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Note from the field

New insights into solar UV-protective properties of natural dye

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Abstract

The protective properties of hats and clothing against solar ultraviolet radiation (UVR) have been the subject of considerable research for some time. However, not all garments provide sufficient protection from UVR. In this study, the ultraviolet protective properties of the fabrics dyed by *Rheum* and *Lithospermum erythrorhizon* were investigated. Experimental results revealed that the fabrics dyed with natural dyes had good ultraviolet protective properties. They could absorb about 80% of the ultraviolet rays. It was demonstrated that the UV-protective effect was strongly dependent on the absorption characteristics of natural dyes for UVR. Natural dyes such as *Rheum* and *L. erythrorhizon* had comparable UV-absorption performance to the common UV-absorber, benzophenone.

Keywords: Natural dye; Ultraviolet protective property; *Rheum*; *Lithospermum erythrorhizon*; Benzophenone

1. Introduction

Sunlight carries the fundamental energy for life on earth by driving photosynthesis, but UVR from the sun has clear detrimental effects. The over-exposure to UVR would cause sunburn, skin damage and an increased risk of developing skin cancer [1,2]. Especially, high levels of exposure in childhood have been associated with greater proneness to develop skin cancer [3,4]. If all current exposure to solar UVR could be significantly reduced, the incidence of skin cancer would eventually decrease significantly. In the past few decades, sun protection campaigns have been initiated in Australia, the United States, and Europe to educate the population about sensible behavior of the sun [5]. Although protecting the skin with clothing is a convenient and valid method, common clothing, including cotton, silk, wool, and synthetic fabrics, is not effective for UVR protection because of the high UV ray transmittance of the fabrics.

In the past decade, investigations about possible uses of natural dyes in textile dyeing processes have been performed by various research groups, on account of their high compatibility with environment, relatively low toxicity, allergic reactions and various natural coloring sources [6,7]. However, most research on natural dyes had been focused on the fundamental aspects of the natural dyes, e.g. the property of dyeing, light fastness and washing fastness [8–10]. Little attention has been given to the other functions of the natural dyes such as UV-protection properties.

In this study, we investigated UV-protection properties of the cotton and silk dyed by natural dyes. It is believed that this study could provide a good insight into UV-protection properties of the natural dyes.

2. Experimental

2.1. Experimental materials

Rheum root and *Lithospermum erythrorhizon* root were purchased from the Chinese Traditional Medicine Hospital of Zhejiang as the source of natural dyes in this experiment. Plain weave cotton fabric and plain weave pure silk were provided by Zhejiang Xidebao Co. Ltd (China). Ethanol, Sodium hydroxide and soap (AR) were obtained from Hangzhou

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Changzhen Chemical Reagent Factory (China). Ferrous sulphate, Potassium dichromate, Potassium aluminium sulphate and stannous chloride (AR) were obtained from Shanghai Chemical reagent Co. Ltd (China).

2.2. Experimental methods

2.2.1. Preparation of the fabrics

The plain weave cotton fabric and plain weave pure silk were soaked in a detergent solution for about 60 min, followed by extensive washing with tap water until free from any detergent. The clean fabrics were then washed with de-ionized water, squeezed, and allowed to dry in an air oven at 60 °C, and were then stored in a vacuum desiccator ready for use.

2.2.2. Extraction of natural dyes

Before extraction of the dyestuffs, the plant materials were dried and ground to powder. The extraction conditions of dyes are listed in Table 1. After the extractions were complete, the extracts were cooled to room temperature. Then the insoluble residues were separated by sedimentation and filtration. The resulting extract was used for the subsequent experiments.

2.2.3. Mordanting

In this experiment, mordanting was done prior to dyeing (called pre-mordanting) to assist the adsorption of the dye and to promote good bonding of dye and fiber. The most commonly used mordants such as alum (potassium aluminium sulfate), chrome (potassium dichromate), iron (ferrous sulfate), and tin (stannous chloride) were chosen. Firstly the cotton fabric and silk were submerged in warm water (about 46 °C) for 30 min to relax the fibers, which would make the cotton fabric and silk more receptive to mordanting and dyeing. Then the specific mordanting process was carried out according to the literature [11].

2.2.4. Dyeing procedures

The dyeing procedures were performed in accordance with the general dyeing method [12,13]. A ratio of dyestuff to fabric of 1:10 was chosen based on the weight of the fresh natural dyes extracted to the fabrics used in the experiment. The fabric was immersed in a dye-bath composed of 0.25% aqueous solution of the dye. The dye liquor ratio (1:40) was kept constant for all samples, and the optimized dye-bath pH value was determined depending on the type of raw material. For *Rheum* root and *L. erythrorhizon* root, the pH values were adjusted by adding drops of sodium hydroxide/hydrochloric acid to pH 9–10 and 3–4, respectively. The temperature of the dye-bath was then gradually raised (about 1 °C/min) to about 100 °C, and was kept at this temperature for about 60 min. The temperature of the dye-bath was then allowed to cool to about 60 °C; then the dyed fabric was squeezed, rinsed thoroughly with water and air dried.

Table 1
Extraction conditions for the natural dyes

Source	Mass (g)	Extract (ml)	Substrate	Temperature (°C)	Time (h)
Rheum root	10	200	Water	100	1.5
Lithospermum erythrorhizon root	10	200	Ethanol and water	100	1.5

2.2.5. Comparison of UV-absorption characteristics between natural dyes and benzophenone

For comparison, benzophenone was selected as a common UV-absorber [14]. The comparison procedure of the UV-absorption between the natural dyes and the common UV-absorber was performed as follows: 1 g dried natural dye extracts was dissolved and diluted to 1% (mass ratio) using 50% ethanol, 0.5 ml of the samples was transferred to 25 ml volumetric flask and diluted by 50% ethanol. The same concentration of aqueous benzophenone was prepared as stated above. Then the measurement of the UV-absorption characteristics was conducted in the range of 280–400 nm by using ultraviolet spectrophotometer (UV-2102PC).

2.3. Analytical procedures

2.3.1. Color fastness tests

The samples selected on the basis of visual evaluation were tested for color fastness to washing, light and cracking. The wash-fastness was determined at 40 °C according to DIN 54004 [15]. A solution containing 0.45 $g\,L^{-1}$ sodium laurylsulfate and 0.5 $g\,L^{-1}$ alkyl poly-glycoside was used as washing liquor. The samples were treated for 30 min at 40 °C in a liquor ratio of 1:50. After rinsing and drying, the change in color of the sample and the bleeding to white fabric (cellulose, wool) was determined. The changes were related to the standard grey scale (marks 1–5, 1 = poor, 5 = excellent). The light fastness was examined using artificial illumination with a xenon light according to DIN 54004 [15] and was related to the standard scale of blue dyeing (marks 1–8, 1 = poor, 8 = excellent). The cracking fastness was determined according to the ISO 105-X12 [16].

2.3.2. Measurement of UV-protective properties

The UV-protective properties of fabrics were measured according to the standard method [17]. Ultraviolet light transmittance and reflectivity of the un-dyed and dyed fabrics were determined using the spectrometer (Lambda 900 UV/Visible/NIR). The UV-protection Factor (UPF) and ultraviolet transmittance rate (T(UV)) were calculated by using Eqs. (1) and (2), respectively,

$$\mathrm{UPF} = \frac{\int_{290}^{400} E_\lambda \times S_\lambda \times \mathrm{d}\lambda}{\int_{290}^{400} E_\lambda \times S_\lambda \times \tau_\lambda \times \mathrm{d}\lambda} \tag{1}$$

where S_λ is erythema action spectrum, E_λ is solar irradiance ($\mathrm{w\,m^{-2}\,nm^{-1}}$), $\mathrm{d}\lambda$ is wavelength increment, and τ_λ is spectral transmittance of the specimen

$$T(\mathrm{UV})_i = \frac{1}{m}\sum_{290}^{400} \tau_\lambda \quad (2)$$

where m is the number of measurement points for UV and τ_λ is spectral transmittance.

2.3.3. Measurement of FTIR

IR characterisation of un-dyed cotton and dyed cotton was performed using a Bruker IFS Equinox 55 FTIR spectrometer (signal averaging 30 scans at a resolution of 4 cm^{-1}). KBr pellets containing ca. 2 mass% of material were analysed.

3. Results and discussion

3.1. Color fastness

Tables 2 and 3 show that the fabrics dyed by the *Rheum* and the *L. erythrorhizon* exhibited excellent fastness characteristics. On comparing the fastness ratings of the samples (cotton and silk) dyed by the *Rheum* and the *L. erythrorhizon*, it was found that the dyed silk had better fastness properties than the dyed cotton utilizing the same type of natural dye. This might be because the silk had a relatively stronger affinity for those dyes. For better fastness to light and washing, the use of mordants may be essential for most of natural dyes. The effect of the mordant is to assist the adsorption of the dye and promote good bonding of dye and fiber as a bridge, which helps to bond fiber and natural dyes at the molecular level. From Tables 2 and 3, it can be seen that the dyed samples that were first treated with mordants had better fastness properties than the dyed samples without mordants.

3.2. Ultraviolet transmittance spectra

The sun emits UV radiation across a broad spectrum from the high-energy UV-C band (wavelength below 280 nm) and the UV-B band (280–315 nm) to the UV-A band (315–400 nm). Continuous depletion of the stratospheric ozone layer has resulted in an increase in UV-B and a little UV-A radiation reaching the earth's surface. No UV-C radiation reaches the earth's surface due to absorption by oxygen and ozone in the upper atmosphere. Therefore, the transmittance of ultraviolet including UV-A and UV-B through the fabrics was evaluated in this experiment. The method used to quantify the UV-protection property of fabrics was the measurement of the transmittance of UV-rays through the fabrics [17]. The less is the UV transmittance of a sample, the better is the UV-protection property that is achieved.

To investigate the UV-protective properties of natural dyes, the ultraviolet transmittance spectra of the cotton and silk fabrics without dyeing and finishing and the dyed cotton and silk fabrics were compared. The ultraviolet transmittance spectra of the fabrics dyed by *Rheum* and *L. erythrorhizon* are displayed in Figs. 1 and 2, respectively. As can be seen, there was a significant difference between the dyed fabrics and un-dyed fabrics for the ultraviolet transmittance spectra. The un-dyed fabrics had a high ultraviolet transmittance. The ultraviolet transmittance of the un-dyed cotton was about 35%. The ultraviolet transmittance of the un-dyed silk was about 10% in the UV-B band and about 45% in the UV-A band. This indicates that the resistance of un-dyed fabrics to ultraviolet ray was very poor. While the ultraviolet transmittance of fabrics dyed by *Rheum* and *L. erythrorhizon* appeared to be lower than 1.5%. Generally, the UV-protective properties of fabrics would be evaluated as good when the ultraviolet transmittance was less than 5% [18]. Evidently, good UV-protective

Table 2
Color fastness of the fabrics dyed by *Rheum*

Mordants	Fabric style	Washing fastness		Cracking fastness		Light fastness
		Fading	Staining	Dry	Wet	
Ferrous sulphate	Cotton	3–4	3–4	4–5	3	3
	Silk	3–4	3–4	4–5	4	3
Potassium dichromate	Cotton	3–4	4–5	4–5	4	4
	Silk	4–5	4–5	4	4	3–4
Potassium aluminium sulphate	Cotton	3	3	4–5	4	3
	Silk	4–5	3–4	4–5	4	3
Stannum chloride	Cotton	3–4	3–4	3–4	4	3–4
	Silk	3–4	3–4	4–5	4	4–5
Without mordants	Cotton	2–3	2–3	3–4	3	3
	Silk	3–4	3–4	3–4	3–4	3

Table 3
Color fastness of the fabrics dyed by *Lithospermum erythrorhizon*

Mordants	Fabric style	Washing fastness		Cracking fastness		Light fastness
		Fading	Staining	Dry	Wet	
Ferrous sulphate	Cotton	3–4	3–4	4–5	4	3
	Silk	3–4	3–4	4–5	4	3
Potassium dichromate	Cotton	4–5	4–5	4–5	4	4
	Silk	4–5	4–5	4	4	4–5
Potassium aluminium sulphate	Cotton	3	3	4–5	4	3
	Silk	3–4	3–4	4–5	4	4
Stannum chloride	Cotton	3–4	3–4	3–4	4	3–4
	Silk	3–4	3–4	4–5	4	3–4
Without mordants	Cotton	2–3	2–3	3	3	3
	Silk	2–3	2–3	3–4	3–4	3

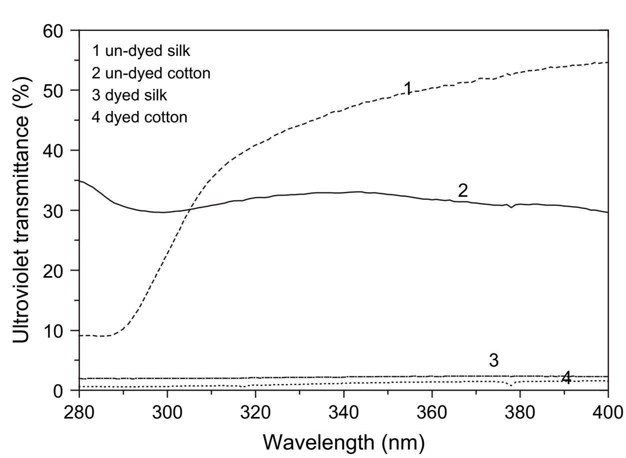

Fig. 1. Ultraviolet transmittance spectra of the fabrics dyed by Rheum.

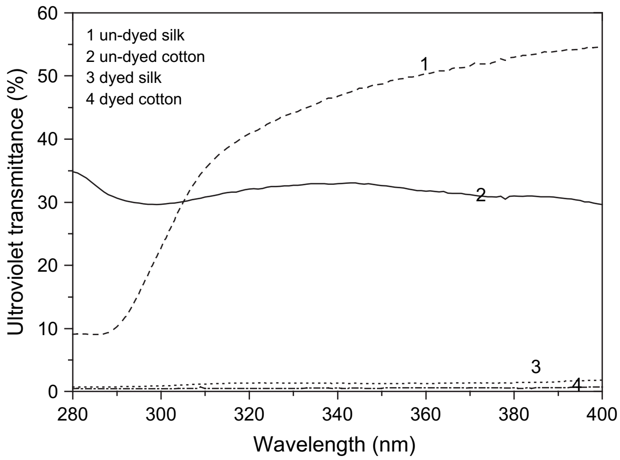

Fig. 2. Ultraviolet transmittance spectra of the fabrics dyed by *Lithospermum erythrorhizon*.

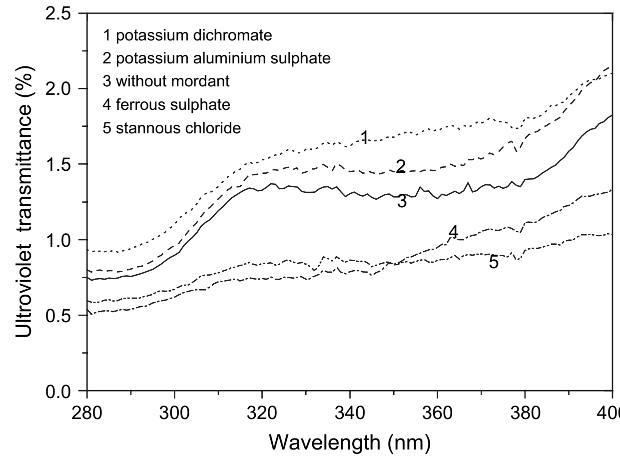

Fig. 4. Ultraviolet spectral transmittance of different mordants for fabrics dyed by *Lithospermum erythrorhizon.*

properties of fabrics occurred when they were dyed by *Rheum* and *L. erythrorhizon*.

Figs. 3 and 4 show ultraviolet spectral transmittance of fabrics dyed by *Rheum* and *L. erythrorhizon* under the conditions of using different mordants. It is clear that different mordants had different effects on the spectral transmittance of fabrics dyed by natural dyes. Compared with the dyed fabric without mordant, the value of the spectral transmittance could be decreased by using mordants such as stannous chloride, ferrous sulphate. On the other hand, potassium dichromate increased the UV transmittance. This could be attributed to the metal salts (mordant) "bridging" the fabrics and the natural dyes resulting in the formation of different conjugated π-bonds.

The degree to which a fabric protects the skin from UVR is given as its UPF. The higher UPF represents more effective blocking and therefore can provide better UV-protection for the wearer of a garment made from the fabric. In this experiment, the UPF of the fabrics dyed by these natural dyes was more than 50 according to Eq. (1), and the value of the $T(\mathrm{UV})_i$ was lower than 1.5% by following Eq. (2). In fact, when the UPF of the dyed fabrics was higher than 50 and the value of the $T(\mathrm{UV})_i$ was lower than 5%, the fabric was considered to be a solar ultraviolet protector [19]. This further demonstrated that the fabrics dyed with natural dyes strongly blocked ultraviolet radiation. Thus, they could effectively protect skin from solar ultraviolet radiation.

3.3. Ultraviolet reflectivity spectra

Apart from ultraviolet transmittance spectra, the ultraviolet reflectivity spectra of the fabrics dyed with natural dyes were also measured in this experiment. Fig. 5 shows the ultraviolet reflectivity spectra of the fabrics dyed by the natural dyes. The reflective values of the fabrics dyed by the *Rheum* and the *L. erythrorhizon* were in the range of 5–15%. As expected, the cotton and silk dyed by the same type of natural dye showed different reflective values. Similarly, the reflective values of the same fabric dyed by the different natural dyes were also different. This indicated that the reflective values were significantly affected by the structure of the fabrics and the natural dyes.

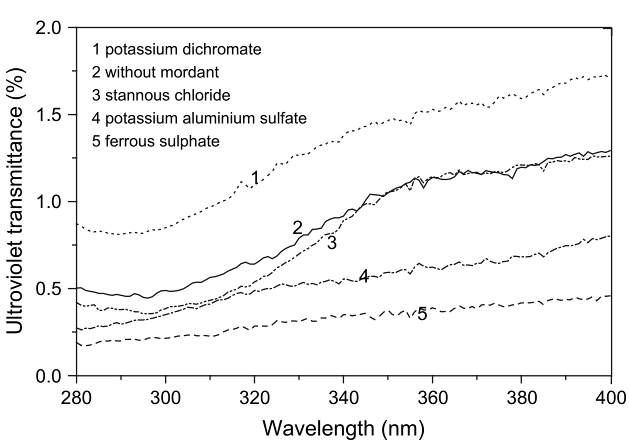

Fig. 3. Ultraviolet spectral transmittance of different mordants for fabrics dyed by Rheum.

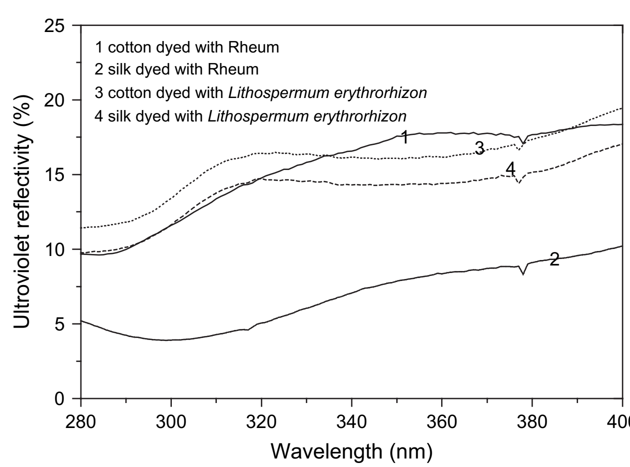

Fig. 5. Ultraviolet reflectivity spectra of the fabrics dyed by Rheum and *Lithospermum erythrorhizon*.

Light is transmitted, reflected and absorbed in nature. As can be seen in Figs. 1 and 2, the ultraviolet transmission value of the fabrics dyed by *Rheum* and *L. erythrorhizon* was about 1%. While Fig. 5 shows that their reflectivity was in the range of 5–15%. According to the energy distributing principle: $\alpha+\rho+\tau=1$ (α – absorptivity, ρ – reflectivity, and τ – transmittance), the fabrics dyed by the natural dyes could absorb about 80% of the ultraviolet light. Thus, it is clear that the UV-protective properties of natural dyes were mainly attributed to their absorption of solar ultraviolet.

3.4. Comparison of UV-absorption between natural dyes and benzophenone

In order to demonstrate the absorption performance of the natural dyes for UVR, benzophenone was selected as a common organic UV-absorber. Table 4 shows the UV-absorption of the natural dyes and benzophenone under the same experimental conditions. The data in Table 4 indicate that the natural dyes such as *Rheum* and *L. erythrorhizon* had comparable UV-absorption performance to benzophenone.

The key reason for the common UV-absorbers to absorb ultraviolet radiation can be attributed to photochemical reactions [20]. When the UV-absorbers absorb ultraviolet light, vibrations of the molecules destroy chemical bonds and cause a chain reaction of free radicals. On the other hand, tautomerism can take place in the process of UV-absorption, which can contribute to the absorption of ultraviolet light. Although, the photochemistry of common UV-absorbers has been the subject of much scrutiny [21,22], the UV-absorption mechanism and the photochemistry reactions of natural dyes has not been reported.

3.5. FTIR absorbability spectra

Fig. 6 shows the FTIR spectra of un-dyed and dyed cotton by *Rheum* and *L. erythrorhizon* natural dyes. It can be seen that the broad band at 3600–3200 cm^{-1} for the un-dyed cotton revealed the presence of numerous hydroxy groups. The band of samples become narrow from 3600–3200 cm^{-1} to 3500–3300 cm^{-1} after dyeing by *Rheum* and *L. erythrorhizon* natural dyes, suggesting the existence of hydrogen bonds. The presence of more than one hydrogen bond donor and one acceptor would be expected to lead to more hydrogen bonds which could make the hydrogen bond behavior more complicated.

The relatively steady hydrogen bonds could form in the molecules of some natural dyes such as *Rheum* and *L. erythrorhizon* [23]. When exposed to UVR, a possible photochemistry reaction of the natural dyes could occur as depicted in Fig. 7. The cleavage of H–O bonds could occur in the reaction, during which UVR could provide sufficient energy. Therefore, it can be proposed that the cleavage of hydrogen bonds in the molecules of the natural dyes contributes to their capacity to absorb UVR.

Table 4
Comparison of UV-absorption between the natural dyes and benzophenone

Wavelength (nm)	Absorption		
	Rheum	*Lithospermum erythrorhizon*	Benzophenone
280	4.34	4.06	4.89
290	4.26	4.92	5.04
300	4.21	4.27	4.19
310	4.65	3.55	4.88
320	4.10	3.33	4.06
330	3.90	3.06	3.48
340	3.52	3.03	
350	3.12	2.87	
360	2.98	2.86	
370	2.65	2.53	
380	2.34	2.55	
390	2.15	2.49	
400	1.34	2.62	

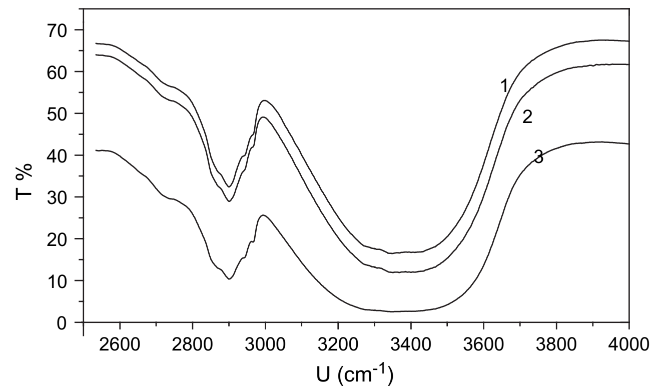

Fig. 6. FTIR spectra of the cotton un-dyed and dyed by Rheum and *Lithospermum erythrorhizon* (1. dyed cotton by *Lithospermum erythrorhizon*; 2. dyed cotton by Rheum; 3. un-dyed cotton).

4. Conclusions

This study demonstrated, for the first time, that *Rheum* root and *L. erythrorhizon* root extracts have excellent UV-protection (including the UV-B band and UV-A band) properties. The following conclusions are drawn from the results presented in document:

1. Cotton fabric and silk can be dyed successfully by the natural dyes extracted from *Rheum* root and *L. erythrorhizon* root;
2. The cotton and silk fabrics dyed by these natural dyes absorb about 80% of the ultraviolet rays. The UV-protection properties were mainly attributed to the absorption of UV radiation by the natural dyes;
3. The natural dyes exhibit a comparable UV-absorption performance to benzeophenone. A possible photochemical reaction is proposed that may account for the natural dyes' excellent UV-adsorption characteristics;
4. It is expected that cotton and silk fabrics dyed with these natural dyes can be applied to manufacture high-quality UV-protective garments. However, the formation of an efficient supplier organization which is able to provide a dye-house with standardized dyes of constant quality has to be fulfilled prior to the utilisation of these natural dyes by garment manufacturers.

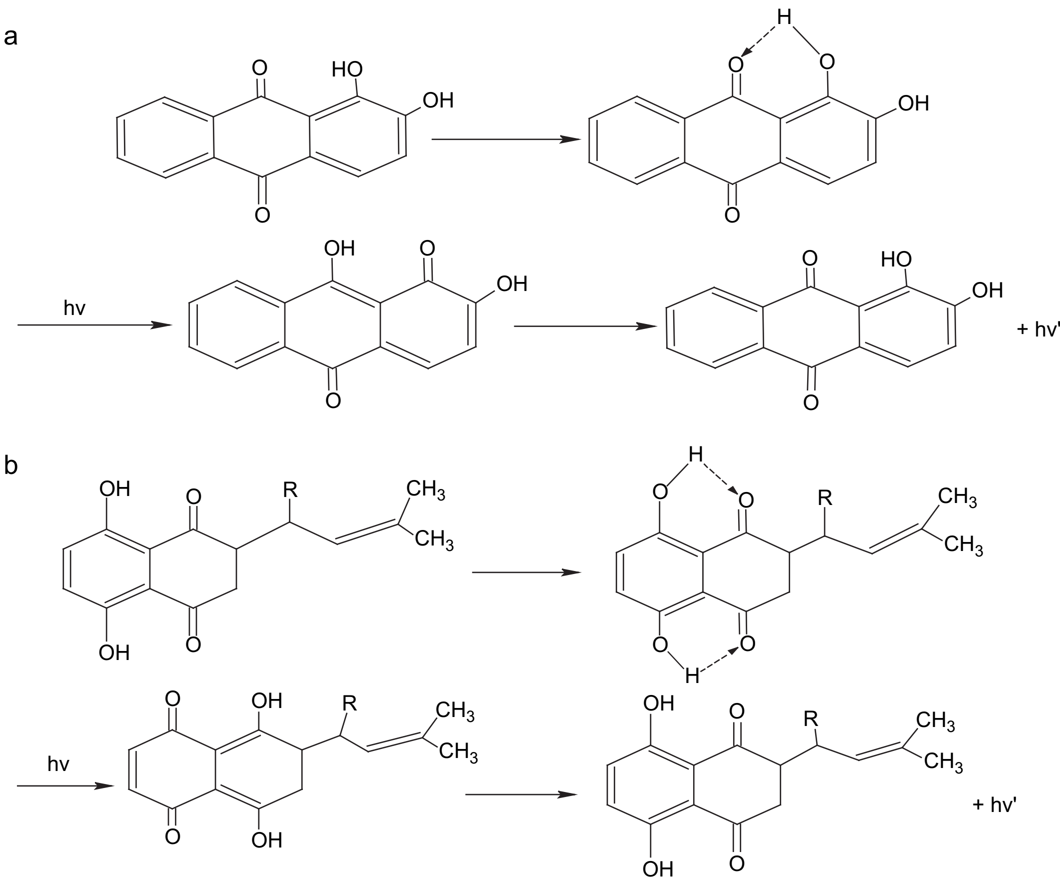

Fig. 7. Depiction of UV-absorptive scheme for the natural dyes (a. Rheum; b. *Lithospermum erythrorhizon*).

The results confirmed that natural dyes from *Rheum* root and *L. erythrorhizon* root had potential applications for UV-protective clothing.

Acknowledgments

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