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TUNISIAN POPULATIONS OF RHUS TRIPARTITA (UCRIA) GRANDE: A PROMISING SOURCE OF NATURAL DYES FOR TEXTILE APPLICATION

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ABSTRACT

Since ancient times, dyes derived from natural sources have been used for dyeing textile fabrics. During last few decades, Environmental awareness in the production and application of synthetic dyes revived interest in natural dyes. The use of plant extracts rich in polyphenols as sources of dyes is drawing attention due to their potent bioactive properties which could be useful for the development of functional dyed textiles.

This work aims the investigation of Tunisian populations of Rhus Tripartita for cotton dyeing. The solvent extraction method yields a highly concentrated dye which has been found to be rich in polyphenol compounds. The colored extract was applied on cotton fabric by exhaust dyeing method. The various parameters that may affect the dyeing process were investigated. Quality control of all dyeing was performed using standard fastness tests and colour measurements. The results were promising for R. Tripartita extract as a natural dye.

KEYWORDS

R.Tripartita; Natural dye; Cotton; Fastness.

1. INTRODUCTION

In recent years, polyphenols from different plants have attracted a great attention. In textile field, several investigations have been undertaken on the dyeing and functional finishing of textiles with polyphenols. Shin et al (1999) has applied polyphenols of green tea to dye protein, polyamide and cationic cotton fibers. Meksi et al (2012) has studied wool dyeing with polyphenols of olive mill wastewater and has shown that polyphenols are soluble in water containing hydroxyl groups and that their molecular structures presented an important electronic density due to their highly conjugated system. Ksibi et al (2015) has investigated phenolics of pepper to dye wool fabric. The use of polyphenols for dyeing rise from a significant interest in using natural dyes with particular biological activities. Thus, efforts are undertaken to identify and investigate potential plants rich in bioactive compounds that can lead to functional dyed textiles.

Rhus species are among the plants which present high contents in polyphenols (Itidel et al., 2013). The genus Rhus contains over 250 individual species in the family Anacardiaceae (Rayne, Mazza, 2007). Various species have been traditionally used for medicinal purposes. *R. Tripartita*, one of the Rhus species, is a low spiny bush of the Tunisian Sahara. Its common name is ''Jedari''. The geographical distribution of *R. tripartita* is primarily in North Africa (Pottier Alapetite, 1981).
In Tunisia, *R. tripartita* has been used for several hundreds of years to treat skins of animals to produce leather making it more durable, less susceptible to decomposition and stained red. Recent works on *R.tripartita* showed high antioxidant activity (Tebourbi et al., 2006). They showed also antibacterial and

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antifungical activities (Abbassi, Hani, 2012). To our knowledge there are no reports about cotton dyeing with *R.Tripartita*.
In this paper, we report a study to produce a solid dye from dried barks. Total phenolic content has been analysed. Dyeing behaviour and colour strength have been tested. Furthermore, pre-mordanting has been carried out to study the effects on the washing, rubbing and light fastness.

2. MATERIAL AND METHODS

2. 1. Plant Materials

Barks of the plant *R.tripartita* were collected at the beginning of January 2014 in Tataouin (South of Tunisia). They were washed with water and dried at 50°C for 6 hours. Dried bark were cut in small pieces, powdered by electronic grinder, sifted and stored in dark.

2. 2. Textile Materials

Bleached cotton fabric with the following specifications (Twill weaved fabric, weight: 370 $g.m^{-2}$) was procured commercially and used for dyeing.

2.3. Extraction and characterization

Solvent extractions are the most commonly used procedures to prepare extracts from plant materials due to their ease of use, efficiency, and wide applicability (Dai, Mumper, 2010). Solvents, such as methanol, ethanol, acetone, hexane and ethyl acetate have been used for the extraction of phenolics, often with different proportions of water. Selecting the right solvent affects the extraction yield. Ethanol and methanol are among the most common used solvents to extract phenolic compounds (Dai, Mumper, 2010). During this work, extraction was done with methanol using Soxhlet technique. 20g of powdered *R.tripartita* bark were taken into a filter paper and placed in a Soxhlet apparatus, set up with 250ml of methanol and extracted according to its boiling point for 18 hours. After completion of extraction, the dark brown extract was then concentrated using rotary evaporator to get the supersaturated solution. Finally we used vacuum filtration to get a crude dried extract which was black in colour. Visible absorption spectrum was determined using an UV-visible spectrophotometer. Fourier transform infrared (FT-IR) spectrum of the crude extract was recorded between 4000 and 400cm^{-1}. The presence of phenolic compounds in the extract was studied by reversed phase HPLC analysis using a binary gradient elution. The phenolic compounds analysis was carried out using an Agilent Technologies 1100 series liquid chromatography (HPLC, Palo Alto, CA) coupled with an UV–vis multiwavelength detector. The separation was carried out on a 250mm × 8mm, particle size 5µm Eurospher-100C18 reversed phase column at ambient temperature. The mobile phase consisted of acetonitrile (solvent A) and water with 0.2% sulphuric acid (solvent B). The flow rate was kept at 0.5$ml.min^{-1}$. The separation was accomplished by gradient elution, as shown in Table 1. The injection volume was 20µL, and peaks were monitored at 280nm. Samples were filtered through a 0.45µm membrane filter before injection.

Table 1. Gradient program used for HPLC separation

Time (min)	Mobile phase A (%)	Mobile phase B (%)
0-12	15	85
12-14	40	60
14-18	60	40
18-20	80	20
20-24	90	10
24-28	100	-

2.4. Dyeing procedure

Cotton fabric samples were dyed at a liquor ratio (LR) of 1:40. Dyeing was performed at different pH and temperature values. The dyeing was carried out in laboratory dyeing machine (Ahiba Data colour International, USA). Then, the dyed fabrics were rinsed with cold water, squeezed and dried at room temperature.

Pre-mordanting technique was used for this study. Different mordants including aluminium sulfate hydrate (alum), copper sulfate, potassium dichromate and iron sulfate were used. Determination of metal content of the mordanted fabric is very important since toxic effects of heavy metals on human health are very well known (Iva Rezić, 2007). During this work, the contents of Cr and Cu ions on the mordanted cotton fabrics were quantified by inductively coupled plasma optical emission spectrometry (ICP OES) after an extraction procedure in an artificial acidic sweat solution which was prepared according to the ISO 3160/2 standard (Menezes et al., 2010). Measurements were obtained with a HORIBA Jobin Yvon ICP–OES spectrometer. Solutions samples are injected in the ICP by a peristaltic pump. The fine aerosol mist containing argon gas and sample is sent to the plasma center where the desolvation and the ionization of the sample occur. Each element exhibited a characteristic radiation with intensity proportional to the concentration of the element. The concentrations are given in $mg.L^{-1}$ (Mechmech et al., 2015).

2.5. Testing of colour strength

Dyed samples colour strengths were evaluated by light reflectance measurements using spectrophotometer (Data Color 650®, USA) under illuminant D65, with a 10° standard observer. The K/S values were assessed using the Kubelka-Munk equation:

$$(1-R)^2 / 2R=K/S \qquad (1)$$

Where, R is the reflectance, K the absorption coefficient and S the scattering coefficient

2.6. Colour fastness testing

The dyed samples were tested for fastness properties according to standard methods: Washing colour fastness (ISO 105-C02), rubbing fastness (ISO 105-X12) and light colour fastness (ISO 105-B02). Fading and staining of samples in colour were evaluated using grey and blue scales.

3. RESULTS AND DISCUSSION

3.1. Extraction and characterization

The efficiency of extraction reached 12%. The UV-visible spectrum of the crude extract is shown in Figure 1. The crude extract showed four maxima absorptions at 292nm, 428nm, 454nm and 478nm. The first band peaking appears due to the presence of aromatic ring(s), and is detected in the spectra of all phenolics. The other long-wave bands are situated in the 400-480nm range and they probably appear due to the presence of flavonoids.

FT-IR spectra (Figure 2) of the crude extract showed characteristic peaks related to the chemical structure of polyphenols. A broad band at $3275cm^{-1}$ belongs to stretching vibration of phenolic hydroxyl group (-OH). Appearance of broad band at wavenumber $2924cm^{-1}$ indicates presence of vibration stretching of aromatic (C-H) group, whereas the appearance of two medium and weak bands at $1610cm^{-1}$ and $1518cm^{-1}$ stretching vibration of aromatic (C=C) group.

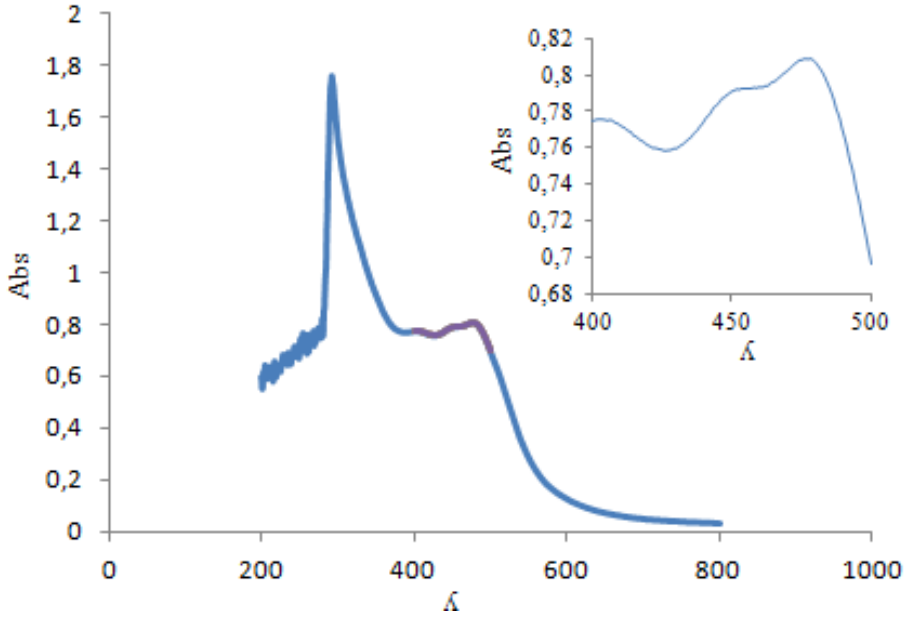

Figure 1: UV-visible spectrum of methanol extract

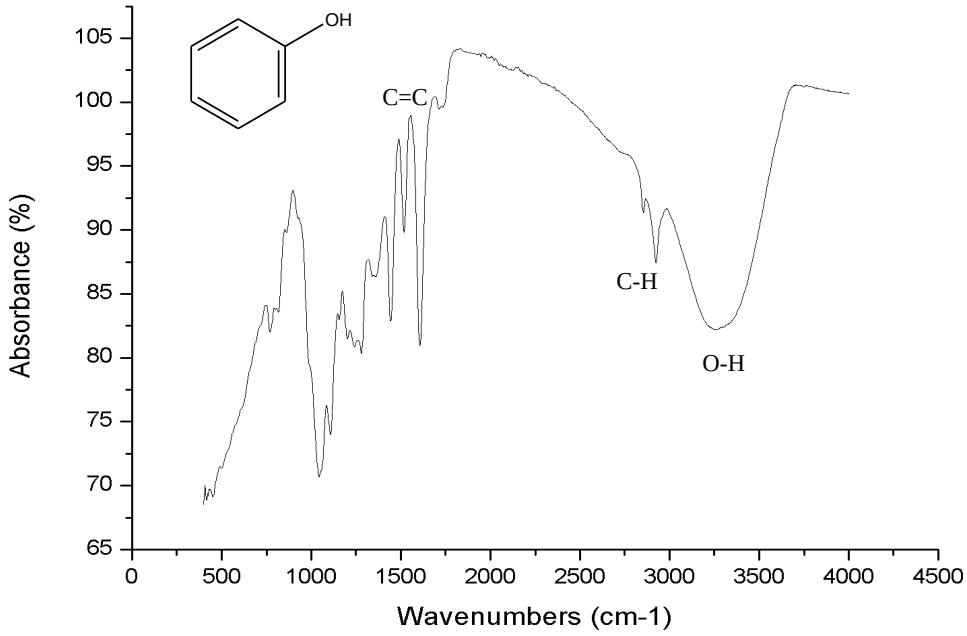

Figure 2: FT-IR spectra of *R.Tripartita* bark extract

HPLC chromatogram of methanol extract is shown in Figure 3. It can be observed that there are significant peaks indicating the presence of many compounds. According to the retention time in reversed phase chromatography and the published literature, some peaks were tentatively identified as **(1)** Kaempferol, **(2)** Butein, **(3)** Sulfuretin, **(4)** Fisetin, **(5)** Kaempferol-3-O-rhamnoside, **(7)** Fustin, **(8)** p-coumaric acid (Chen et al., 2014; Cho et al., 2013; Lee et al., 2009).

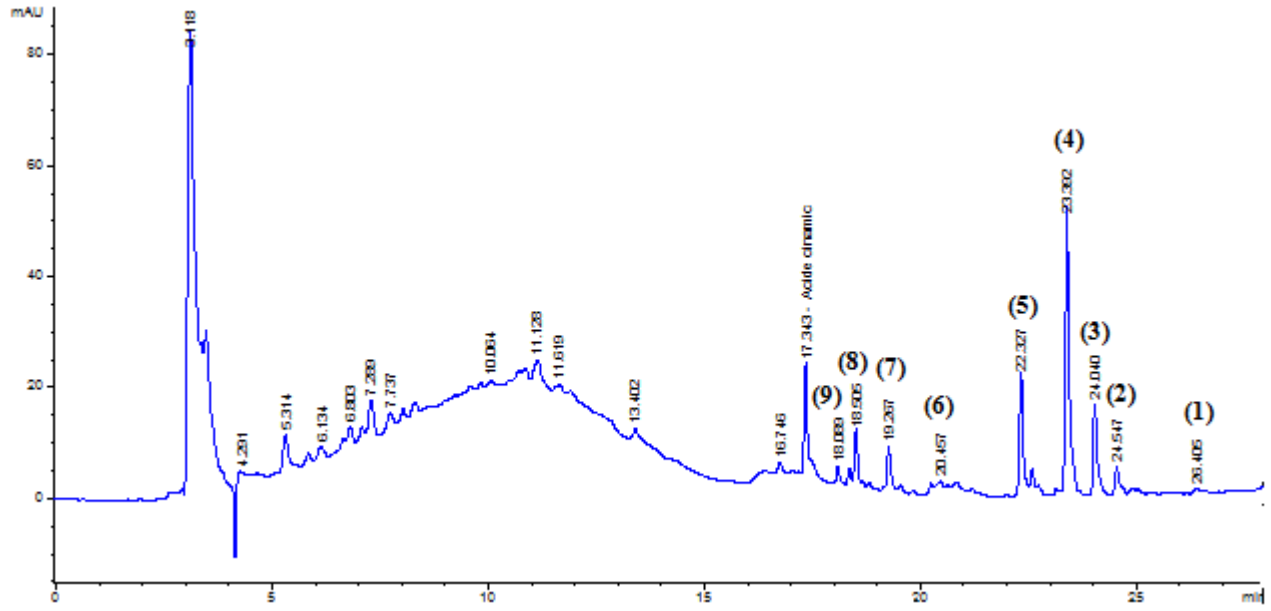

Figure 3: HPLC profile of methanol extract at 280nm wavelength

In the previous studies with *Rhus* bark extracts, 2,4-dihydroxybenzoic acid, protocatechuic acid, caffeic acid, chlorogenic acid, p-coumaric acid, phloretin-20 -O-glucoside, kaempferol-3-Oglucoside, quercetin, butein, and kaempferol, gallic acid, 2,6,3',4' -tetrahydroxy-2-benzylcoumaran-3-one, fustin, fisetin, and sulfuretin have been reported as major phenolic compounds (Kim et al., 2013). The composition and contents of the ingredients varied as the Rhus specie was different. However, the main ingredients were generally fustin or fisetin, which is consistent with the chemical profile of the present work. Due to the complexity of chemical composition in plant extracts, it is costly to separate each compound. In addition the desired colour of natural extract results from a cooperative action of all compounds.

3.2. Determination of total phenolic content

Total phenol content was determined by Folin- Ciocalteu method according to Scalbert et al. (1999). 0.5mL of water extract at appropriate dilutions was mixed with 2.5mL of Folin–Ciocalteu's reagent and 2mL of 7.5%Na_2CO_3. The mixture was allowed to stand for 5min at 50◦C in a water bath. The absorbance was measured at 760nm. A gallic acid aqueous solution was used for calibration. Results were reported as mg Gallic Acid Equivalent (GAE) per g of dry weight (DW) (Scalbert et al., 1989). Results revealed the highest amount of total phenols: 181±30mg(GAE).g^{-}1(DW).

3.3. Dyeing

3.3.1. Effect of dyeing pH

Figure 4 shows that Yellow red colour was observed only at acidic pH values. This enhancement in K/S values at acidic pH may be attributed to better dye uptake and building up of dye molecules onto the protonated active sites of cotton fibers. Higher K/S value is achieved at pH 5. For pH>5 K/S values decreased markedly. According to these results, the pH of dye bath in all next experiments was fixed at 5. In conventional dyeing processes, treatments at acidic pH are not suitable for cotton fabric since they damage mechanical properties. However garment processes, especially enzyme treatments, are treating denim fabrics at pH 4 and 5.

Khan et al has reported that cellulase enzyme treatment of denim fabric conducted at pH 5.5 and a temperature of 70°C resulted in a tensile strength decrease by 22% for warp yarns and 30% for weft yarns (Khan et al., 2013). As such as difference is acceptable for designers since they aim to create eco-friendly,

fashionable and low cost clothing collections. They did not search to provide the strength required in high-quality suits.

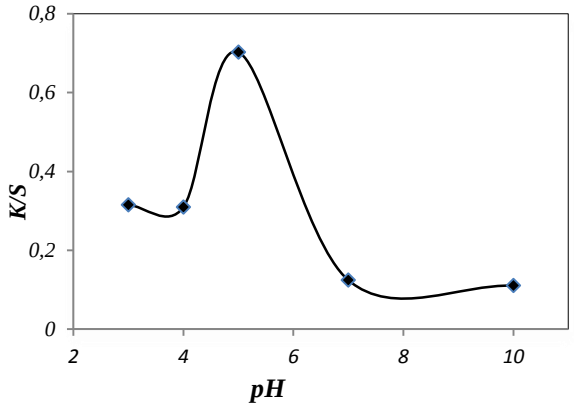

Figure 4: Effect of dye bath pH on the colour strength of dyed cotton fabrics

Dyeing conditions: dye concentration 0.25g/100ml, 45min, LR 40:1 and T=70°C.

3.3.2. Effect of dyeing temperature

As shown in Figure 5, colour strength of dyed samples increases as the temperature increases up to 70°C and then decreases. This finding can be explained by the fact that heating increases the cotton fiber swelling, and leads to a more dye dispersion and solubility. Beyond 70°C, the K/S values decrease with a pronounced manner. These data are probably due to the dye desorption from the fiber (Guesmi et al., 2013).

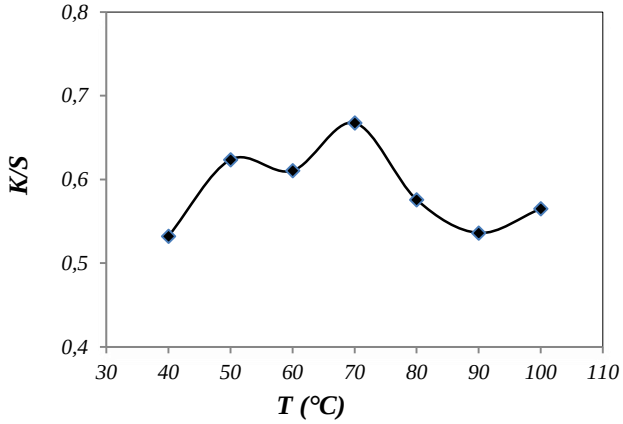

Figure 5: Effect of dye bath Temperature on the colour strength of dyed cotton fabrics.
Dyeing conditions: dye concentration 0.25g/100ml, 45min, LR 40:1 and pH=5.

3.3.3. Mordanting Effect

The type of shades produced and the color strength values were affected by using the different mordants (Table 2). Pre-modanting has increased the color strength of dyed fabrics and iron sulfate gave the highest value (K/S=2.22). According to Meksi et al (2012), metallic mordants enhance the interaction between the fiber and the dye by forming coordination complexes between both the hydroxyl groups of the dye molecules and the fiber functional groups resulting in an improvement of dye uptake. In addition, chemical reaction between natural dyes and mordants depended on the unique structures of the colour components

and on the strength of the metal dye coordination complex formed during the dyeing process (Wanyama et al., 2011). Chromium and copper concentrations extracted from dyed mordanted fabrics were 0.125 and 13.91mg.L^{-1}. These concentrations did not exceed the limits suggested by different ecological standards (Iva Rezić, 2007).

Table 2. Mordant effect on the colorimetric data of dyed fabrics

Pre-mordanting	L^*	a^*	b^*	C^*	h	K/S
None	77.31	7.82	11.49	13.90	55.76	0.66
Alum	74.90	8.07	13.04	15.34	58.25	0.81
Copper sulfate	71.72	10.24	15.50	18.58	56.56	1.14
Potassium dichromate	77.50	7.48	13.30	15.26	60.64	0.69
Iron sulfate	59.75	6.31	15.69	16.91	68.09	2.22

3.3.4. Colour fastness

The rating of fastness (washing, rubbing and light fastness) of pre-mordanted and un-mordanted cotton fabrics dyed with *R.tripartita* extract is shown in Table 3. It was found that rubbing fastness of un-mordanted cotton fabrics showed excellent properties. However, washing fastness was relatively good and light fastness was fair. Generally, it is well known that the poor light fastness was a problem for natural dyes. The wash fastness of pre-mordanted cotton fabrics was found to be better. From these results, it can be concluded that some mordants improve the wash fastness of cotton fabrics. Iron sulfate is the best mordant to improve light fastness.

Table 3. Colour fastness

	Dry rubbing fastness	Wet rubbing fastness	Washing fastness	Light fastness
None	4-5	4-5	3	2
Alum	4-5	4-5	3-4	2
Copper sulfate	4-5	4-5	4	2
Potassium dichromate	4-5	4-5	3-4	2
Iron sulfate	4-5	4-5	4	2-3

4. CONCLUSION

This study provided evidence of the highest polyphenolic content of *R.Tripartita* bark extract. The production of a concentrated dyestuff was achieved using Soxhlet extractor. The extraction method requires only basic equipment that can be installed at the industrial site. In addition, having a concentrated dye made possible the standardization of the dyeing process for better reproducibility. Dyeing of cotton fabric with the crude extract is found to be effectively realized at pH 5 and a temperature of 70°C. The pre-mordanted dyed samples showed better fastness properties and colour strength values. Fastness properties ranged from good to excellent while light fastness was fair. R. tripartita, an abundantly available plant in Tunisia, offers a potential for future use as natural dye for textile application. Based on the results of this work, we anticipated that *R. Tripartita* used as natural dye might impart bio-functional properties to textiles since polyphenols are well known as natural bio-acting agents.

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