-methyl-propanol.

Bath in medium A: the dyeing experiment was made dissolving or dispersing the dye in a solution prepared by mixing 75% of water, 20% of benzyl alcohol, and 5% of 2-propanol (V/V). For each mixture the pH was adjusted to the required value using a 1 M aqueous solution of citric acid or 2-amino-2-methyl-propanol.

Bath in Medium B (used as described in Supporting Information): the dyeing experiment was made using a benzyl alcohol 1% v/v aqueous solution.

White yak hair samples were divided in locks of 0.150 g weight and 4–5 cm length and were immersed in the 10 mL of a freshly

Table 2
Dyeing tests using alizarin.[a]

Entry	pH	Time (h)	% (w/V)	Medium	L^*	a^*	b^*	ΔE
Yak[a]	–	–	–	–	69.7 ± 0.4	1.2 ± 0.2	12.5 ± 0.5	–
1	8.0	0.5	0.1	Water	55 ± 1	9.0 ± 0.5	1.5 ± 0.1	20 ± 1
2	8.0	0.5	0.1	A[b]	50 ± 1	13.7 ± 0.9	−2.3 ± 0.6	27.8 ± 0.9
3	8.0	0.5	0.5	A[b]	41 ± 2	15.4 ± 0.4	−5.9 ± 0.2	37 ± 1
4	8.0	0.5	1.0	A[b]	46 ± 1	16.2 ± 0.5	−4.4 ± 0.2	33 ± 1

[a] Starting yak hair parameters.
[b] Water/2-propanol/benzyl alcohol (75/20/5).