



Dyeing of Wool Fibers with Natural Fungal Dye from *Suillus luteus*

NURDAN KASIKARA PAZARLIOGLU^{1,*}, ALPER AKKAYA¹, A. MERIH SARIISIK², GOKHAN ERKAN² and E. PERRIN AKCAKOCA KUMBASAR³

¹Department of Biochemistry, Faculty of Science, Ege University, Bornova, Izmir, Turkey

²Department of Textile Engineering, Faculty of Engineering, Dokuz Eylul University, Buca, Izmir, Turkey

³Department of Textile Engineering, Faculty of Engineering, Ege University, Bornova, Izmir, Turkey

*Corresponding author: Fax: +90 232 3438624; Tel: +90 232 3884000/2396 E-mail: nurdan.pazarlioglu@ege.edu.tr

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Suillus luteus is a pored, edible mushroom of the genus *Suillus* in the *Suillaceae* family in *Boletales* order. The wool fabrics were dyed with the ethanolic extract of *S. luteus* fruit bodies at different pH values with various mordants. The greatest colour yield was obtained at pH 3 without mordant. Highest K/S values were obtained at pH 5 and 6 mordanting with copper sulfate. However at pH 4, 3 and 2 the highest K/S values were obtained mordanting with tin(II) chloride. Although, all dyed samples have good washing and crocking fastness, poor washing fastness colour change values were observed at pH 2 and 3 without mordanting.

Key Words: *Suillus luteus*, Natural dye, Wool, Mordant, Dyeing, Suillusin.

INTRODUCTION

Colour plays a significant role in the use of textiles. The pleasure derived from imparting colour to textile material has existed since the time of the earliest civilization. Dyes and pigments were traditionally obtained from natural sources, but by the second half of the 19th century the first synthetic dye had been synthesized by William Henry Perkin and the introduction of synthetic dyes led to an almost complete replacement of natural dyes, due to the favourable application properties of synthetic dyes. Compared to their natural counterparts, synthetic dyes made available a wide range of shades, higher fastness and reproducibility¹⁻⁷.

Today, the textile industry produces and uses *ca.* 1.3 million tones of dyes, pigments and dye precursors, valued at around \$ 23 billion, almost all of which is manufactured synthetically. However, manufacturing of synthetic dyes suffers from the following limitations: environmentally unfriendly, increase in cost of feedstock or energy, hazardous waste generation, increasing transportation costs, toxic and allergic reactions. In addition, today natural dyes are used in limited quantities in part due to the fact that they are environmentally-friendly. Conventional wisdom leads to the belief that natural dyes are friendlier to the environment than synthetic dyes^{2-5,7,8}.

The limitations of the natural dyes, which were responsible for their failure: minor availability, weak colour yield, complex dyeing process, non-repeatability of shade, limited

number of suitable dyes, mixing difficulty of dyes, only suitable for wool, natural silk, linen and cotton, non-standardized, inadequate fastness properties, water pollution by heavy metal mordants and large amount of organic substances.

In addition, the following properties are considered being the advantages of natural dye. They are obtained from renewable resources, no health hazards, practically no or mild chemical reactions are involved in their preparation, no disposal problem, they are unsophisticated and harmonized with nature^{2,6}.

Besides, even though usage of natural dyes in textile dyeing is limited in comparison to the commercial synthetic dyes, scientific and artistic concern in these dyes has never decreased⁹. Especially dyeing of wool, silk, mohair, *etc.*, with natural dyes causes them to obtain an additional value. Also natural dyes are obtained from renewable sources such as crops, may decrease the dependence to the petrochemical sources^{1,3,10}. The future demand for more sustainable processes can be seen as a driving force for new strategies which could bring a revival of natural dyes in textile dyeing².

Recently many researchers have interested in natural dyes due to reasons that mentioned above^{1-8,10}. Plants, such as barberry, Canadian golden rod, walnut tree, *Rubia* sp. and so forth, are the major sources of natural dyes. In addition new dyeing techniques like ultrasound or usage of modified cotton for natural dyes have also investigated¹¹⁻¹³. However a few reports have been published about fungal sources of natural dyes. The fungus *Monascus*, traditionally used for manufacturing food colourants (*e.g.* red rice), has been studied by

De Santis *et al.* to produce red or orange pigments in a well-established production media and to determine the dyeing capacity of ethanolic extracts on raw wool specimens differently premordanted. Assessment of the resistance to fading of dyed specimens by carrying out some fastness standard tests was done¹⁴. Nagia and El-Mohamedy were studied on dyeing of wool with natural anthraquinone dyes from *Fusarium oxysporum*. Their study shows that natural anthraquinone dyes can provide bright hues and colour fastness properties¹⁵.

The aim of this research is to isolate natural dye from the fruit bodies of *Suillus luteus* for dyeing wool and to evaluate their effectiveness on dye ability and fastness properties. To the best of our knowledge, this is the first study on dyeing wool fiber with a natural pigment from *S. luteus*.

EXPERIMENTAL

The fruit bodies of *S. luteus* were harvested from habitat around Bornova in Izmir, Turkey (Fig. 1). Macroscopic discrimination of this macro fungus was carried out in Ege University, Faculty of Science, Biology Department, Basic and Applied Microbiology Section.



Fig. 1. *Suillus luteus* (harvested in October-2007; Bornova, Izmir, Turkiye)

Scoured and bleached 100 % wool woven fabric was used in the experiments. Properties of fabric are shown in Table-1.

TABLE-1
PROPERTIES OF WOOL FABRIC

| Construction | Twill |
|---------------------|---------------------|
| Weight | 271 |
| Yarn count (Warp) | 60/2 Nm |
| Yarn count (Weft) | 60/2 Nm |
| Yarn density (Warp) | 45 cm ⁻¹ |
| Yarn density (Weft) | 35 cm ⁻¹ |

Metallic salts such as copper sulfate, potassium dichromate, aluminum sulfate and tin(II) chloride were used as mordant. All chemicals were commercially available and reagent grade.

Dye extraction: Whole fresh fruit bodies of *S. luteus* were cleaned, frozen and kept at -20 °C until extraction of their pigments. 650 g of frozen mushrooms were macerated in 95 % (v/v) ethanol for 24 h and extracted three-times by a mechanical shaking with ethanol and then ethanol extract was evaporated under reduced pressure. Residual fraction of extract

was re-extracted with CHCl₃ to exclude hydrophobic fraction of crude preparate and then freeze dried to dryness. The final extract (38.7 g) was partitioned and diluted before using at desired concentration.

UV/vis absorption spectra and fluorescence spectra:

The UV/vis and fluorescence spectra were measured by using a Perkin-Elmer Lambda 25 UV/vis spectrophotometer and an RF-5301 PC spectrofluorometer (Shimadzu), respectively. The emission wavelength was fixed at 460 nm and the sample was excited at 348 nm. All samples were measured at 25 ± 0.1 °C.

Dyeing: Extracted dye solution was diluted 1:1 ratio with water. Dyeing was starting at room temperature and raising the temperature 1.5 °C/min to the 90 °C. Dyeing was carried out at 90 °C for 1 h, then the mordants were added to the dyeing liquor and mordanting was performed for 0.5 h at 90 °C. All dyeing were done at pH 2, 3, 4, 5 and 6. After dyeing the samples were rinsed with tap water and washed at 90 °C for 15 min. Finally the samples were rinsed with cold water and dried at ambient temperature. All treatments were performed at 1:10 liquor ratio and achieved at laboratory type dyeing machine (Labortex IR-Dyer, Taiwan).

Fastness tests: Colour fastness to rubbing was performed according to EN ISO 105-X12. Washing fastness was carried out according to EN ISO 105-C06. Colour fastness to light was done according to 1008 EN ISO 105-B02.

Colour yield and CIELabCH values: Colour yield was evaluated by using of K/S values which were calculated from Kubelka-munk formula. Reflectance and CIELabCH values were measured by Minolta 3600D spectrophotometer, (specular included, illuminant D 65, 10° observer).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where R: % remission value, K: light absorption, S: light reflection.

Dye exhaustion: Dye exhaustion was monitored spectrophotometrically at 360 nm. All dyeing were carried out at pH 6, 5, 4, 3 and 2 and 90 °C. Absorbance values of all dyeing liquor samples were measured at definite intervals of dyeing. Initial absorbance assumed as 100 % and absorbance percentage was expressed by following formula:

$$\%A_r = 100 - \left(\frac{A_i - A_t}{A_i} \times 100 \right) \quad (2)$$

where A_i is the initial absorbance, A_t is the absorbance at time, A_r is the absorbance percentage in the dye liquor.

The absorbance of solution is directly related to the concentration by Lambert-Beer's law. Therefore concentration gradient of dye molecules can be easily observed by changes in absorbance values of liquor. Equation 2 can be converted as eqn. 3:

$$\%C_r = 100 - \left(\frac{C_i - C_t}{C_i} \times 100 \right) = \%A_r \quad (3)$$

where C_i is the initial concentration, C_t is the concentration at time, C_r is the concentration percentage in the dye liquor.

RESULTS AND DISCUSSION

Structural properties of isolated dye: Fruiting bodies of some macromycetes can give a range of pinks, blues, yellows, reds and browns (*e.g.* *Boletus*, *Cortinarius*, *Hydnellum*, *Hygrocybe* spp) using mordant such as alum or iron¹⁶. The *Suillus* genus, included in the Boletal order, is widely distributed throughout the world and has been used as a model in the exclusive symbiotic interaction with pines¹⁷. In previous chemical studies of this genus, precedents of quinone-type compounds isolated from *Suillus granulatus*, *S. luteus* and *S. placidus*¹⁸, as well as tetraprenylphenols from *S. granulatus* and *S. bovinus*, with antibacterial activity and cytotoxicity against KB cells¹⁹, have been described. The methanolic extract from *S. luteus* exhibited potent antioxidant²⁰ and cytotoxic activities²¹. This genus has also produced yellow pigments as secondary metabolites²².

In this study, isolation of these yellow pigments from *S. luteus* was carried out by extraction with ethanol and then, hydrophobic fraction of the extract was removed with chloroform extraction. Final ethanolic extracts with different pH were diluted and analyzed at spectrophotometrically. Fig. 2a shows the absorption spectra of the corresponding isolated pigment at pH 4.0, 6.5 and 11.0. The absorption spectra showed the same profile which are between pH 2.0 and pH 10.0. UV absorption maxima of the pigment were at 348 nm. However, the spectral curve of pigment, could be confusing as the higher part of the curve, at the region of *ca.* 380- 400 nm.

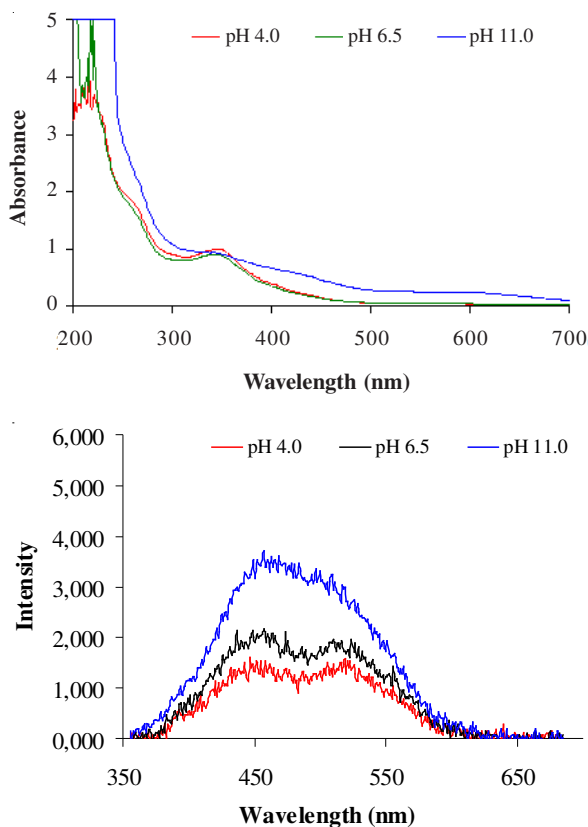


Fig. 2. (a) Absorption spectra of clarified extract of *S. luteus* fruit bodies at different pHs (b) Fluorescence spectra of clarified extract of *S. luteus* fruit bodies at different pHs

Since isolated pigment has fluorescent properties, it was also analyzed at fluorometrically (Fig. 2b). Aqueous solutions of dye with pH 4.0, 6.5 and 11.0 proved to exhibit intense fluorescent emission ($\lambda_{em} = 460$ nm) when excited at $\lambda_{ex} = 348$ nm (Fig. 2b). It was observed that fluorescent emission of dye in solution is strongly dependent on pH changes and dye fluorescent emission ($\lambda_{em} = 460$ nm) increases with increasing pH. This should be ascribed to the chemical structure change of dye at different pH values (Fig. 3).

An extensive compilation of the chemical and biosynthetic aspects of macromycete pigments by Gill & Steglich and structural formulae and further references can be found in the review of these authors²³. Important pigments from *Suillus* were briefly characterized as terpenyl quinones, cyclopentenones, pulvinic acid derivatives, grevillins, 1,2,4-trihydrobenzene, prenylated phenols, prenylated benzoquinones, cavipetins and carotenoids. During the biosynthesis of atromentin, a pulvinic acid derivative, a benzoquinone ring is produced by forming two C-C bonds. In the case of one C-C bond is formed, the resulting lactonization yields grevillins. This kind of pigment virtually appears only in the genus *Suillus*. The rearrangement is needed for the transition from grevillin B to grevillin D²².

A benzofuran pigment suillusin, which has the same UV absorption maxima at 348 nm with present pigment from *S. luteus*, was isolated from the methanolic extract of fruiting body of the mushroom *S. granulatus* by Yun *et al.*²⁴. They reported that the structure of this compound was assigned on the basis of various spectroscopic analysis as a highly substituted novel 1*H*-cyclopenta[*b*]benzofuran(I), suillusin and it was suggested to be biogenerated from polyporic acid. However, Gill was reported that there is a very close biosynthetic relationship between suillusin (I) and grevillin D (II), which was isolated from *S. granulatus* by Besl and co-workers¹⁸. Grevillin D (II) is isomeric with the carboxylic acid corresponding to the ester I. It seems very likely that both suillusin and grevillin D are descendents of a common biosynthetic precursor in the form of the tautomerically-fluid keto-enol III, as was originally proposes by Gill and Steglich^{23,25}. In this case, it is convenient to be called this pigment as grevillin D.

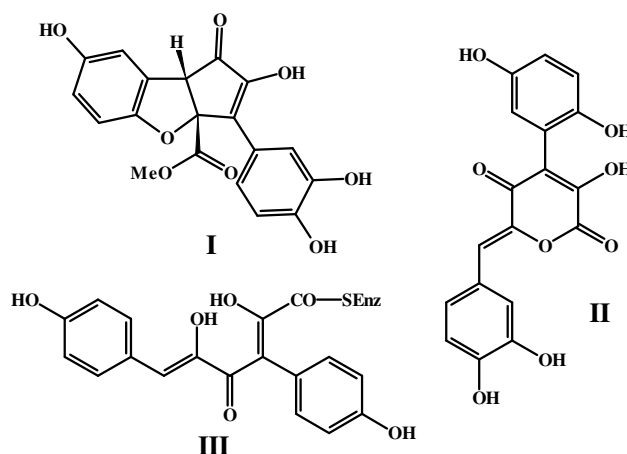


Fig. 3. Chemical structures of pigments (I) suillusin (II) grevillin D (III) biosynthetic precursor of suillusin and grevillin D

Dye exhaustion: For this research dye exhaustion is given as absorbance percentage change of dyeing liquors at 90 °C and at different pH values is shown in Fig. 4. For all pH values first 0.5 h of dyeing shows a rapid decrease of absorbance percentage. A slow decrease of absorbance percentage was observed after 30th minute of dyeing.

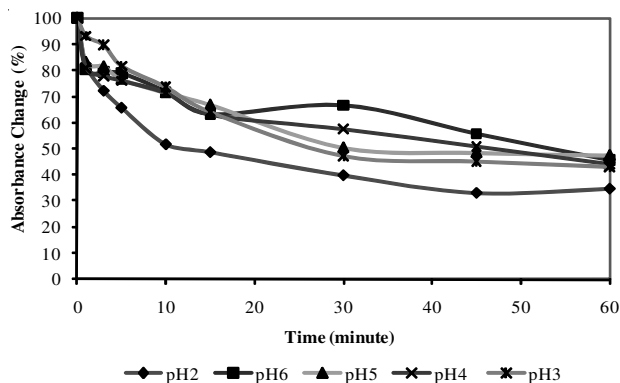


Fig. 4. Dye exhaustion according to absorbance percentage change at dye liquor

At highly acidic conditions, wool fibers were positively charged. Thus the maximum absorbance change occurs at pH 2. The increase of pH value decreased the dye uptake due to decreasing of positive charge of wool fibers.

Colour yield and colour hue changes: As it is known isoelectric point is the state when all the acidic and basic groups in the wool are electrostatically in equilibrium. When excess of hydrogen ions are present they will be attracted by the electro-negative carboxyl ions leaving a positive charge on the wool. In a similar manner an excess of hydroxyl ions will result in a negative charge on the fiber by neutralizing the NH_3^+ groups. This property affects dye uptake of anionic dyes on wool.

Fig. 5 shows K/S values at different pH values at maximum absorbance wave length (400 nm) without mordant. The highest colour yield was obtained at pH 3 for unmordanting samples. This result can be related to dyes behaviour at different pH values, which is mentioned above. Fig. 6 illustrates dyed samples. As shown in Figs. 6 and 7; Table-2, the different mordants not only cause difference in hue colour and significant changes in K/S values but also changes in L^* values and brightness index values. Although yellowish camel colours were obtained with unmordanting, alum and stannic chloride mordanting dyeing, copper sulfate and potassium dichromate gave green-camel colour. When the pH value decrease, the highest K/S values were obtained for all dyeing.

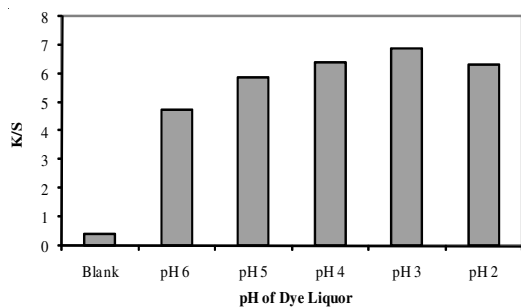


Fig. 5. Effect of pH on K/S values (at maximum absorbance wave-length 400 nm)

| Fabric sample | L^* | a^* | b^* | C | H |
|---------------|---------|--------|--------|--------|--------|
| pH 2 | 62,45 | 3 | 28,521 | 28,679 | 83,996 |
| pH 3 | 58,948 | 2,783 | 25,344 | 25,496 | 83,732 |
| pH 4 | 55,407 | 2,435 | 21,044 | 21,184 | 83,401 |
| pH 5 | 55,2164 | 2,792 | 20,979 | 21,164 | 82,419 |
| pH 6 | 55,991 | 3,282 | 18,8 | 19,084 | 80,098 |
| pH 2 Cu | 45,242 | 4,584 | 19,116 | 19,658 | 76,515 |
| pH 2 Cr | 43,23 | 5,113 | 18,856 | 19,537 | 74,83 |
| pH 2 Sn | 59,844 | 10,703 | 39,032 | 40,472 | 74,666 |
| pH 2 Al | 58,346 | 5,144 | 28,867 | 29,322 | 79,897 |
| pH 3 Cu | 44,28 | 4,999 | 19,124 | 19,766 | 75,35 |
| pH 3 Cr | 44,584 | 4,344 | 18,882 | 19,375 | 77,044 |
| pH 3 Sn | 59,967 | 10,034 | 38,553 | 39,837 | 75,412 |
| pH 3 Al | 58,923 | 6,059 | 30,066 | 30,67 | 78,606 |
| pH 4 Cu | 42,574 | 4,208 | 18,644 | 19,113 | 77,28 |
| pH 4 Cr | 43,68 | 4,65 | 18,549 | 19,123 | 75,926 |
| pH 4 Sn | 58,875 | 7,36 | 35,862 | 36,609 | 78,402 |
| pH 4 Al | 58,38 | 4,77 | 26,773 | 27,194 | 79,898 |
| pH 5 Cu | 43,094 | 4,336 | 18,636 | 19,134 | 76,902 |
| pH 5 Cr | 44,883 | 4,48 | 18,676 | 19,206 | 76,512 |
| pH 5 Sn | 57,299 | 4,743 | 29,669 | 30,046 | 80,918 |
| pH 5 Al | 56,575 | 4,222 | 24,14 | 24,506 | 80,078 |
| pH 6 Cu | 47,296 | 3,81 | 18,71 | 19,094 | 78,489 |
| pH 6 Cr | 50,032 | 3,665 | 17,193 | 17,58 | 77,966 |
| pH 6 Sn | 59,2962 | 3,881 | 25,68 | 25,972 | 81,407 |
| pH 6 Al | 54,021 | 4,649 | 21,65 | 22,143 | 77,881 |

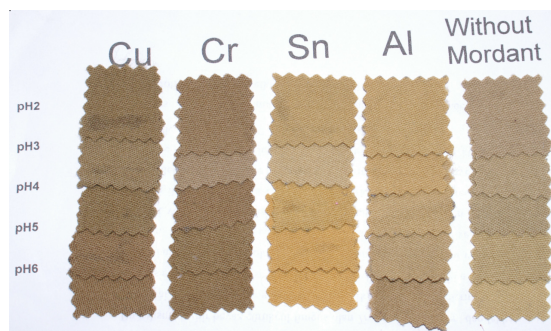


Fig. 6. Colour of the dyed samples

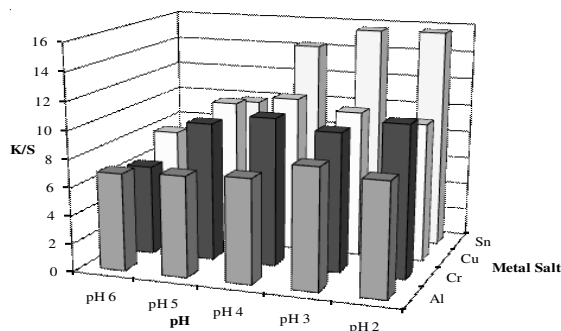


Fig. 7. Effects of different pH and mordant on K/S values (at maximum absorbance wave length 400 nm)

Fastness properties: Although all dyed samples have generally high washing and crocking fastness values, colour change of dyed samples at pH 2 and 3 after washing obtained 1-2 and 3-4, respectively. All of the dyed samples have poor light fastness values and mordanting process did not increase light fastness values significantly (Table-3).

TABLE-3
FASTNESS PROPERTIES OF DYED SAMPLES

| Fabric sample | Light fastness | Crocking fastness dry | Crocking fastness wet | Color change | Washing Fastness | | | | | |
|---------------|----------------|-----------------------|-----------------------|--------------|------------------|----|----|-----|-----|-----|
| | | | | | Staining | | | | | |
| | | | | | CA | Co | PA | PES | PAC | Wo |
| pH 6 | 2-3 | 4-5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 5 | 2-3 | 5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 4 | 2-3 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 3 | 2-3 | 5 | 4-5 | 3-4 darker | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 2 | 2-3 | 4-5 | 4-5 | 1-2 darker | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 6 Cu | 3 | 4-5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 6 Cr | 3 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 6 Sn | 2-3 | 5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH6 Al | 3 | 5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 5 Cu | 3 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 5 Cr | 3 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 5 Sn | 3 | 4-5 | 4-5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH5 Al | 3 | 4-5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 4 Cu | 3 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 4 Cr | 3 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 4 Sn | 3 | 4-5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 4 Al | 3 | 4-5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 4-5 |
| pH 3 Cu | 3 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 3 Cr | 3 | 4-5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 3 Sn | 3 | 4-5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 3 Al | 3 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 2 Cu | 3 | 5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 2 Cr | 3-4 | 4 | 5 | 4 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 2 Sn | 3 | 4-5 | 5 | 4 | 5 | 5 | 5 | 5 | 5 | 5 |
| pH 2 Al | 3 | 4-5 | 5 | 4-5 | 5 | 5 | 5 | 5 | 5 | 5 |

Conclusion

First time, a natural dye isolated from *S. luteus* was used for dyeing wool. Based upon the literature and present spectral results, this dye was proposed as grevillin D, but further structural characterization studies can be carried out.

The shade of dyeing is dependent on the mordant used. Although yellowish camel colours were obtained with unmordanting, alum and stannic chloride mordanting dyeing, copper sulfate and potassium dichromate gave green-camel colour. In addition the K/S values of dyed samples are strongly affected by pH. The highest K/S value is obtained at pH 3 without mordant. pH values of highest K/S values are affected by mordant type. For over all the highest K/S values are obtained by stannic mordant.

Conventionally, heavy metal ions such as copper, cadmium, iron, aluminum and tin are used in mordanting procedure. These heavy metals can cause an environmental problem and in this study indicated that using of mordant is not improving fastness properties. Although using of mordant develops colour yield extract of *Suillus* gives good shades with good wet fastness and crocking fastness properties without mordanting.

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