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Ellagic acid from gallnut (*Quercus infectoria*): Extraction and determination of its dyeing conditions for natural fibres

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The dyestuff of ellagic acid in gallnut (*Quercus infectoria*) was extracted and used in dyeing of woolen strips, feathered-leather and cotton using three types of mordanting methods at various pH values. Selected transition element salts [$CuSO_4$ $5H_2O$, $FeSO_4$ $7H_2O$, $ZnSO_4$ $7H_2O$, $Al(NO_3)_3$. $9H_2O$] were used as mordant agent at various pH. The dyed samples with highest fastness were obtained by Cu(II) for all samples except for cotton and by Al(III) for only cotton at pH 8 in the pre-mordanting method. It was also observed that gallnut plant based ellagic acid dyestuff would probably be an important raw material in dyeing process of natural textile fibers.

Keywords: Dyestuffs, Ellagic acid, Gallnut, Natural fibres
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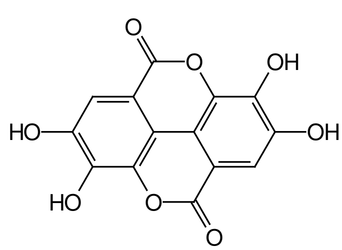
Introduction

Natural dyes have high importance in hand made-carpet, kilim and the similar industrial dying applications because of high colour fastness, cheapness, long-term color stability and authentic property. Natural dyes are being produced in the Asian countries (Turkey, Iran, India, Azerbaijani), and the products of natural dyes are being used in the most countries of the world.

Gallnut (*Quercus infectoria*) contains the mixture (60-70%) of gallotannin, ellagic acid, starch and glucose[1]. The dyestuff in the tannin of gallnut is ellagic acid[2], which exhibits dyeing properties because of its auxochrome group (-OH) together with other chromogen groups. Wool molecules consist of amino acid units, which contain free amino and carboxyl groups[3]. During the dyeing of wool, hydrogen bonds occur between the auxochrome groups of dyestuff and amino groups.



Ellagic acid

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No study was available on the dyeing properties of ellagic acid. So, the present paper is aimed to study the dyeing properties of ellagic acid for wool, feathered leather and cotton. In order to investigate the most proper mordant and pH value in terms of the wash, crock and light fastness in dyeing by ellagic acid, some selected transition element salts [$CuSO_4$ $5H_2O$, $FeSO_4$ $7H_2O$, $ZnSO_4$ $7H_2O$, $Al(NO_3)_3$ $9H_2O$] were used as mordant agent at various pH. Woolen strips (48), cotton (35), feathered-leather (16) were dyed using transition element salts as mordant agents.

Materials and Methods

Extraction of Ellagic Acid

Gallnut was picked up from areas of Tokat city, Turkey. Gallnut cups were dried and powdered. Extraction of the dyestuff was carried out by the following method[2]: 2 *N* H_2SO_4 (1 ml) and powdered tannin (10 g) are placed into a round-bottomed flask (2 l) and heated for 24 h at 100°C. After cooling, pyridine (100 ml) is added and filtered. Sample (1 l) is mixed with pyridine (1.1 l) in dried flask and HCl (100 ml) is added and then $NaNO_2$ (100 ml) is placed into this mixture at 30°C. The absorbance of the obtained mixture (λ, 538 nm) is recorded by UV-visible spectrophotometer. Absorbance is recorded after 36 min again. The absorbance change during 36 min is well proportioned with concentration of ellagic acid. Consequently, the free ellagic acid (1.6%) is produced.

Dyeing of Wool

The dyeing procedures of wool were carried out using the following three types of mordanting methods at pH:2, 4, 6, 8 successively for each mordant:

Pre-Mordanting

White fowl woollen strips (1g) were placed into 0.1 *M* mordant solution (100 ml) and heated for 1 h at 90°C. After cooling, it was rinsed, dried and placed into 100 ml of dye-bath. After heating for 1 h at 90°C, it was allowed to cool. The dyed product was rinsed with distilled water and dried.

Together Mordanting

0.1 *M* mordant dyestuff solution (100 ml) and woollen strips (1g) were placed into 250 ml Erlenmeyer flask. This mixture was heated for 1 h at 90°C. After cooling, it was filtered, rinsed with distilled water and dried.

Last Mordanting

Woollen strips (1g) were heated in dye-bath (100 ml) for 1 h at 90°C. After cooling, the woollen strips were filtered and dried. Then it was put into 0.1 *M* mordant solution (100 ml) and heated for 1 h at 90°C. Finally, it was filtered, rinsed with distilled water and dried.

The dyed-woollen strips, dyed from each of these three methods, were kept in 3% ammonia solution (100 ml) to increase the fastness of colours.

Dyeing of Feathered-Leather

Dyeing of feathered-leather process was carried out using mordanting and together mordanting methods. The third procedure (Last mordanting) did not give positive results since the feathered-leather lost its water and shrinks at higher temperature (35-40°C). The length of the feather in the feathered lambs-leather used in this work was 1.5 cm. For these two methods, the dyeing pH was selected as 2 and 4.

Pre-Mordanting

The white feathered-leather treated with $K_2Cr_2O_7$ (approx 15 cm^2) was heated for 1 h at 35-40°C in 0.1*M* of mordant solution (100 ml) in a 300 ml Erlenmeyer flask. After cooling, it was added into dyestuff solution (100 ml) and shaken at frequent intervals for 1 h at 35-40°C. After completion of the dyeing process, the dyed-feathered-leather was filtered, rinsed with distilled water and dried.

Together Mordanting

The feathered-leather following pre-mordanting was added to dyestuff solution (100 ml) and mordant agents were mixed in 250 ml Erlenmeyer flask. This mixture was shaken at frequent intervals for 1 h at 35-40°C and finally, dyed matter was filtered, rinsed with distilled water and dried.

Dyeing of Cotton

Cotton has different structure and properties than wool and leather. It consists of glycoside units and can occur coordinative and intermolecular hydrogen bonding with the mordant agent and dyestuff. The dyeing in cotton was obtained as follows:

Pre-Mordanting

Cotton (1.5g, 50 cm^2) was heated for 1 h at 95°C in 0.1 *M* mordant solution (100 ml). After cooling, the cotton was taken out, rinsed with distilled water, dried, put into dye-bath (100 ml) and heated for 1h at 95°C. It was allowed to cool, then filtered. Finally, the dyed-cotton was rinsed with distilled water and dried.

Together Mordanting

Dyestuff solution (100 ml) was added to the cotton and 0.1 *M* mordant agent and heated for 1 h at 95°C. After cooling, it was taken out, rinsed with distilled water and dried.

Last Mordantating

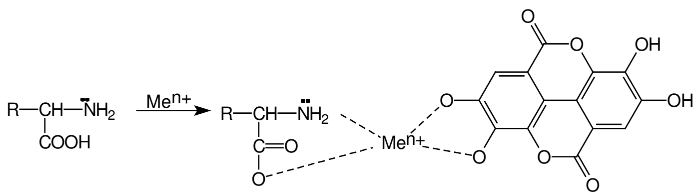
Cotton (1.5g, 50 cm^2) was dyed in dyestuff solution (100 ml) for 1 h at 95°C. After filtering, it was heated in 0.1 *M* mordant solution (100 ml) for 1 h at 95°C. The dyed cotton samples were filtered, rinsed with distilled water and dried.

Colour codes were determined using Pantone Colour Guide[4]. The crock, light and wash fastness of dyed samples, which were established according to DIN 54021, DIN 54004 and to ISO 105-C06, C1S, respectively[5], were determined by a LHTP model Alas Laundero meter, a 255 model crockmeter and a Fadeometer (xenotest), respectively.

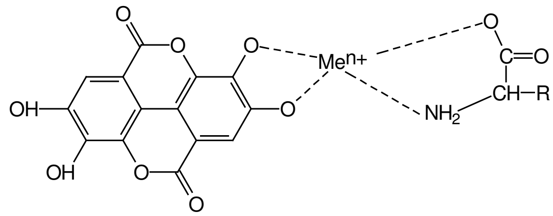
Results and Discussion

The dyeing mechanisms of wool and feathered-leather with ellagic acid by pre-mordanting (1), together mordanting (2) and last mordanting (3) can be considered as follows[6]:

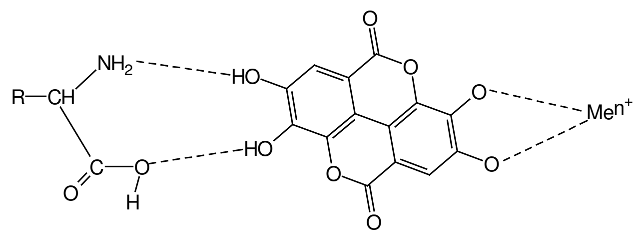
(1) Wool ....Mordant (Me^{n+})...............Dyestuff



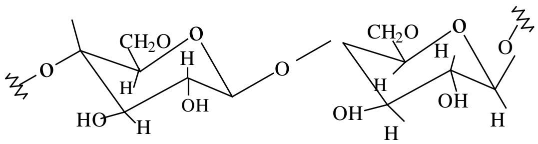
(2) Dyestuff...............Mordant (Me^{n+})...............Wool



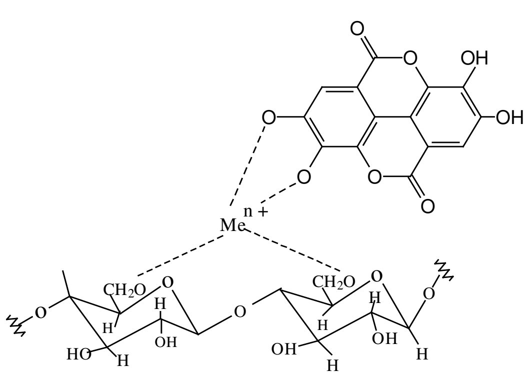
(3) Wool...............Dyestuff (Me^{n+})...............Mordant



On the other hand, cotton contains cellulose (90%), which is a linear polymer of 1,3- β-D glucoses as shown below:



Cotton can be dyed without using any mordant agent. However, when a mordant agent is used in dyeing process, a lot of colour tones can be obtained. The dyeing mechanism of cotton with ellagic acid can be suggested as below:



For wool and feathered-leather, the fastness increases when the pH is varied from 8 to 2 (Fig. 1). This result means that the dyeing with high fastness can be achieved in acidic pH range. This is because in the acidic pH range, the proton of acid is bonded with free carboxyl group of amino acids in the structure of wool or feathered-leather and the anion of acid is bonded to nitrogen atom with positive charge in the structure[6]. Moreover, in dyeing process by acidic dyestuff, the bonding tendency of dyestuff molecule to the wool decreases in the alkali medium (pH ≥8). The dissociation of carboxyl groups increases by the effect of alkaline and the anion of the dyestuff is to be free since the positive charged amino acid groups are bonded to the carboxyl anions. Therefore, the desired bonding does not occur in the alkaline medium.

The fastness for cotton increases with increase of pH (Fig. 1). This is because the oxygen atoms in cellulose units of the cotton are free in slightly alkaline medium and the cellulose units are easily bonded to the metal cations of mordant agent. The highest fastness (Fig. 2) were obtained by pre-mordanting method for each of the four metal salts, Cu(II), Zn(II), Fe(II) and Al(III).

The average fastness values of the all dyed samples by Cu(II) and Fe(II), respectively, are as follows: Pre-

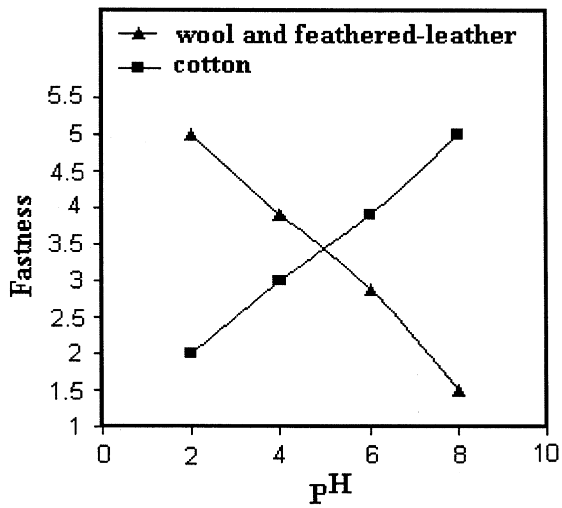


Fig. 1—The variation of fastness with pH

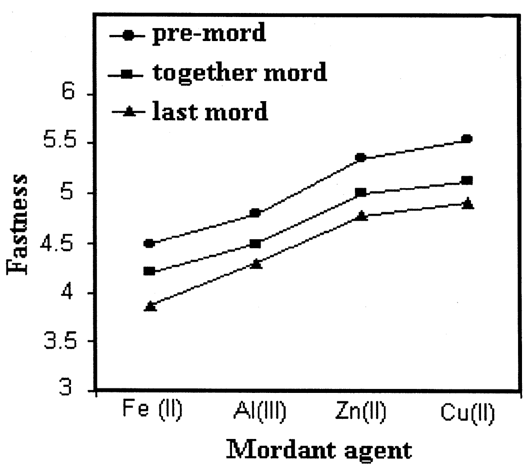


Fig. 2—The variation of average fastness for wool with respect to the mordant agent

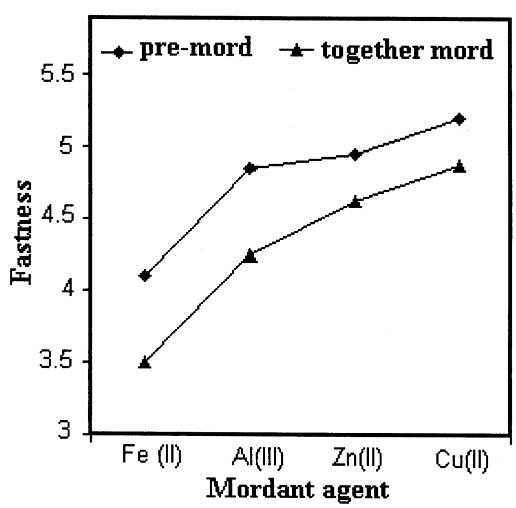


Fig. 3—The variation of average fastness for feathered-leather with respect to the mordant agent

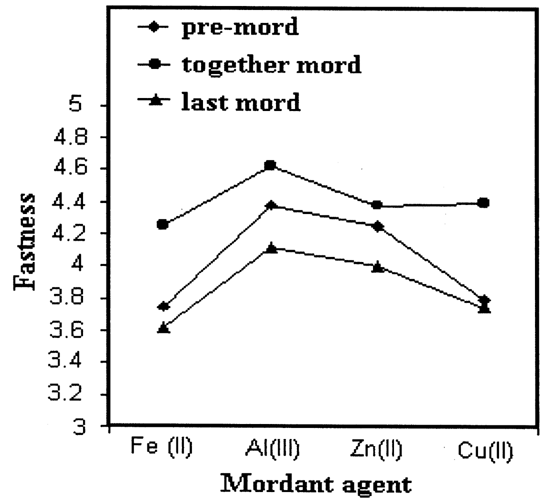


Fig. 4—The variation of average fastness for cotton with respect to the mordant agent

mordanting, 5.75, 4.50; Together mordanting, 5.12, 4.20; and Last mordanting, 4.91, 4.15. The effect of mordanting agent on the fastness of the investigated samples can be ordered as Cu(II)>Zn(II)>Al(III) >Fe(II). This is because the Cu(II) mordanting agent forms the more stable complex with dyestuff molecules compared to the other mordant.

For dyed feathered-leather samples, fastness values by Cu(II) are changed from 4.87 to 5.20 and by Fe(II) mordant agent from 3.5 to 4.10 in pre-mordanting and together mordanting method, respectively (Fig. 3).

Under average fastness values (wash, crock, light) of dyed cotton samples by Al(III), Cu(II), Zn(II) and Fe(II) for the three mordanting methods, the best result was obtained in presence of Al(III) by together mordanting method (Fig. 4). The average fastness values by Fe(II), Al(III), Zn(II) and Cu(II) respectively are as follows: Pre-mordanting, 3.75, 4.30, 4.25 and 3.85; Together mordanting, 4.25, 4.65, 4.30, and 4.45; and, Last mordanting, 3.60, 4.41, 4.0 and 3.80. Thus, the effect of mordant agent on the fastness of the cotton samples can be sequenced as Al(III)> Cu(II) > Zn(II)> Fe(II).

Conclusions

The results show that it is possible to dye natural fibers using mordanting methods by some transition metal salts at various pH values. Generally, different colour and colour tones and excellent fastness dyeings were obtained with ellagic acid. The highest colour depths on cotton and protein fibres (wool and feathered-leather) were obtained at 90°C for 60 min for wool and cotton, and at 35°-40°C for 60 min for feathered-leather, because the water of feathered-leather extracts and shrinks above the 40°C. The best result were obtained using pre-mordanting method for wool and feathered-leather by Cu(II) mordant salt at pH≤4. In addition, the dyed samples with highest fastness were also obtained by Cu(II) for the samples except cotton and by Al(III) for only cotton at pH 8 in the pre-mordanting method. However, a further experimental study should be made to investigate the reason for the highest fastness value obtained by Al(III) for cotton. Consequently, if gallnut *(Quercus infectoria)* is used in dyeing process of natural textile fibres, it will probably be an important raw material for commercial use.

Acknowledgement

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