*Asian Journal of Chemistry* Vol. 20, No. 1 (2008), 608-614

# Extraction of Total Dyestuff from Centaury (*Hypericum scabrum* L.) and Dyeing of Natural Fibres under Different Conditions

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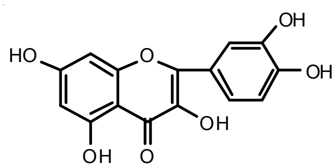
In this present work, the flowers of the centaury (*Hypericum scabrum* L.) were extracted with distilled water. Different transition element salts were used to obtain stable and different colours with high fastness. $AlK(SO_4)_2 \cdot 12H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $K_2Cr_2O_7$, $MnSO_4 \cdot 7H_2O$, $SnCl_2 \cdot 2H_2O$, $ZnCl_2$ were used as mordant substances. According to preliminary, together and last mordanting methods, wool, silk and cotton fibres were dyed at pH 4, pH 8 and at 90 ºC, seperately. In addition, the effect of the artificial animal urine system ($NH_2CONH_2$ (3 %, m/v), $NH_3$ (3 %, v/v), $CaC_2O_4$ (3 %, m/v)) as a mordant substance on dyeing of woollen materials was studied using together-mordanting method. The optimum dyeing conditions were determined and the results were evaluated in terms of fastness of dyed samples.

**Key Words: St. John'st Wort, *Hypericum scabrum* L, Extraction, Dyestuff, Mordant, Animal urine system.**

## INTRODUCTION

For thousands of years, dyes were obtained from natural sources, such as plants and animals. Natural dyes still hold a fascination and are used extensively by artisans around the world although synthetic dyes have replaced many natural dyes for commercial use[1].

Centaury (*Hypericum scabrum* L.) grow up in Europe, North Africa, Asia and Persia[2]. The main dyestuff in centaury is quercetin[3] and this plant contains little amount of hyperican[4]. The molecular structures of the compounds which play important role on dyeing process of natural fibres are given below:




Quercetin

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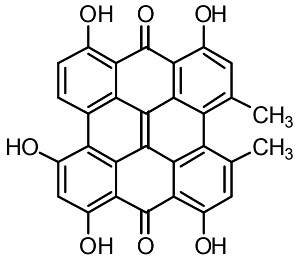



Hyperican

The dyestuffs in the plant

These compounds exhibit dyeing properties for wool, silk and cotton fibres due to their auxochromo groups (-OH) and chromogen groups (C=O and benzene ring).

Wool and silk mainly consist of amino acid units, which contain free amino and carboxyl groups[5]. During the dyeing process auxochromo groups of dyestuff bind with amino groups of the fibres *via* hydrogen bonding. On the other hand, cotton contains 90 % cellulose. The hydrogen bond between the groups of -$CH_2O$ in cellulosic structure and auxochromo groups of dyestuffs (quercetin and hyperican) is responsible for dyeing of cotton.

The literature search reveals that there is no study on dyeing properties of centaury for natural fibres. Therefore, this paper is aimed to determine the dyeing features of quercetine and hyperican in centaury for wool, silk and cotton as natural fibres in terms of wash, crock and light fastnesses. In order to obtain the highest fastness values in dyeing of each fibres, some selected transition metal salts such as $AlK(SO_4)_2 \cdot 12H_2O$, $Bi(NO_3)_2 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $K_2Cr_2O_7$, $MnSO_4 \cdot 7H_2O$, $SnCl_2 \cdot 2H_2O$, $ZnCl_2$ were used as mordant agent. The effect of pH on dyeing of the samples was also studied. Dyeing of the samples was carried out using pre-mordanting, together-mordanting and last-mordanting methods.

## EXPERIMENTAL

**Extraction of the dyestuffs:** Centaury (*Hypericum scabrum* L.) flowers were picked up in Tokat city, Turkey. The flowers were dried in shade, cleaned, powdered by grinder before the experiments. To transfer the dyestuff from centaury to aqueous solution, the powder (150 g) was extracted with distilled water (1 L) by soxhlet apparatus. By use of pre-mordanting, together-mordanting and last-mordanting methods and various mordants wool, silk and cotton samples were dyed. The selected mordants were $AlK(SO_4)_2 \cdot 12H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $K_2Cr_2O_7$, $MnSO_2 \cdot 7H_2O$, $SnCl_2 \cdot 2H_2O$, $ZnCl_2$ and selected pH were 4 and 8.

**Dyeing procedures of the natural fibres**

**Pre-mordanting method:** The fibre material (1 g) was placed into 0.1 M mordant solution (100 mL) and heated at 90 °C for 1 h. After cooling the sample to room temperature, it was rinsed, dried and placed into 100 mL of dye-bath and then heated for 1 h at 90 °C and at pH 4 and pH 8. Finally, the dyed sample was removed from the bath, rinsed with distilled water and dried.

**Together-mordanting method:** Mordant (in solid state which equivalent to 0.1 M mordant solution), dyestuff solution (100 mL) and fibre material (1 g) were mixed together into a flask and heated at 90 °C for 1 h. After cooling of sample, it was removed and rinsed with distilled water and dried.

**Last-mordanting method:** Fibre material (1 g) was heated in dye-bath (100 mL) for 1 h at 90 °C. After cooling, the dyed fibre was removed and dried. It was put into 0.1 M mordant solution (100 mL) and heated for 1 h at 90 °C. Finally, it was rinsed with distilled water and dried.

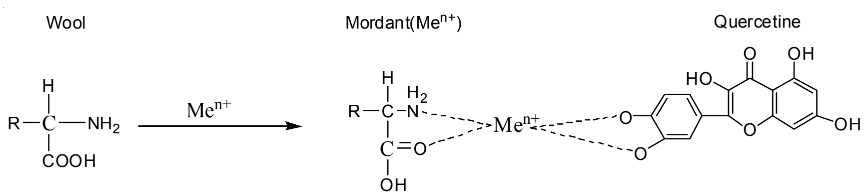
**Dyeing procedure of woollen, silk and cotton materials using artifical animal urine system (AAUS):** The woollen materials were kept into AAUS, $NH_3$ (3 %, v/v), $CaC_2O_4$ (3 %, m/v) and urea (3 %, m/v) for 12 h and dyed with $AlK(SO_4)_2{\cdot}12H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$, $CoCl_2{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, $FeSO_4{\cdot}7H_2O$, $K_2Cr_2O_7$, $MnSO_4{\cdot}7H_2O$, $SnCl_2{\cdot}2H_2O$, $ZnCl_2$ mordants using together-mordanting method at pH 4 and 90 °C.

**Determination of fastnesses:** The light-, wash-, crock (wet, dry)-fastness of all dyed samples, which were established according to DIN 54021 and to ISO 105-C06, ClS, respectively[6] were determined by Atlas Weather-ometer, a Launder-ometer and a 255 model crock-meter, respectively. Colour codes were determined using pantone colour guide.

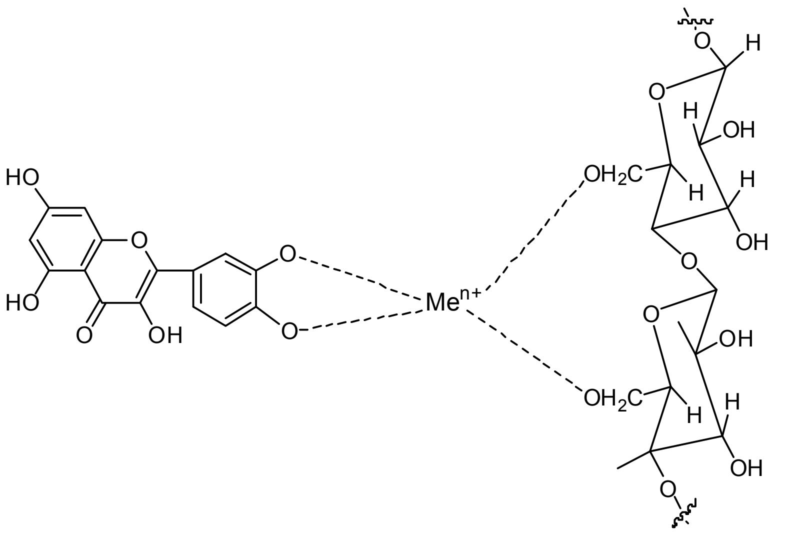
## RESULTS AND DISCUSSION

In this study, dyeing processes of wool, silk and cotton fibres with centaury (*Hypericum scabrum* L.) were carried out using some selected transition element salts as mordant agents by three methods at pH 4, 8 and 90 ºC, respectively.

The dyeing mechanisms of wool and silk fibres with quercetin as a main dyestuff in centaury can be considered as follow[7,8].



On the other hand, the dyeing mechanism of cotton with quercetine can be written as below:




The effects of mordant types and mordanting methods on the fastness of wool, silk and cotton fibres are shown in Figs. 1-3, respectively.

The variation of arithmetic average fastnesses (wash, crock, and light) of dyed wool samples with respect to mordant types is presented in Fig. 1. The effect of the mordanting agent on the fastness of the wool samples can be ordered as:

Cr(VI)>Zn(II)>Al(III)>Cu(II)>Mn(II)>Sn(II)>Fe(II)>Bi(III)>Co(II)

As can be seen from Fig. 1, in case of all mordanting agents the fastnesses obtained from both pre-mordanting and together-mordanting methods are higher than that obtained from last-mordanting method. The highest fastness (5.0) was achieved using Al(III) ($AlK(SO_4)_2 \cdot 12H_2O$) mordant and pre-mordanting method for wool samples at pH 4 and 90 °C. Morover, the lowest fastness was found as 4.25 for together-mordanting, 4.0 for last-mordanting by using Fe(II) mordant when it was found as 3.9 for pre-mordanting by using Bi(III) $Bi(NO_3)_3 \cdot 5H_2O$ mordant.

Fig. 2 shows the effect of mordanting agent and dyeing methods on the fastness of the silk samples. The sequence of average fastness for silk fibres with respect to mordanting agent type and dyeing method was given below:

Mn(II)>Zn(II)> Sn(II)> Cr(VI)> Al(III)> Co(II)>Cu(II)> Bi(III)>Fe(II)

It can be clearly observed from Fig. 2, there is no considerable difference in fastnesses for all types of mordanting methods. The highest fastness was found as 5.0 in case of using Cr(VI), Sn(II), Al(III) with last-mordanting method, Cr(VI), Mn(II), Al(III) with together-mordanting method, Sn(II) and Mn(II) with pre-mordanting method.

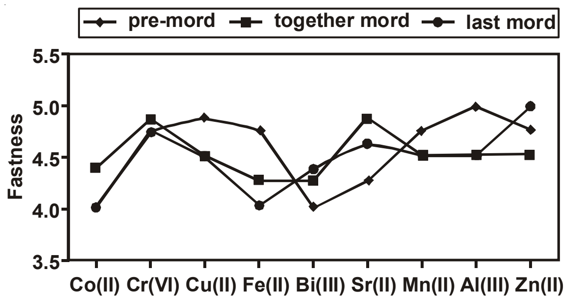



Fig. 1. Variation of average fastness for wool with respect to the mordant agent

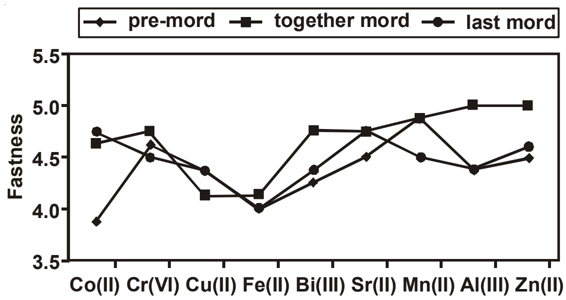



Fig. 2. Variation of average fastness for silk with respect to the mordant agent

Fig. 3 shows the variation of average fastnesses for dyed cotton samples by using different mordanting agents and mordanting methods. From this figure, the effect of mordanting agents on the fastness of cotton samples can be ordered as:

Mn(II)>Cr(VI)>Sn(II)>Al(III)>Bi(III)>Cu(II)>Co(II)>Zn(II)>Fe(II)

As seen from the curves the highest fastness (5.0) of dyed cotton samples obtained by using Cu(II) in pre-mordanting method, it was found by using Mn(II) pre-mordanting and together-mordanting methods. Furthermore, Fig. 4 indicates the variation of fastness of dyed wool samples treated with AAUS and different mordanting agents according to together-mordanting method. The highest fastness was 5.0 when used Fe(II) and Bi(III) mordants. This result is opposite to that obtained for dyed wool samples (Fig. 1) by using the same mordanting methods. Based on the results it can be noted that the treatment of wool with AAUS caused an increase in the fastness of dyed wool using different mordanting agents especially Fe(II) and Bi(III). This is because the components of AAUS (the mixture of ammonia, urea and oxalate) affect the structure of the wool fibre. Ammonia expands the misels of the wool fibre, urea serves as a pH regulator and oxalate makes stable the complex formed onto wool fibres during dyeing process. On the other hand, the pH of dye solution influenced the fastness of only both wool and silk fibres. The fastness at acidic pH (pH 4) was better than that at basic pH (pH 8). This is due to the hydrogen bonding between the free carboxyl group of amino acids in the structure of wool or silk and the hydrogen proton of the acid, and the bonding of anion of the acid with positive charge in the structure[5]. Moreover, in dyeing process by acidic dyestuff, the bonding tendency of dyestuff molecule to the wool decreases in the alkali medium (pH $\geq$ 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 bonded to the carboxyl anions[5,8]. Therefore, the desired bonding does not occur in the alkaline medium. The fastness of cotton was better in case of basic pH. This is because the oxygen atoms in cellulose units are easily bonded to the metal cations of mordant agent.

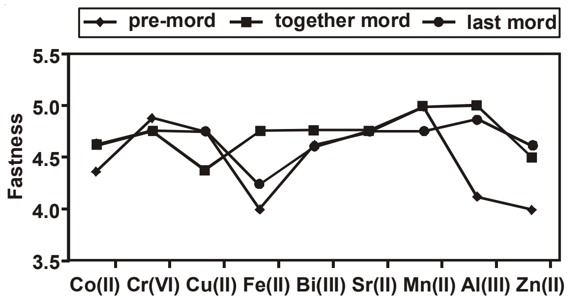



Fig. 3. Variation of average fastness for cotton with respect to the mordant agent

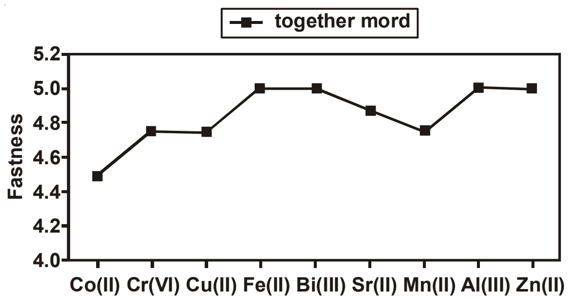



Fig. 4. Variation of fastness for wool with respect to the mordant agent with AAUS using together-mordanting method

## Conclusion

Wool, silk and cotton fibres were dyed using $AlK(SO_4)_2 \cdot 12H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $CoCl_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $K_2Cr_2O_7$, $MnSO_4 \cdot 7H_2O$, $SnCl_2 \cdot 2H_2O$, $ZnCl_2$ mordant agents with pre-mordanting, together-mordanting and last-mordanting method method at pH 4 and 90°C. The best results were obtained using pre-mordanting and together-mordanting method for silk by Cr(VI) at pH 4. In addition, Al(III) is the best mordant for wool in the presence of pre-mordanting method at pH 4. On the other hand, the highest fastnesses for cotton samples were obtained using pre-mordanting with Cu(II) and Mn(II), together-mordanting method with Mn(II) at pH 8. Genarally, the highest average fastnesses were obtained for wool and silk fibres at pH 4 and for cotton samples at pH 8. Morover, the fastnesses of wool fibres were increased with the effect of AAUS using same mordant agents.

The results show that it is possible to dye natural fibres using mordanting methods by some transition metal salts at acidic and basic pH with centaury (*Hypericum scabrum* L.). Generally, different colour and colour tones and excellent fastness dyeings were obtained with quercetine. Consequently, if the curative plant centaury is used in dyeing process of natural textile fibres, it will probably be an important raw material for commercial use. Further investigations are going on.

## ACKNOWLEDGEMENT

This study has been supported by Gazi University Scientific Research Project Commission (GUBAP), Project no : 08/2005-03

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(*Received*: 16 December 2006; *Accepted*: 14 September 2007) AJC-5868