Asian Journal of Chemistry;   Vol. 23, No. 12 (2011), 5441-5446

ASIAN JOURNAL OF CHEMISTRY

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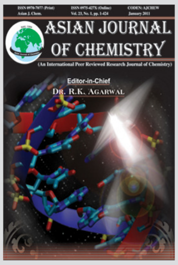

Dyeing Properties and Analysis by RP-HPLC-DAD of Silk Fibers Dyed with Weld (*Reseda luteola* L.) and Walloon Oak (*Quercus ithaburensis* Decaisne)

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(*Received*: 15 February 2011;   *Accepted*: 24 August 2011)   AJC-10302

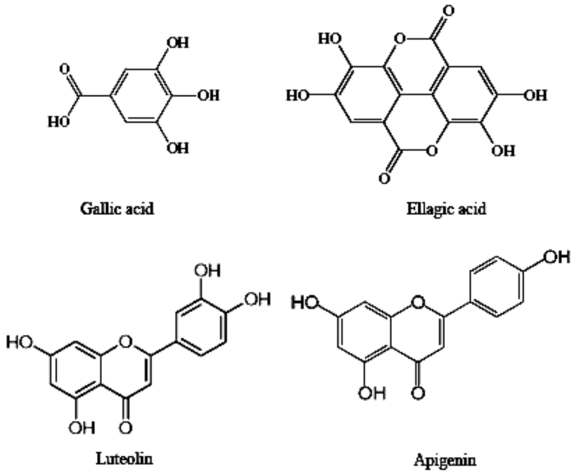
The purpose of this study is to analyse and to determine their colour values and rubbing and light fastness properties of the silk fabrics dyed with the natural dyes present in weld (*Reseda luteola* L.) and walloon oak (*Quercus ithaburensis* Decaisne). A reversed-phase high performance liquid chromatography (RP-HPLC) with diode-array detection (DAD) method was utilized for the identification of natural dyes present in the dyed silk fabrics. The extraction of dyes from the silk fabrics was carried out with 37 % hydrochloric acid/methanol/water mixture (2/1/1 v/v/v). CIEL*a*b* and fastness values of the fabrics were determined. In the study reported here, for the analysis and the dyeing of silk fabrics an analytical method was developed.

Key Words: Weld, Walloon oak, Natural dyeing, Fastness, HPLC, CIEL*a*b*.

INTRODUCTION

Weld (*Reseda luteola* L.) is an annual or biennial herb[1]. The branched erect stems grow up to 150 cm tall. The leaves of plant form in the first year. And, the evolution of plant is complete the second year. It grows in parts of North Africa and most of the eastern Mediterranean[2]. The whole of the plant was used for dyeing of wool and silk. The yellow dyes as the colouring matters are concentrated mainly in the leaves, inflorescences and fruit[1]. The yellow dyes are known as flavonoids[3,4]. Luteolin and apigenin flavonoids are the effective dyes present in the weld plant[5]. Luteolin from these dyes is known to possess antibacterial and antiinflammatory properties[6]. The weld-dyed textiles have a very good light fastness[7]. The fastness of a mordant dye depends on the mordant and the mordanting method. The light fastness is influenced by several factors such as the chemical structure and the physical state of dye, the dye concentration, the mordant type, the nature of the fibers[8].

Walloon oak (*Quercus ithaburensis* Decaisne) is a tree growing to 15-20 m in open forests in Turkey and Greece[2]. Their acorn cups contain 25-35 % tannin[1,6]. The complicated chemistry of tannins has been explained by Schweppe[9]. The hydolyzable tannin-ellagic acid is found in the bark of the oak[10]. This plant has been used for the tanning and the dyeing of leather in the past[2]. Interest relating to ellagic acid has increased lately due to antimutagenic, antiviral and anticarcinogenic effects[11]. On the other hand, HPLC provides the identification of natural dyes (ellagic acid, luteolin, *etc.*) present in the various historical textiles such as the some pieces of 15-17th centuries Ottoman silk textiles[12]. The molecular structures of natural dyes are given in Fig. 1.



Gallic acid   Ellagic acid

Luteolin   Apigenin

Fig. 1. Molecular structures of natural dyes

Cristea *et al.*[13] have accomplished quantitative HPLC analysis of the main flavonoid components present in weld (*Reseda luteola* L.). Sanyova[14] has identified various flavonoid and glycosides in weld lakes. The natural dyes present in the pigments have been prepared from walloon oak (*Quercus ithaburensis* Decaisne) dye plant were qualitatively identified by Deveoglu *et al.*[15].

The main aim of present study is to identify dyes present in the silk fabric dyed *via* weld (*Reseda luteola* L.) and walloon oak (*Quercus ithaburensis* Decaisne) dye plants by reversed-phase high performance liquid chromatography-diode-array detection.

EXPERIMENTAL

100 % silk, 1/1 plain woven fabric was used throughout in this experimental work. The fabrics was pre-treated and ready for dyeing. The sample sizes were approximately 0.7 g for the all treatments.

Dye plants and chemicals: Weld (*Reseda luteola* L.) and walloon oak (*Quercus ithaburensis* Decaisne) were obtained from Turkish Cultural Foundation, Research and Development Laboratory for Natural Dyes, 34775, Istanbul, Turkey. The following standard dyes have been used as references: rhamnetin(3,5,3',4'-tetrahydroxy-7-methoxyflavone), isorhamnetin (3,5,7,4'-tetrahydroxy-3'-methoxyflavone), kaempferol(3,5,7,4'-tetrahydroxyflavone), emodin (1,3,8,trihydroxy-6-metyl-anthraquinone) and apigenin(5,7,4'-trihydroxy-flavone) from Carl Roth (Karlsrube, Germany). Alum [$KAl(SO_4)_2.12H_2O$], hydrochloric acid and methyl alcohol were obtained from Merck (Darmstadt, Germany, www.merck.de).

Procedure for the mordanting of silk fabrics: For mordanting 16.75 g of silk fabric samples (10 cm × 10 cm, 25 pieces), was used 5.86 g alum [$KAl(SO_4)_2.12H_2O$]. The alum mordant was dissolved in 1675 mL of warm ultra pure water. Then, the fabrics were wetted by ultra pure water and these were added to the mordant bath at 60 ºC. The mordant bath was heated to 90 ºC and then, it was kept at 70 ºC for 1 h. The fabrics were mordanted in the mordant bath for 24 h at the room temperature. Afterwards, the wet fabrics were taken out from the mordant bath. The mordanted silk fabrics were dried at room temperature.

Procedure for the dyeing of silk fabrics

Procedure I: According to this procedure, the mordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added to 150 mL ultra pure water at 55 ºC. The fabrics were separately dyed with 50, 40, 30, 20 and 10 % wt. walloon oak (*Quercus ithaburensis* Decaisne) with 50 % wt. weld (*Reseda luteola* L.) in the same dye bath for 1 h at 70 ºC. Then, they were taken out from the dye baths and these were washed with ultra pure water. Later, the samples were dried at the room temperature. Table-1A shows the amounts used for silk fabrics dyed in walloon oak-weld dye baths.

Procedure II: The mordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added to 150 mL ultra pure water at 55 ºC. First, the fabrics were separately dyed with 50 % wt. weld (*Reseda luteola* L.) dye bath for 1 h at 70 ºC. Then, the dyed silk fabrics were taken out from the dye baths and these were washed by ultra pure water. Secondly, the silk fabrics dyed *via* the weld dye baths were added to 50, 40, 30, 20 and 10 % wt. walloon oak (*Quercus ithaburensis* Decaisne) dye baths at 55 ºC. Then, the dyeing processes were kept at 70 ºC for 1 h. The dyed samples were washed with ultra pure water. Then, they were dried at the room temperature. Table-1B shows the amounts used for silk fabrics dyed in walloon oak and weld dye baths, separately.

Procedure III: The mordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added to 150 mL ultra pure water at 55 ºC. First, the silk fabrics were separately dyed with 50, 40, 30, 20 and 10 % wt. walloon oak (*Quercus ithaburensis* Decaisne) dye baths for 1 h at 70 ºC. Then, the dyed silk fabrics were taken out from the dye baths and these were washed with ultra pure water. Secondly, the silk fabrics dyed with walloon oak dye baths were added to 50, 40, 30, 20 and 10 % wt. weld (*Reseda luteola* L.) dye baths at 55 ºC and the dye baths were kept at 70 ºC for 1 h. Then, the dyed silk fabrics were washed with ultra pure water. Table-1C shows the amounts used for silk fabrics dyed in walloon oak and weld dye baths, separately.

Procedure IV: The mordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added to 150 mL ultra pure water at 55 ºC. The silk fabrics were separately dyed with 50, 40, 30, 20 and 10 % wt. walloon oak (*Quercus ithaburensis* Decaisne) dye baths for 1 h at 70 ºC. Then, the dyed silk fabrics were washed with ultra pure water. Table-1D shows the amounts used for silk fabrics dyed in walloon oak dye baths, separately.

Procedure V: The wet unmordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added to 150 mL ultra pure water at 55 ºC. First, the unmordanted silk fabrics were separately dyed with 50, 40, 30, 20 and 10 % wt. walloon oak (*Quercus ithaburensis* Decaisne) dye baths for 1 h at 70 ºC. Then, the dyed silk fabrics were washed with ultra pure water. Secondly, the silk fabrics dyed *via* walloon oak were mordanted with 35 % alum [$KAl(SO_4)_2.12H_2O$] mordant solution in 150 mL ultra pure water at 55 ºC. Then, the silk fabrics were stood in the mordant baths for 24 h at room temperature. The mordanted silk fabrics were taken out from the mordant baths and then dried at room temperature. Thirdly, the wet mordanted silk fabrics were added in 150 mL ultra pure water at 55 ºC, separately. The silk fabrics were dyed with 50 % wt. weld (*Reseda luteola* L.) baths for 1 h at 70 ºC, respectively. Then, the dyed silk fabrics were washed with ultra pure water, and, the silk fabrics were dried at room temperature. Table-1E shows the amounts used for silk fabrics mordanted with alum mordant and dyed in walloon oak and weld dye baths, separately.

Procedure VI: The wet unmordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added to 150 mL ultra pure water at 55 ºC. First, the silk fabrics were separately dyed with 50, 40, 30, 20 and 10 % wt. walloon oak (*Quercus ithaburensis* Decaisne) dye baths for 1 h at 70 ºC. Then, the dyed silk fabrics were taken out from the dye baths and these were washed with ultra pure water. Secondly, the silk fabrics dyed with walloon oak dye baths were added to 50 % wt. weld (*Reseda luteola* L.) dye baths at 55 ºC and the dye baths were kept at 70 ºC for 1 h. Then, the dyed silk fabrics were washed with ultra pure water. Table-1F shows the amounts used for silk fabrics dyed with walloon oak and weld dye baths, separately.

TABLE-1
AMOUNTS USED FOR UNMORDANTED AND MORDANTED SILK FABRICS DYED WITH WALLOON OAK AND WELD

	Mordanted silk fabrics	Walloon oak%* + weld%		
A	1	50 + 50		
	2	40 + 50		
	3	30 + 50		
	4	20 + 50		
	5	10 + 50		
	Mordanted silk fabrics	Weld % I. Dyeing	Walloon oak % II. Dyeing	
B	6	50	50	
	7	50	40	
	8	50	30	
	9	50	20	
	10	50	10	
	Mordanted silk fabrics	Weld % I. Dyeing	Walloon oak % II. Dyeing	
C	11	50	50	
	12	40	40	
	13	30	30	
	14	20	20	
	15	10	10	
	Mordanted silk fabrics	Walloon oak %		
D	16	50		
	17	40		
	18	30		
	19	20		
	20	10		
	Unmordanted silk fabrics	Walloon Oak % I. dyeing	Alum % mordanting	Weld % II. dyeing
E	21	50	35	50
	22	40	35	50
	23	30	35	50
	24	20	35	50
	25	10	35	50
	Unmordanted silk fabrics	Walloon Oak % I. dyeing	Weld % II. dyeing	
F	26	50	50	
	27	40	50	
	28	30	50	
	29	20	50	
	30	10	50	
	Unmordanted silk fabrics	Walloon Oak %		
G	31	50		
	32	40		
	33	30		
	34	20		
	35	10		
	Mordanted silk fabrics	Weld %		
H	36	50		
	37	40		
	38	30		
	39	20		
	40	10		

A: Procedure I, B: procedure II, C: Procedure III, D: Procedure IV, E: Procedure V, F: procedure VI, G: Procedure VII, H: Procedure VIII, *(o.w.f.)

Procedure VII: The wet unmordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added in 150 mL ultra pure water at 55 ºC. The silk fabrics were separately dyed with 50, 40, 30, 20 and 10 % wt. walloon oak (*Quercus ithaburensis* Decaisne) dye baths for 1 h at 70 ºC. Then, the dyed silk fabrics were washed with ultra pure water. Table-1G shows the amounts used for silk fabrics dyed in walloon oak dye baths, separately.

Procedure VIII: The mordanted silk fabrics (10 cm × 10 cm, 5 pieces) were added to 150 mL ultra pure water at 55 ºC. The silk fabrics were separately dyed with 50, 40, 30, 20 and 10 % wt. weld (*Reseda luteola* L.) dye baths for 1 h at 70 ºC. Then, the dyed silk fabrics were washed with ultra pure water. Table-1H shows the amounts used for silk fabrics dyed in weld dye baths, separately.

Colour measurements for dyed silk fibers: The colour measurements were performed by GretagMacbeth SpectroEye Spectralphotometer and the colour differences were calculated in accordance the CIEL*a*b* system. The average of the measurements for the samples was recorded as colour differences (ΔE^*).

The colour difference is expressed as ΔE^* and is calculated by the following equation (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (1)$$

where ΔE^* is the CIEL*a*b* colour difference between batch and standard. Here ΔL^*, Δa^*, Δb^* and hence ΔE^* are in commensurate units. ΔL^* denotes the difference between lightness (where $L^* = 100$) and darkness (where $L^* = 0$), Δa^* the difference between green ($-a^*$) and red ($+a^*$) and Δb^* the difference between yellow ($+b^*$) and blue ($-b^*$)[16].

Fastness tests for dyed silk fibers: Rubbing and light fastness properties were carried out respectively in accordance with the methods described in ISO 105-X12 (February 2000) and ISO 105-B02 (April 2001) standards. The samples were exposed to the light for 80 h from a Xenon arc lamp (250 Watt).

HPLC equipment: Chromatographic experiments were carried out using an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including a G1329A ALS autosampler, a G1315A diode-array detector. Chromatograms were obtained by scanning the sample from 191 to 799 nm with a resolution of 2 nm and the chromatographic peaks were monitored at 255 nm. A G1322A vacuum degasser and a G1316A thermostatted column compartment were used. The data were analyzed using Agilent Chemstation. A Nova-Pak C_{18} analytical column (3.9 mm × 150 mm, 4 μm, Part No WAT 086344, waters) protected by a guard column filled with the same material was used. Analytical and guard columns were maintained at 30 ºC. The HPLC gradient elution was performed using the previously described method[17,18]. Chromatographic separations of the hydrolyzed samples were performed using a gradient elution program that utilizes two solvents: solvent A: H_2O-0.1 % TFA (trifluoroacetic acid) and solvent B: CH_3CN - 0.1 % TFA. The flow rate was 0.5 mL/min and the applied elution program is described in Table-2.

Extraction procedure for HPLC analysis: The extraction from the dye plants and the dyed silk fabrics was done by using the previously described method[19-25].

The samples were prepared as follows: The dye extraction from the dye plants and the dyed silk fabrics was performed by using the following procedure. The dyed silk fabrics (7.1-9.9 mg) and dye plants (approximately 2.5 mg) were hydrolyzed by using water/methanol/37 % hydrochloric acid mixture (1/1/2 v/v/v 400 μL) in conical glass tubes for precisely 8 min in a water-bath at 100 ºC to extract the organic dyes. After rapid cooling under cold running water, the solution was evaporated just to dryness in a water-bath at 50-65 ºC under a gentle stream of nitrogen. The dry residues were dissolved in 400 µL of the mixture of methanol/water (2/1 v/v). Then 95 µL of the supernatant were injected into the HPLC apparatus.

TABLE-2
GRADIENT ELUTION PROGRAM FOR HPLC

Time (min)	H_2O + 0.1 % TFA (%)	CH_3CN + 0.1 % TFA (%)
0.00	95.0	5.00
1.00	95.0	5.00
20.0	70.0	30.0
25.0	40.0	60.0
28.0	40.0	60.0
33.0	5.00	95.0
35.0	5.00	95.0
45.0	95.0	5.00

TFA = Trifluoroacetic acid

RESULTS AND DISCUSSION

The unmordanted silk fabrics and silk fabrics mordanted with alum mordant were dyed with weld (*Reseda luteola* L.) and walloon oak (*Quercus ithaburensis* Decaisne) dye plant baths according to the various procedures. To identify the natural dyes present in silk fibers, the dyed silk fibers were analyzed qualitatively by a reversed phase high performance liquid chromatography (RP-HPLC) with diode-array detection (DAD). The dye extractions for HPLC analysis were done by using the previously described method[19-25]. The composition was identified based on the absorption spectra acquired with standard reference dye compounds. According to the results of HPLC analysis the gallic acid and ellagic acid in the acid hydrolyzed walloon oak (*Quercus ithaburensis* Decaisne) plant and luteolin and apigenin in the acid hydrolyzed weld (*Reseda luteola* L.) plant were identified (Fig. 2).

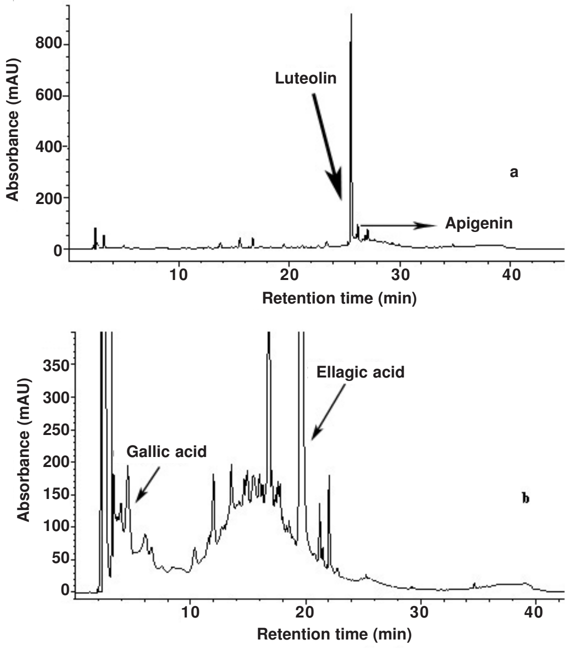


Fig. 2. HPLC chromatograms of the hydrolyzed weld (a) and walloon oak (b) plants

To identify the natural dyes, the dyed silk fibers were analyzed by reversed phase high performance liquid chromatography (HPLC) with photodiode array (PDA) dedection. As shown in Fig. 3, ellagic acid, luteolin and apigenin compounds in the silk textiles dyed according to the procedure I were determined by using the standard reference compounds.

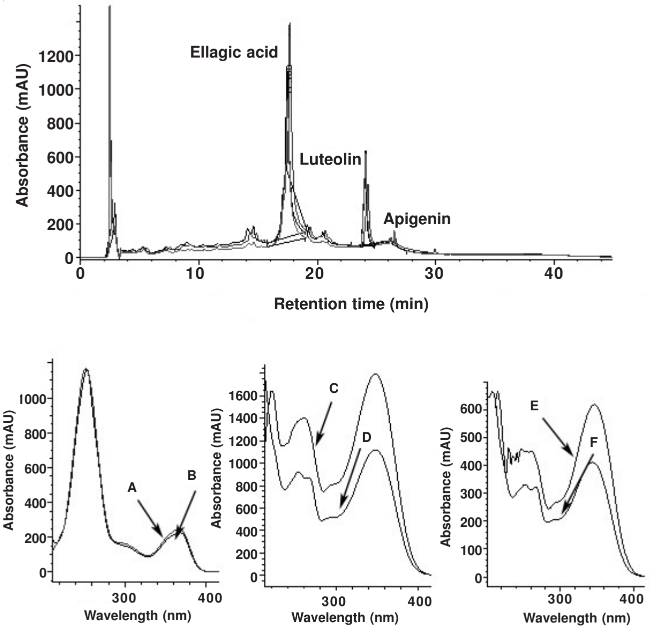


Fig. 3. HPLC chromatograms of the silks dyed according to the procedure I. The below figures show photodiode array spectra of the dyes identified in the dyed silk fibers: ellagic acid (A), luteolin (C) and apigenin (D)

Except for this, these dyes in the silk fabrics dyed according to the procedures II, III, IV and V were also determined as shown in Fig. 4 and Fig. 5(a). As shown in Fig. 5(b-c), only ellagic acid in the fabrics dyed according to the procedures VI and VII were determined.

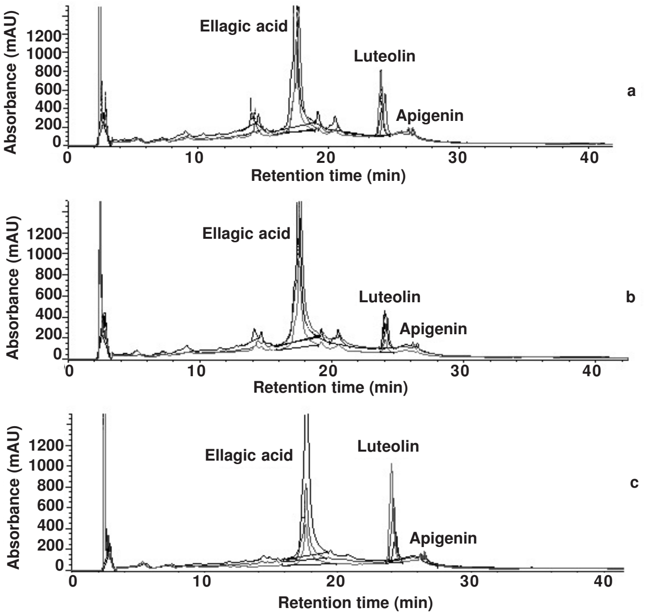
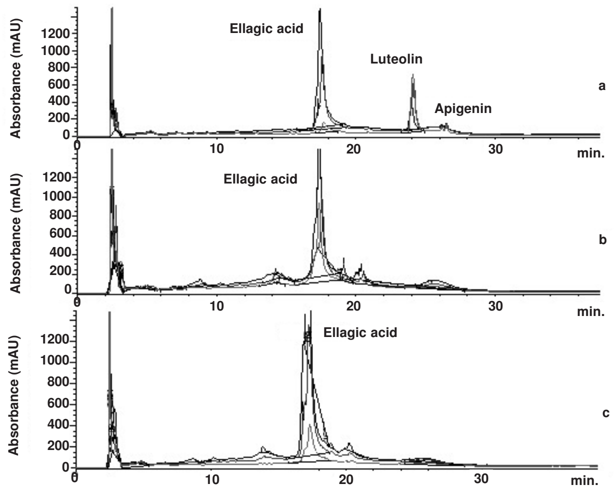


Fig. 4. HPLC chromatograms of the dyed silk fibers according to the procedure II (a), III (b) and IV (c)



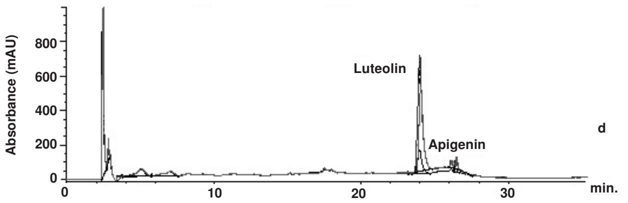


Fig. 5. HPLC chromatograms of the dyed silk fibers according to the procedure V (a), VI (b), VII (c) and VIII (d). In the figures, the each one chromatogram denote black colour for the first dyeing, red colour for third dyeing and green colour for fifth dyeing related to the silks dyed according to the each one procedure

In spite of the identification of gallic acid in the acid hydrolyzed walloon oak plant, gallic acid in the fabrics dyed by using walloon oak plant was not identified. At the same

TABLE-3
CIE L*a*b* VALUES, COLOUR DIFFERENCES, RUBBING AND LIGHT FASTNESS TEST RESULTS FOR DYED SILK FABRICS WITH NATURAL DYE PLANT BATHES

Numbers of dyed fabrics	L^*	a^*	B^*	C^*	h	ΔE^*	LF	RF**	
								Dry	Wet
Unmordanted fabtic	95.89	-0.22	1.45	1.47	98.56	-			
Mordanted fabric	93.37	0.61	4.11	4.16	81.59	-			
1	70.43	-0.06	32.03	32.02	90.21	36.07	1	4	5
2	72.37	-0.34	30.26	30.63	90.63	33.84	2	5	5
3	73.43	-0.69	31.15	31.16	91.18	33.74	2	5	5
4	75.44	-0.80	30.64	30.54	91.40	31.21	3	5	5
5	77.43	-1.54	30.45	30.45	92.63	30.98	4-5	5	5
6	67.88	1.83	27.44	27.79	86.28	34.95	3	5	5
7	68.24	2.83	26.58	26.55	85.93	33.73	2	5	5
8	69.02	1.63	26.50	26.43	86.37	32.97	3	5	5
9	72.26	0.94	26.28	26.69	87.91	31.15	4	5	5
10	74.72	0.52	26.08	25.94	88.91	28.63	5	5	5
11	70.72	-0.19	29.69	29.52	90.36	34.05	3	5	5
12	71.60	-0.56	29.45	29.46	91.08	33.43	4	5	5
13	72.62	-0.30	27.99	28.22	90.43	32.03	4	5	5
14	73.56	-0.42	27.21	27.14	90.88	30.38	5	5	5
15	76.67	-0.05	25.26	25.27	90.12	26.96	5	5	5
16	67.88	0.97	29.35	29.37	88.11	35.87	2	5	5
17	68.75	0.68	29.32	29.33	88.67	35.24	2	5	4-5
18	71.20	0.34	28.27	27.94	89.49	32.35	3	5	5
19	73.32	0.29	27.64	27.64	89.40	30.92	3	5	5
20	71.12	1.61	28.23	27.85	86.92	32.52	4	5	5
21	66.44	2.32	24.95	84.69	75.83	37.70	4	5	5
22	65.86	1.61	29.30	86.83	75.33	40.77	5	5	5
23	67.84	0.93	30.92	88.34	76.86	40.68	5	5	5
24	70.31	-0.16	32.16	90.28	78.83	39.98	6	5	5
25	75.17	-2.48	36.79	93.95	82.59	41.76	6	5	5
26	66.31	3.58	19.76	79.75	75.66	34.92	5	5	5
27	67.52	3.36	18.95	79.80	76.43	33.79	5	5	5
28	68.74	3.20	18.60	80.02	77.47	32.41	6	5	5
29	71.40	2.76	17.23	80.94	79.79	29.13	5	5	5
30	76.79	2.15	14.34	81.26	83.83	23.16	7	5	5
31	69.15	3.48	19.93	79.98	77.91	32.82	3	5	4-5
32	69.61	3.48	19.53	79.88	78.27	32.11	4	5	5
33	71.00	3.27	18.59	80.07	79.60	30.05	5	5	5
34	74.66	2.65	16.83	80.97	82.21	26.38	6	5	5
35	79.40	2.16	13.38	80.84	85.77	20.45	6	5	5
36	90.43	-8.00	39.24	101.53	93.63	36.65	1	5	5
37	89.09	-6.87	38.52	100.12	92.70	35.88	1	5	5
38	89.35	-8.24	44.82	100.42	92.88	42.25	3	5	5
39	91.03	-7.47	33.00	102.76	94.04	30.42	3-4	5	5
40	90.77	-7.23	29.68	103.69	93.86	27.18	4	5	5

**At the evaluation realizing by the gray scale, 5 is the most, 1 is the lowest. For 1-20, 36-40 the mordanted fabric was taken as standard. For 21-35 the unmordanted fabric was taken as standard.

time, the most sharp peak present in the chromatograms relating to the silk fabrics dyed by using walloon oak and weld plants belongs to ellagic acid compound.

CIEL*a*b* values and fastness properties of the dyed silk fibers with weld (*Reseda luteola* L.) and walloon oak (*Quercus ithaburesis* Decaisne) were shown on Table-3.

The best brightness values were obtained from (5, 10, 15, 19, 25, 30, 35 and 39 number) dyeings for the each one procedure, respectively. The light fastness test results of the dyed materials were examined. Nevertheless, the silk fabrics dyed according to the procedures I, IV and VIII present mostly a very low light fastness values. However, the rubbing fastness properties for inter-procedures was better.

Conclusion

In this study, the various procedures for dyeing of silk fabrics were developed with different weld (*Reseda luteola* L.) and walloon oak (*Quercus ithaburensis* Decaisne) dye plant percentages. The identification of natural dyes from the dyed silk fabrics were achieved by RP-HPLC with DAD. The HPLC method provide a good qualitative determination for the natural dyes.

As a result, 100 % silk fabric can be dyed with the natural dyes (weld and walloon oak) using various dyeing procedures. In general, the best dyeing condition for the silk fabrics with natural dyes was procedure V. In overall results, the silk fabrics dyed by procedure VIII, which are dyed with weld, have quite better brightness (C*) values compared to the other dyed fabrics. The dyed fabrics by procedure VII are also high brightness values. Hue angle (h) are showed that, the dyed fabrics by procedure VIII have yellowish and pale colours. The wet and dry rubbing fastness values of all the dyed fabrics are 5 and 4-5 respectively. The non-mordanted dyed fabrics showed higher light fastness test results. Finally, we believe that dyeing protein fibers with natural dyes (weld and walloon oak) can be an important advantage for the enviromental processes.

ACKNOWLEDGEMENTS

The support by Turkish Cultural Foundantion is gratefully acknowledged. The authors would like to thank Dr. Chris Cooksey for a critical review.

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