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UV protective properties of cotton and flax fabrics dyed with multifunctional plant extracts

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ABSTRACT

Ultraviolet radiation (UVR) blocking properties of textiles depend on fibre type, fabric construction and nature of finishing chemicals. Natural dyes can provide vegetable fibres with strong colours if mordants are used.

In this study UV protection properties of dyeing extracts from Mediterranean flora (*Helichrysum italicum* Roth, *Rubia peregrina* L., *Daphne gnidium* L., *Lavandula stoechas* L., *Cynara scolymus* L.) were tested in combination with fabrics made of vegetable fibres (cotton and flax) and different types of mordants (potassium alum and chestnuts tannins). Pre- and post-dyeing solutions were analyzed quali-quantitatively by HPLC/DAD/ESI-MS in order to calculate the dye uptake on fabrics during the dyeing process.

UVR transmittance of fabrics was measured using a spectrophotometer equipped with an integrating sphere. After the dyeing process only flax fabrics mordanted with alum and dyed with Lavandula and Rubia, and flax fabrics mordanted with tannin and dyed with Rubia and Helychrysum reached the minimum protection level. A very good protection level was reached by flax mordanted with alum and dyed with Helychrysum. Chestnut tannins provided a slight support in phenols uptake for Lavandula and Helichrysum plant dyes with respect to potassium alum, but without an improvement of the fabrics UV protection properties; flax samples dyed with Helichrysum extract showed an improvement in UV protection properties when mordanted with potassium alum instead of tannins. Colour fastness and the persistence of UV protection characteristics were also tested after light/sun exposure and after several washes.

1. Introduction

Overexposure to solar UV radiation has been identified as causing an increased incidence in skin problems such as sunburn, premature aging, allergies and skin cancers [1,2]. In order to avoid or limit these health risks, it is important to reduce the UV ray exposure with clothing, accessories and shade structures made of protective materials. Textiles have been shown to provide UV blocking properties but these characteristics depend on fibre type, fabric construction and nature of finishing chemicals. Dyed fabrics are more protective than undyed ones and the protection level rises with the increase in dye concentration [3]. In general, light colours reflect solar radiation more efficiently than dark ones [4], but part of the radiation penetrates more easily through the fabric thanks to multiple scattering. Moreover, most of the studies on this topic concern synthetic dyes. The high compatibility with the environment of naturally dyed textiles and their lower toxicity and allergic reaction have been arousing growing interest in the last 15 years and, for this reason, many studies have focused on the multifunctional properties of dyeing plants extracts, as shown by Islam et al. [5]. Nonetheless, as regards the UV-protection properties of natural dyes, few researches have been performed on natural fabrics [6–8] and most of these concern animal fibres, as reported by Grifoni et al. [9].

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Very few studies exist on the UV protection properties of natural dyes in combination with fabrics made of vegetable fibres [5,6,9–13] maybe because very few natural dyes provide vegetable fibres with strong colours without the aid of mordants. An ecofriendly natural dyeing can however be achieved by replacing metal mordant with natural mordant, like tannic acid or other vegetable tannins [14], even if metal mordants such as potassium alum and aluminium sulphate can also be used in ecofriendly natural dyeing as their environmental toxicity is almost nil [15]. Tannins are water-soluble phenolic compounds that have been used on textiles for several hundred years both as a pre-treatment and post-treatment factor to increase wash fastness [16] and light fastness [17], e.g. in cotton fabrics. The evaluation of the level of UV protection properties of natural colours needs to be supported by knowledge of the dyes chemical structure, absorption characteristics in the UV region, interaction and complexation with the premordanted substrate, as well as the ability to block or absorb the hazardous UV rays [9]. In addition, improvement of the UV protection properties is determined by the physical state/chemical structure of the natural dye extract, the type of mordant as well as fabric structure [18].

In order to test UV-protection properties of natural fabrics dyed with vegetal extracts, this study focuses on the i) characterization of the quali-quantitative profile of secondary metabolites in vegetal dyeing extracts from Mediterranean flora: *H. italicum* (Roth) G. Don, *R. peregrina* L., *D. gnidium* L., *L. stoechas* L., *C. scolymus* L.; ii) investigation of UV-protection properties of textiles made of vegetable fibres (cotton, flax), with different textile structures/weight and dyed with these extracts; iii) comparison of the effects from the application of *Castanea sativa* Mill. tannins or metal mordants (potassium alum and soda) on UV-protection properties of cotton and flax fabrics; iv) evaluation of the persistence of UV protection characteristics and colour fastness after laboratory light exposure and in the open-air. v) evaluation of the persistence of UV protection characteristics after washing.

2. Materials and methods

2.1. Dyeing materials

All the fabrics were dyed with extracts of wild native plants such as *H. italicum* (Roth) G. Don (curry plant), *R. peregrina* L. (wild madder), *D. gnidium* L. (daphne), *L. stoechas* L. (wild lavender) and *C. scolymus* L. (artichoke). The wild native plants were harvested in the province of Sassari (Sardinia, Italy) and Grosseto (Tuscany, Italy), while artichoke leaves were waste from artichokes cultivated in Southern Italy and processed by Biotech Company (Fasano, Bari, Italy).

All the plant extracts were obtained by an industrial extractor (TIMATIC FC 100, Tecnolab) using hot water. At the end of the process, the extracts were concentrated by an industrial heat pump evaporator.

In the paper the names of the plant extracts will be abbreviated as: Helichrysum, Rubia, Daphne, Lavandula and Cynara.

2.2. HPLC/DAD/ESI-MS quali-quantitative analysis

In order to characterize polyphenols, dye extracts were analyzed with HPLC/DAD/ESI-MS using the HP 1100 MSD API-electrospray (Agilent Technologies, Palo Alto, CA) operating in negative and positive ionization mode under the following conditions: nitrogen gas temperature = 350 °C; nitrogen flow rate = 10 l/min; nebulizer pressure = 30 psi; quadrupole temperature 30 °C; capillary voltage = 3500 V. The mass spectrometer operated at 80–200 eV to optimize fragmentation conditions of the different analyzed compounds. Phenolic compounds were separated using a 3 × 150 mm Luna C18 (5 μm) column (Phenomenex, Germany) with water (adjusted to pH = 3.2 by HCOOH)/CH_3CN as eluent. A four-step linear gradient solvent system was used, starting from 100% H_2O to 100% CH_3CN during a 30-min period, at a flow rate of 0.6 ml/min. Individual phenolics were identified using their retention times with UV–Vis and MS spectra. The single phenolic compounds were quantified by HPLC/DAD using a five-point regression curve built with the available standards. Specifically, hydroxycinnamic acid amounts were calculated at 330 nm using chlorogenic as reference; coumarins were calibrated at 320 nm using daphnetin as reference; flavonoids were calculated at 350 nm with apigenin 7-O-glucoside and luteolin 7-O-glucoside; madder antraquinone classes were calculated at 410 nm and 480 nm, respectively, with 1,8-dihydroxyantraquinone and 1,4-dihydroxyantraquinone as reference compounds.

2.3. Fabric characteristics

Cotton (CO) and flax (FL) fabrics were chosen among those more frequently used for summer clothing.

The characteristics of CO and FL fabrics are shown in Table 1.

The fabrics cover factor (CF), a parameter that measures fabric porosity (calculated as 100-CF, where CF is defined as the percentage area occupied by warp and weft yarns in a given fabric area), was estimated by image analysis technique. Fabric sample images were acquired by a high resolution scanner (HP Scanjet 7400C) and then processed using the supplied software.

2.4. Dyeing procedure

All the fabrics were washed in a boiling soda solution (5% on fabric dry weight) for a few minutes; the fabrics were then wrung out. The effect of temperature increase due to this preliminary treatment on possible fabric shrinkage and, thus, on CF, was verified estimating the CF of each sample before starting the dyeing process (in this paper these samples are designated as "undyed-boiled"). Fabrics were mordanted prior to dyeing in order to increase the natural dyes affinity for cellulosic fibers. The possible effect of mordant on UV protection was tested by applying two types of mordants, *C. sativa* Mill. (chestnut) tannins, designated as "mordant-T" and a metal mordant of potassium alum and soda, "mordant-A". *C. sativa* tannins were provided by the Gruppo Mauro Saviola srl (Viadana, MN, Italy), potassium alum and soda was obtained from Sigma–Aldrich S.r.l. (Milan, Italy). 6% of chestnut tannins or 26% of potassium alum plus 6% of soda on the dry weight of the fabric were used. The samples were kept in the mordanting tannins bath for 2 h at 80 °C and then cooled to room temperature. In the potassium alum plus soda mordanting process, samples were maintained for 2 h at boiling temperature and then cooled and left in the solution for 12 h. The possible mordant UV-absorbing capacity was tested on samples of each fabric mordanted with chestnut tannins or with potassium alum plus soda ("undyed-mordant-T" and "undyed-mordant-A", respectively). After mordanting, the fabrics were well wrung out and dyed. The ratio between the fabric dry weight and aqueous solution weight was 1:20. The fabrics dyed with Helichrysum, Daphne, Lavandula and Cynara

Table 1
Parameters of undyed fabrics used in the experiment. CO, cotton fabrics, FL, flax fabrics.

Fabric	Weight (g/m^2)	Count (warp × weft/cm)	Cover factor (%)		Weave
			Undyed	Undyed-boiled	
CO	108	13 × 21	97.3	97.9	Plain
FL	159	24 × 15	96.5	97.4	Plain