

# The evaluation of procedures for dyeing silk with buckthorn and walloon oak on the basis of colour changes and fastness characteristics

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In this study, silk fabric samples were dyed according to various procedures with buckthorn (*Rhamnus petiolaris* Boiss) and walloon oak (*Quercus ithaburensis* Decaisne) extracts. Reversed-phase high-performance liquid chromatography with diode-array detection was utilised for the identification of dyes present in the dyed silk fabrics and the plant extracts. The extraction of dyes was carried out with a hydrochloric acid/methanol/water (2:1:1; v/v/v) mixture. The colour coordinates of the silk fabrics were measured, and the rubbing, wash and light fastness properties of the dyed silk materials were determined and are discussed.

## Introduction

In recent years, natural dyes have attracted renewed attention because of their biodegradability, sustainable production and uncommon, soothing shades. Synthetic dyes are often economical and available in a wide variety of colours, but they (e.g. MAK III category 2 dyes, which belong to the carcinogenic dyes used in the textile industry [1]) may cause skin allergies and other harm to the human body, in addition to producing toxic waste. Natural dyes are obtained from renewable sources such as crops, insects and so forth, and they may decrease the dependence on petrochemical sources [2–4]. These considerations have led to the publication of several studies on natural dyes from a number of sources [5–11]. In former times, wool or silk fibres were always dyed with natural dyes extracted from plants or animals [12]. Compounds present in extracts obtained from the most widely used natural dyes belong to a few main classes: flavonoids (yellow dyes), anthraquinoids (red dyes), indigoids (purple and blue dyes) and tannins (brown and black dyes) [13,14]. The buckthorn (*Rhamnus* spp.) plant contains a large number of flavonoids [15]. Flavonoids are particularly important compounds due to reported medicinal properties, including antibacterial, antiinflammatory, antiallergenic, antimutagenic, antiviral and anticancer activities [16]. Buckthorn berries also contain non-flavonoid colouring compounds such as the anthraquinone emodin. Buckthorn berries have a very

important place in the history of natural dyes and have long been used in Turkey [15]. The acorn caps of the walloon oak plant contain 25–35% tannin [17]. The complicated chemistry of tannins has been discussed [18]. The hydrolysable tannin, i.e. ellagic acid, is found in the bark of oak [19]. The most commonly used mordanting material is alum, which gives bright colours with most natural dyes [20]. Several analytical techniques have been used for the identification of natural dyes, for example, thin-layer chromatography (TLC) [21–23], high-performance liquid chromatography (HPLC) [24–31], Raman spectroscopy [32], Fourier Transform-infrared (FTIR) spectroscopy [33], UV-visible spectrophotometry [34] and nuclear magnetic resonance (NMR) spectroscopy [35].

The aim of the present work was to investigate various procedures for dyeing silk fibres with a common species of buckthorn (*Rhamnus petiolaris* Boiss) and with walloon oak (*Quercus ithaburensis* Decaisne) in terms of the colour changes and fastness characteristics (light, wash and rubbing fastness) produced, and to analyse qualitatively the natural dyes present in the dyed silk fabrics using reversed-phase high-performance liquid chromatography (RP-HPLC) with diode-array detection (DAD).

## Experimental Methods

### Materials

Degummed, bleached, woven mulberry silk fabric 20 ends/cm, 18 picks/cm weighing 89.6 g/m<sup>2</sup> (obtained from the



Turkish Cultural Foundation) was used. ECE non-phosphate standard detergent, adjacent multifibres and blue wool standard fabrics were purchased from SDC Enterprises Limited (UK).

All reagents were analytical grade, unless stated otherwise. Buckthorn (with its dried green berries) and walloon oak acorn caps were obtained from the Turkish Cultural Foundation (Natural Dyes Research and Development Laboratory, Turkey). The following dye standards were used as references: rhamnetin, isorhamnetin, emodin, kaempferol and ellagic acid, all obtained from Carl Roth (Germany). Quercetin dihydrate was also provided by ABCR GmbH & Co KG (Germany). High-purity water was obtained by passing water through a Milli-Q treatment system (Millipore, USA), and the HPLC mobile phase was prepared using Milli-Q water. Alum [ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ], hydrochloric acid, gallic acid and methanol were obtained from Merck (Germany).

### Mordanting procedure

Mordanting was accomplished using  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (alum) as a 35% proportion of the quantity of the textile. The alum mordant was dissolved in warm (55 °C) ultrapure water (alum/water 1/100) in a large (2 l) beaker. Then, the silk fabric samples were wetted with ultrapure water and added to the mordant solution. This was performed at 75 °C for 1 h in a liquor ratio of 35:1. The silk fabrics were mordanted in the mordant bath for 24 h at room temperature. Afterwards, the wet silk fabrics were removed from the mordant bath and added directly to the dyebath.

### Dyeing procedure

Each dyeing procedure was performed in a dyebath ratio of 33:1 at 65 °C for 60 min, and dye concentrations are listed in Table 1. The washing procedures included washing with ultrapure water and drying at room temperature. All dyeing processes were separate for each dye, except for procedure I, where walloon oak and buckthorn were added to the dyebath together.

### Colour measurements

All colour measurements were performed using a Minolta (Japan) 3600D (D65, specular inclusion, 10°) spectrophotometer. The spectrophotometer was equipped with software able to automatically calculate CIELab,  $\Delta E^*$  and colour strength ( $K/S$ ) values from the reflectance values at the appropriate wavelength for each dyeing. Colour strengths of fabrics were determined using the Kubelka–Munk formula:

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

where  $K$  is the scattering coefficient,  $S$  is the absorption coefficient and  $R$  is the reflectance.

The colours are given in CIELab coordinates:  $L^*$  corresponding to the brightness (100 = white, 0 = black),  $a^*$  to the red-green coordinate (+ = red, - = green),  $b^*$  to the yellow-blue coordinate (+ = yellow, - = blue), and  $C^*$  to vividness-dullness (100 = vivid, 0 = dull).

The colour difference  $\Delta E^*$  was calculated by the equation:

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

### Fastness standard tests

Wash fastness, light fastness and rubbing fastness of the dyed silk fabrics were tested according to ISO 105-C06 [45], ISO 105-B02 [46] and ISO 105-X12 [47], respectively. The specific tests were applied using the following instruments: Atlas Xenotest Alpha for light fastness (SDL Atlas, USA), the Atlas rubbing fastness tester and Atlas Linitest for wash fastness. The changes in shades and staining to adjacent multifibre fabrics and rubbing fastness fabrics were related to the standard greyscale rating (where 1 is poor and 5 is excellent). The changes in shades under artificial light were evaluated according to standard blue wool fabrics (SDC) protocols. ECE non-phosphate standard detergent was used in wash fastness trials.

### HPLC method

Chromatographic separations were carried out using an Agilent 1200 series system (Agilent Technologies, Germany) including a G1329A ALS autosampler, a G1315A diode-array detector, a G1322A vacuum degasser and a G1316A thermostatted column compartment. Chromatograms were obtained by scanning the sample from 191 to 799 nm with a resolution of 2 nm; eluted peaks were monitored at 255 nm. Data were analysed using an Agilent Chemstation. A Waters Nova-Pak (USA)  $C_{18}$  analytical column (3.9 × 150 mm, 4 μm) protected by a guard column filled with the same material was used. Analytical and guard columns were maintained at 30 °C. The HPLC gradient elution was performed using previously described methods [36,37]. Chromatographic separations of the hydrolysed samples were performed using a gradient elution programme utilising two solvents: solvent A consisted of water and 0.1% trifluoroacetic acid (TFA), and solvent B consisted of acetonitrile ( $\text{CH}_3\text{CN}$ ) and 0.1% TFA. The flow rate was 0.5 ml/min; the elution programme was as described earlier [14,15,17,38–40].

### Extraction procedure for HPLC analysis

Extraction from the dye plants and the dyed silk fabrics was carried out as described in earlier reports [14,15,17,38–41]. Organic dyes were extracted from the dyed silk fabrics (7–10 mg) and dye plants (approximately 2.5 mg) and hydrolysed by heating in 400 μl of water:methanol:37% hydrochloric acid (1:1:2; v/v/v; 400 μl) in conical glass tubes for 8 min in a water bath at 100 °C. After rapid cooling under running cold water, the solution was evaporated just to dryness in a water bath at 50–65 °C under a gentle stream of nitrogen. The dry residues were dissolved in 400 μl of a methanol:water (2:1; v/v) mixture. All mixtures were filtered using polypropylene syringe filters (0.2 μm). Then, 95 μl of the supernatant was injected into the HPLC apparatus.

## Results and Discussion

### HPLC analysis

In this study, dyes from the silk samples dyed by two dye plants (buckthorn and walloon oak) were extracted after treatment with methanolic hydrochloric acid, as described earlier [41]. The extracts were then analysed qualitatively by RP-HPLC with DAD. The identification of dye components was based on previous reports [15,38,39], and the

**Table 1** Amounts used for unmordanted and mordanted silk fabrics dyed with walloon oak (acorn caps) and buckthorn (dried green berries)

Dyeing procedure	Procedure no.	Sample (Trial) no.	Mordant (%)	Walloon oak (%)	Buckthorn (%)
Premordanted fabrics were dyed (together walloon oak and buckthorn)	I	1	35	50	20
		2	35	40	20
		3	35	30	20
		4	35	20	20
		5	35	10	20
Premordanted fabrics were separately dyed (before buckthorn, after walloon oak)	II	6	35	50	20
		7	35	40	20
		8	35	30	20
		9	35	20	20
		10	35	10	20
Premordanted fabrics were separately dyed (before walloon oak, after buckthorn)	III	11	35	50	20
		12	35	40	16
		13	35	30	12
		14	35	20	8
		15	35	10	4
Premordanted fabrics were dyed (walloon oak)	IV	16	35	50	–
		17	35	40	–
		18	35	30	–
		19	35	20	–
		20	35	10	–
Unmordanted fabrics were separately dyed and mordanted (before walloon oak, then alum mordanted, after buckhorn)	V	21	35	50	20
		22	35	40	20
		23	35	30	20
		24	35	20	20
		25	35	10	20
Unmordanted fabrics were separately dyed (before walloon oak, after buckthorn)	VI	26	–	50	20
		27	–	40	20
		28	–	30	20
		29	–	20	20
		30	–	10	20
Unmordanted fabrics were dyed (walloon oak)	VII	31	–	50	–
		32	–	40	–
		33	–	30	–
		34	–	20	–
		35	–	10	–
Premordanted fabrics were dyed (buckthorn)	VIII	36	35	–	20
		37	35	–	16
		38	35	–	12
		39	35	–	8
		40	35	–	4

All concentrations were owf.

absorption spectra were acquired using reference compounds. By means of HPLC analysis, quercetin, rhamnetin and emodin could be identified in the extracts of the acid-hydrolysed buckthorn berries, as shown in Figure 1.

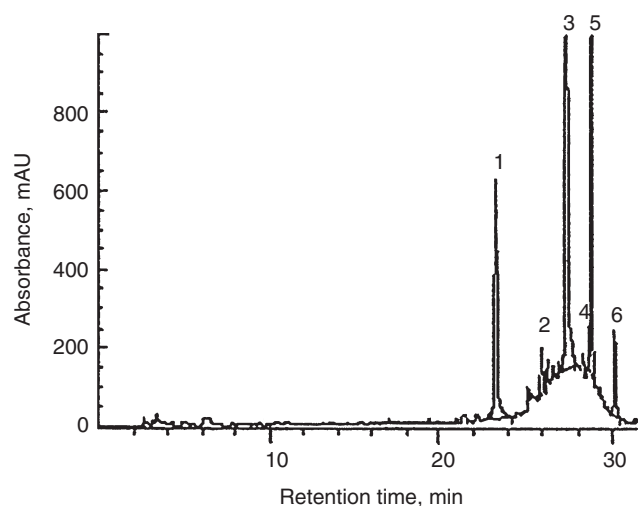
The peak at 23.2 min ( $\lambda_{\max}$  254, 295 and 371 nm) is related to quercetin, based on its retention time and UV-vis spectra. The peak at 28.6 min ( $\lambda_{\max}$  263, 293, 320 and 367 nm) was probably rhamnazin (dimethyl quercetin), but there was no reference compound for it. Gallic acid ( $R_t$  4.5 min) and ellagic acid ( $R_t$  16.8 min) were identified in acid-hydrolysed walloon oak acorn caps (Figure 2). A peak at 19.8 min ( $\lambda_{\max}$  253, 307, 355 and 369) was also observed, but was not identified. It is likely that this peak is related to ellagic acid derivative, based on its UV spectrum, as shown in Table 2.

The main colouring components of buckthorn and walloon oak that could be fully separated, detected and identified by their UV-vis spectra are gallic acid, ellagic acid, quercetin, rhamnetin, rhamnazin and emodin. The retention time ( $R_t$ ) and corresponding spectral characteristics of the main colouring components of buckthorn and walloon oak, as detected in Figures 1 and 2, are presented in Table 2.

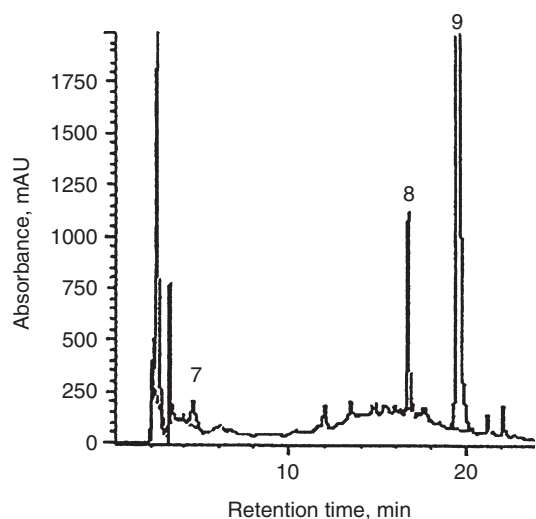
Although gallic acid, ellagic acid and probably an ellagic acid derivative were determined in the acid-hydrolysed walloon oak acorn caps, both ellagic acid (PVII31) and gallic acid (PVII35) were found in the unmordanted samples, while only ellagic acid (PIV16 and PIV20) was identified in the alum-mordanted silk samples dyed with walloon oak acorn caps. For an explanation of the abbreviations used here, please see Table 3.

Emodin, rhamnetin, rhamnazin (dimethyl quercetin) and quercetin were identified in the acid-hydrolysed buckthorn berries, whereas quercetin (PVIII36), rhamnetin and rhamnazin (PVIII36 and PVIII40) were determined in the acid hydrolysate of the hydrolysed alum-mordanted silk samples dyed with buckthorn berries. In the alum-mordanted silk samples that were firstly dyed with buckthorn berries and overdyed with walloon oak acorn caps, ellagic acid, rhamnetin, rhamnazin (PII6 and PII10) and quercetin (PII10) were identified.

In the alum-mordanted silk samples that were firstly dyed with walloon oak acorn caps and overdyed with buckthorn berries, rhamnetin, rhamnazin (PIII11 and PIII15), ellagic acid and quercetin (PIII11) were determined.



**Figure 1** HPLC chromatogram of the acid-hydrolysed buckthorn berries. Numbers correspond to the dyes as follows: 1, quercetin; 2, kaempferol or isorhamnetin; 3, rhamnetin; 4, unidentified; 5, rhamnazin (dimethylquercetin); 6, emodin



**Figure 2** HPLC chromatogram of the acid-hydrolysed walloon oak acorn caps. Numbers correspond to the dyes as follows: 7, gallic acid; 8, ellagic acid; 9, ellagic acid derivative

The unmordanted silk fabrics were dyed first with walloon oak acorn caps. Then the walloon oak-dyed silk samples were mordanted with alum, after which they were

**Table 2** Chromatographic and spectral characteristics of the investigated standard dyestuffs

Dyestuff source	Colouring component	$R_t$ , min	Absorbance maxima, nm
Walloon oak acorn caps	Gallic acid	4.4	215, 271
	Ellagic acid	17.5	253, 307, 369
Buckthorn berries	Quercetin	23.9	254, 295, 371
	Kaempferol	26.8	263, 293, 319, 365
	Isorhamnetin	26.9	255, 301, 369
	Rhamnetin	28.0	255, 299, 371
	Rhamnazin	28.6	263, 293, 320, 367 <sup>a</sup>
	Emodin	31.7	253, 267, 289, 439

<sup>a</sup> Mantzouris *et al.* [43] and Petrovicu *et al.* [44].

dyed with buckthorn berries. Rhamnetin, rhamnazin (PV21 and PV25) and ellagic acid (PV21) were determined in the dyed silk samples.

Quercetin, rhamnetin and rhamnazin (PVI26 and PVI30) and ellagic acid (PVI26) were identified in the dyed silk samples that had been dyed first with walloon oak acorn caps and then with buckthorn berries.

Ellagic acid, rhamnetin, rhamnazin (PI1 and PI5) and quercetin (PI5) were determined in the silk samples that had been dyed with a mixture of walloon oak acorn caps and buckthorn berries.

Emodin was not observed in any of the dyed silk samples, although it was identified in the acid hydrolysate of hydrolysed buckthorn berries. Therefore, it is concluded that it had no effect on the colour of any of the dyed silk samples.

Table 3 presents the dye compositions found in silk samples dyed according to the various procedures summarised in Table 1.

### Colour analysis

The colorimetric values for dyed fabrics are listed in Table 4. Analysis of the data shows that increasing the concentration of walloon oak results in darker shades. The darkest shade was obtained using procedure V, in which higher concentrations of both buckthorn and walloon oak were used. The fabrics showed more greenish shades with a decrease in walloon oak concentration (procedure I). However, the green-red and blue-yellow axes of the dyed samples showed no correlation with the concentration of walloon oak. The dyeing procedures had different effects on  $a^*$  and  $b^*$  values. When the premordanted silk fabrics were dyed together with both walloon oak and buckthorn, more greenish and yellow fabrics were obtained. This can be attributed to flavonoids such as quercetin, etc., in the dyebath. Given that the concentration of quercetin remained the same because the buckthorn concentration was constant, as the walloon oak concentration decreased, the colour shades became more green and yellow. Similar results were obtained for procedure II. In the case of procedure III, both  $b^*$  and  $a^*$  values decreased with decreasing amounts of both walloon oak and buckthorn. To observe the effect of mordanting, procedures II and V can be compared. Without mordanting, which binds the dye to the fibre by chelation, dye molecules may only bind loosely, which results in poor wash fastness. Comparison of colorimetric data for procedure III, where mordanting with alum was carried out before dyeing with walloon oak and buckthorn, and procedure V, where mordanting was carried out after first dyeing with walloon oak, showed that procedure V gave more reddish and yellowish hues than procedure III did. When the silk samples were mordanted with alum, they had more yellow and green shades because of the decreasing concentration of walloon oak extract. However, premordanted samples (procedures I, II, III, IV and VIII) were more reddish and yellowish than the unmordanted samples. The value of  $a^*$  was positive and  $b^*$  was maximal at the lowest level of walloon oak concentration. The vividness of dyeings increased with a decrease in the walloon oak concentration in procedures I, II, V and VI. In the case of a decreasing amount of buckthorn, the dyed fabrics became duller. The vividness of dyeing decreased with decreasing concentrations of walloon oak in procedures IV and VII.



**Table 3** Chromatographic characteristics of the investigated sample extracts

Hydrolysed dyed silk sample extract <sup>a</sup> (abbreviation)	Compound identified	Retention time, min	Area,%	Peak height
PI1	Ellagic acid	17.3	50.3	70.8
	Rhamnetin	27.2	27.2	102
	Rhamnazin	28.7	13.3	54.3
PI5	Ellagic acid	17.3	38.0	79.6
	Quercetin	23.2	7.9	29.2
	Rhamnetin	27.3	35.3	199
PII6	Rhamnazin	28.7	18.8	112
	Ellagic acid	17.3	41.4	76.2
	Rhamnetin	27.3	40.5	194
PII10	Rhamnazin	28.7	18.1	89.4
	Ellagic acid	17.3	20.7	28.8
	Quercetin	23.2	7.2	21.7
PIII11	Rhamnetin	27.3	51.1	205
	Rhamnazin	28.7	21.0	88.6
	Ellagic acid	17.3	34.5	39.9
PIII15	Quercetin	23.3	8.3	21.9
	Rhamnetin	27.3	43.6	163
	Rhamnazin	28.7	13.5	53.3
PIV16	Rhamnetin	27.3	65.3	32.5
	Rhamnazin	28.7	34.7	20.9
	Ellagic acid	17.3	49.2	104
PIV20	Ellagic acid	17.3	59.2	42.0
	Ellagic acid	17.1	29.0	35.7
	Rhamnetin	27.2	42.2	139
PV21	Rhamnazin	28.7	17.1	67
	Rhamnetin	27.2	67.8	205
	Rhamnazin	28.7	32.2	109
PVI26	Ellagic acid	17.3	22.9	38.3
	Quercetin	23.1	11.4	33.6
	Rhamnetin	27.2	49.5	238
PVI30	Rhamnazin	28.7	16.1	80.6
	Quercetin	23.2	14.4	29.6
	Rhamnetin	27.3	66.5	178.4
PVII31	Rhamnazin	28.7	19.2	55.7
	Ellagic acid	17.3	69.8	83.2
	Gallic acid	4.8	100.0	26.7
PVII35	Quercetin	23.2	10.0	26.8
	Rhamnetin	27.3	63.3	237
	Rhamnazin	28.7	26.7	111
PVIII36	Rhamnetin	27.3	34.5	29.6
	Rhamnazin	28.7	22.5	21.6
	Rhamnetin	27.3	34.5	29.6

<sup>a</sup> For example, PI1 signifies first dyeing according to procedure I as indicated in Table 1

The values of  $\Delta E^*$  between procedures IV and VII are shown in Figure 3. As can be seen in Figure 3, the values were very high and far from the desired value of 1. There are two possible explanations for this. The first is the effect of mordant salt; the second one is inadequate binding of dyes to fibre active sites when mordant salts are not present.

To observe the effect of dyeing at a constant concentration of buckthorn,  $\Delta E^*$  values for procedures II, V and VI were compared (Figure 4). The  $\Delta E^*$  values for the unmordanted and mordanted dyeings were very high. However,  $\Delta E^*$  values for mordanted (procedures II and V) and unmordanted (procedure VI) dyeings become closer with increasing amounts of walloon oak.

With decreasing amounts of both walloon oak and buckthorn extracts, the colour strength decreased. If colour strength values of procedure IV and VII are compared (Figure 5), it can be seen that the values dramatically decreased in the absence of a mordant. If colour strengths of procedures II and V are compared, it can be seen that the differences in  $K/S$  values were comparable with their  $\Delta E^*$

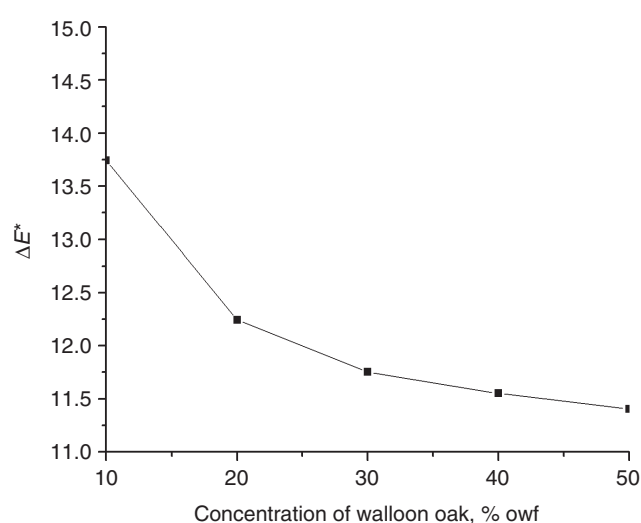
values. Comparison of colour strengths at constant buckthorn concentrations showed that mordanting between dyeing gave higher  $K/S$  values (Table 4).

#### Fastness tests

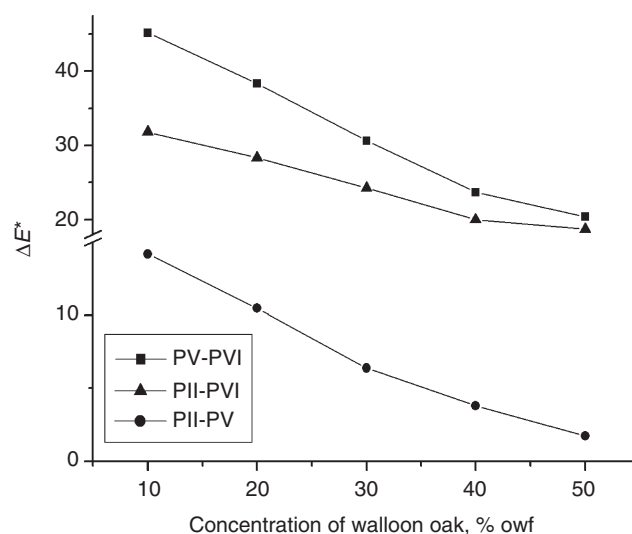
Colour and wash fastness results are listed in Table 5. Mordanting with alum gave moderate light fastness values. However, in the absence of the mordanting process, good values of light fastness were observed. The dry rubbing fastness properties of the dyed samples varied between 5 and 4–5. Although the wet rubbing fastness of the dyed samples varied generally between 4 and 5, a slight decrease was observed in procedure V. That slight decrease could be partly attributed to the physical binding of the mordant–dye system to the fibre surface. Staining values of adjacent fibres (i.e. bleeding) varied between 5 and 4–5. In other words, the adjacent fibres were not stained by the washing bath, so very good values were obtained. However, for all of the samples, the colour change values for wash fastness were very poor, ranging from 2 to 1–2.

**Table 4** Colorimetric values of samples

Procedure	Trial no.	$L^*$	$a^*$	$b^*$	$C^*$	$h$	$\lambda_{\max}$	$K/S$
I	1	70.590	-1.915	40.846	40.891	2.685	400	15.756
	2	71.299	-2.395	45.747	45.809	2.997	400	17.48644
	3	71.934	-2.543	46.381	46.450	3.138	400	16.76556
	4	72.415	-2.849	52.692	52.769	3.094	400	18.14572
II	5	75.156	-3.400	57.045	57.146	3.411	400	17.69333
	6	67.434	-0.930	45.374	45.383	1.174	400	18.19462
	7	67.485	-1.027	46.640	46.651	1.261	400	18.54405
	8	68.169	-1.397	51.240	51.259	1.562	400	19.75894
III	9	68.395	-1.148	54.780	54.792	1.200	400	19.36506
	10	70.878	-1.012	59.704	59.712	0.971	400	18.5695
	11	69.251	-1.801	48.942	48.975	2.107	400	18.7755
	12	69.610	-2.139	50.404	50.450	2.430	400	19.2826
IV	13	70.943	-2.770	49.009	49.087	3.235	400	17.17357
	14	72.168	-2.820	46.520	46.606	3.468	400	14.65728
	15	74.427	-2.387	41.223	41.292	3.315	400	9.491434
	16	69.956	-0.024	30.133	30.133	0.046	400	9.29129
V	17	70.610	-0.069	29.559	29.559	0.134	400	8.162568
	18	71.084	-0.127	28.851	28.852	0.251	400	7.42374
	19	72.920	0.053	27.958	27.908	89.890	400	5.888927
	20	74.886	0.389	25.147	25.150	89.115	400	3.786171
VI	21	67.266	-1.006	47.094	47.104	1.224	400	18.62059
	22	67.265	-1.197	50.428	50.443	1.360	400	19.03919
	23	67.681	-1.272	57.613	57.627	1.265	400	21.0055
	24	68.827	-0.550	65.165	65.165	0.048	400	21.07016
VII	25	72.023	1.896	73.526	73.550	88.523	400	20.65657
	26	71.226	1.366	27.214	27.249	87.127	400	16.99951
	27	72.040	1.173	27.358	27.383	87.544	400	17.37347
	28	72.902	1.023	27.544	27.563	87.873	400	17.81029
VIII	29	75.129	0.502	27.343	27.348	88.947	400	16.6405
	30	78.929	-0.249	28.956	28.957	0.492	400	16.0215
	31	71.200	2.940	19.190	19.414	81.291	400	3.024036
	32	72.019	2.968	18.502	18.738	80.886	400	2.616599
IX	33	73.183	2.817	17.669	17.893	80.941	400	2.155717
	34	75.523	2.613	16.271	16.479	80.876	400	1.530185
	35	81.358	1.900	13.120	13.257	81.759	400	0.736384
	36	75.746	6.411	84.916	85.158	85.683	400	20.78217
X	37	76.907	5.425	84.099	84.274	86.309	400	19.96165
	38	77.620	5.660	85.055	85.243	86.193	400	19.36506
	39	79.662	3.908	81.406	81.500	87.251	420	14.01667
	40	84.435	0.064	72.954	72.954	89.950	420	6.54455

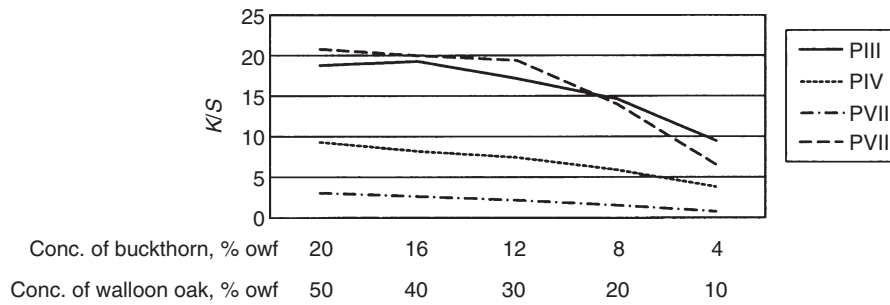
**Figure 3**  $\Delta E^*$  values between procedures IV and VII

This colour change was manifested in a change to more reddish and darker hues. As can be seen in Figure 6, the  $a^*$  values of washed fabrics were more positive and higher than for the unwashed fabrics.

**Figure 4**  $\Delta E^*$  values between procedures II, V and VI

## Conclusions

It has been observed that buckthorn and walloon oak can be used for the dyeing of both unmordanted and alum-mordant-



**Figure 5** Effect of walloon oak and buckthorn concentration on colour strength

**Table 5** Fastness properties of samples

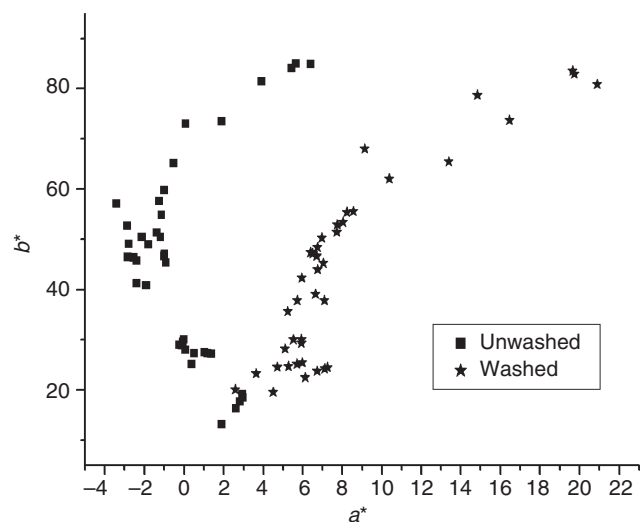
Procedure	Trial no.	Fastness to light	Colour fastness on washing								
			Rubbing fastness		Colour change <sup>a</sup>	Bleeding					
			Dry	Wet		CA <sup>b</sup>	Co <sup>b</sup>	PES <sup>b</sup>	PA <sup>b</sup>	PAC <sup>b</sup>	Wo <sup>b</sup>
I	1	3	4-5	4-5	1-2	5	5	5	5	4-5	5
	2	3	4-5	4-5	1-2	5	5	5	5	5	5
	3	4	5	4-5	1-2	5	5	5	5	5	5
	4	3	5	4	1-2	5	5	5	5	5	5
	5	4	5	4-5	1-2	5	5	5	5	5	5
II	6	3	5	4-5	1-2	5	5	5	5	5	5
	7	3	5	4-5	1-2	5	5	5	5	5	5
	8	4	5	4-5	1-2	5	5	5	5	5	5
	9	3-4	5	4-5	1-2	5	5	5	5	4-5	5
	10	4	5	4-5	1-2	5	5	5	5	4-5	5
III	11	3	5	4-5	1-2	5	5	5	5	5	5
	12	3-4	5	4-5	1-2	5	5	5	5	5	5
	13	3	5	5	1-2	5	5	5	5	5	5
	14	3-4	5	5	1-2	5	5	5	5	5	5
	15	4	5	4-5	1-2	5	5	5	5	5	5
IV	16	3-4	5	4-5	1-2	5	5	5	5	5	5
	17	3-4	5	5	1-2	5	5	5	5	5	5
	18	4	5	5	1-2	5	5	5	5	5	5
	19	3-4	5	5	1-2	5	5	5	5	5	5
	20	4	5	4-5	2	5	5	5	5	5	5
V	21	3-4	4-5	3-4	1-2	5	4-5	5	5	5	5
	22	3-4	4-5	3-4	1-2	5	4-5	5	5	5	5
	23	3-4	4-5	3-4	1-2	5	4-5	5	5	5	5
	24	3-4	4-5	3-4	1-2	5	5	5	5	5	5
	25	3-4	4-5	4	1-2	5	5	5	5	5	5
VI	26	5	4-5	4-5	1-2	5	4-5	5	5	5	5
	27	5	4-5	4-5	1-2	5	4-5	5	5	5	5
	28	5	5	4-5	1-2	5	4-5	5	5	5	5
	29	5	5	4-5	2	5	4-5	4-5	5	5	5
	30	5	5	4-5	2	5	4-5	5	5	5	5
VII	31	5	5	5	1-2	5	4-5	5	5	5	5
	32	5	5	5	1-2	5	4-5	5	5	5	5
	33	5	5	5	1-2	5	4-5	5	5	5	5
	34	5-4	5	5	1-2	5	4-5	5	5	5	5
	35	4	5	5	1-2	5	4-5	4-5	5	5	5
VIII	36	3	4-5	4	1-2	5	4-5	5	5	5	5
	37	3	4-5	4	1-2	5	4-5	5	5	5	5
	38	3	5	4-5	1-2	5	4-5	5	5	5	5
	39	3-4	5	4-5	1-2	5	5	5	5	5	5
	40	3-4	5	5	1-2	5	5	5	5	5	5

<sup>a</sup> Colour change values had reddish hues.

<sup>b</sup> CA: cellulose diacetate, Co: cotton, PES: polyester, PA: polyamide, PAC: polyacrylic, Wo: wool

ed silk fabrics. The identification of natural dyes from the dyed silk fabrics was achieved here by reversed-phase high-performance liquid chromatography (RP-HPLC) with diode-

array detection (DAD). The HPLC method provides a good qualitative determination of the natural dyes. The extraction of dyes prior to HPLC analysis was successful using



**Figure 6**  $a^*$  and  $b^*$  values of washed and unwashed fabrics

previously reported methods. The dye components were identified on the basis of literature values and absorption spectra acquired with the standard reference compounds, as shown in Table 6.

**Table 6** Identified dyes (colouring compounds) in the sample extracts

Dye plant	Plant extract or Dyeing procedure	Identified sample (Trial) no.	Identified dyes (colouring compounds)
Walloon oak	Acid-hydrolysed walloon oak extract	–	Gallic acid Ellagic acid Possible ellagic acid derivative
Buckthorn	Acid-hydrolysed buckthorn extract	–	Quercetin Rhamnetin Rhamnazin Emodin
Walloon oak + Buckthorn	Premordanted fabrics were dyed (together walloon oak and buckthorn)	1 5	Ellagic acid, rhamnazin, rhamnetin Ellagic acid, rhamnazin, rhamnetin, quercetin
Buckthorn + Walloon oak	Premordanted fabrics were separately dyed (before buckthorn, after walloon oak)	6 10	Ellagic acid, rhamnazin, rhamnetin Ellagic acid, rhamnazin, rhamnetin, quercetin
Walloon oak + Buckthorn	Premordanted fabrics were separately dyed (before walloon oak, after buckthorn)	11 15	Rhamnetin, rhamnazin ellagic acid, quercetin Rhamnetin, rhamnazin
Walloon oak	Premordanted fabrics were dyed (walloon oak)	16 20	Ellagic acid Ellagic acid
Walloon oak + Buckthorn	Unmordanted fabrics were separately dyed and mordanted (before walloon oak, then alum mordanted, after buckthorn)	21 25	Rhamnetin, rhamnazin, ellagic acid Rhamnetin, rhamnazin
Walloon oak + Buckthorn	Unmordanted fabrics were separately dyed (before walloon oak, after buckthorn)	26 30	Quercetin, rhamnetin, rhamnazin, ellagic acid Quercetin, rhamnetin, rhamnazin
Walloon oak	Unmordanted fabrics were dyed (walloon oak)	31 35	Ellagic acid Gallic acid
Buckthorn	Premordanted fabrics were dyed (buckthorn)	36 40	Quercetin, rhamnetin and rhamnazin Rhamnetin and rhamnazin

Addition of mordant had effects on CIE  $L^*a^*b^*$  and  $K/S$  values. The  $\Delta E^*$  values decreased with increasing concentrations of walloon oak. However, at the highest concentration of walloon oak, the type of mordanting had no effect on colour parameters. In spite of displaying moderate light and rubbing fastness, the level of staining of adjacent fibres was very low. However, the colour changes of fabrics after washing were high, with the result that the fabrics took on reddish hues.

This study shows that compatible natural dyes could be combined with each other or used separately. Thus, trichromy dyeing can be applied to natural dyes. However, mordanting plays an important role for natural dyes. The present results show that dyeing of unmordanted silk fabrics with walloon oak and buckthorn (procedure VI) is the most suitable dyeing procedure owing to its good fastness properties and higher colour strength values.

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