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Dyeing of Wool and Nylon 6.6 with Henna and Lawsone

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ABSTRACT

HPLC was employed to show that Henna extract contained 0·57% Lawsone together with a high proportion of another colorant. When applied to wool and nylon 6.6, both Henna extract and Lawsone behaved as acid levelling, non-metallised acid dyes in so fas as dye uptake increased with decreasing pH. Afterchroming improved both the wash and light fastness of Henna extract and Lawsone on each substrate and also altered the depth, chroma and colour of the dyeings, this being attributable to the formation of a dye–chromium complex.

INTRODUCTION

Henna (*Lawsonia inermis* Linn) is a glabrous shrub, extensively distributed in the tropics and sub-tropics, whose leaves have been used for thousands of years as a medicine,[1] as a cosmetic to dye hair[1–4] and to stain hands and feet[1,5] and also for dyeing textiles,[1,6–8] being applied either alone or on an alum mordant to wool and silk fibres. The dyeing properties of Henna accrue[1] from Lawsone (2-hydroxy-1,4-naphthaquinone (**I**)) (Scheme 1) which was first isolated and identified by Tommasi.[9] Cox[10] showed that Henna comprised 1% Lawsone and 6% gallic acid but was free of tannin; Karawaya[11] employed spectrophotometry to demonstrate that Lawsone was most abundant in the leaf of the Henna bush and recent phytochemical studies of Henna leaves have resulted in the isolation of Lawsone (0·43%) and other crystalline compounds including a flavonoid colorant, Luteolin (**II**).[12]

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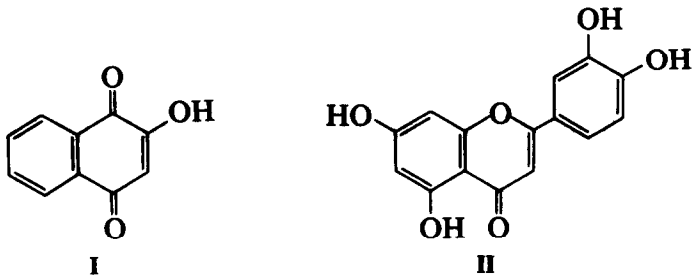


Scheme 1

Despite its long established use as a dye for animal fibres, no systematic investigation has been carried out of the dyeing behaviour of Henna; the present work concerns the application of both Henna extract and Lawsone to nylon 6.6 and wool fabrics as both non-metallised acid dyes and mordant dyes.

EXPERIMENTAL

Materials

Henna
Dry, powdered leaves of Henna bush (*Lawsonia inermis* Linn) cultivated in Sudan were used.

Lawsone
2-Hydroxy-1,4-naphthoquinone (98% purity) was obtained from Aldrich Chemicals.

Fabrics
Scoured and bleached wool (235 g m^{-2}) fabric obtained from Whalleys, and scoured nylon 6.6 (230 g m^{-2}) provided by ICI Fibres were employed.

PROCEDURES

Determination of Lawsone content of Henna extract

A sample (2·0 g) of powdered Henna leaves was extracted with 100 cm^3 of 0·1 M sodium hydroxide solution in a mechanically shaken, stoppered conical flask at ambient temperature for 48 h. The ensuing solution was filtered under vacuum and then separated by using a Varian 5000 HPLC

system, incorporating a C_{18} reverse phase, Apex Octadecyl 15 cm column (Jones Chromatography). The method used was as follows:

Eluent	55% deionised water containing $3{\cdot}33 \times 10^{-3}$ M acetic acid and $8{\cdot}9 \times 10^{-4}$ M potassium hydroxide/45% methanol containing $3{\cdot}33 \times 10^{-3}$ M acetic acid and $8{\cdot}9 \times 10^{-4}$ M potassium hydroxide
Flow	1 cm^3 min^{-1}
Pressure	50 atm
Detection	420 nm.

The above extraction and HPLC separation were repeated using two further samples (2·0 g) of powdered Henna leaves.

The concentration of Lawsone in each of the three Henna extracts was determined by reference to a calibration curve of Lawsone concentration versus integrated peak area. An aqueous (distilled water) solution (4 g $litre^{-1}$) of Lawsone was prepared and an aliquot (2, 4, 6, 8 or 10 cm^3) removed and diluted to 100 cm^3 using distilled water. The ensuing diluted solution of Lawsone was then separated by HPLC using the conditions and procedure described above; a linear plot of Lawsone concentration versus integrated peak area curve was obtained.

Dyeing

All dyeings were carried out using 300 cm^3 capacity glass dyepots housed in a Zeltex Vistacolor laboratory-scale dyeing machine; after dyeing, the dyed sample was thoroughly rinsed in tap water and allowed to dry in the open air.

Dyeing wool and nylon 6.6 with henna

Powdered henna leaves (100 g) were extracted by stirring in 1 litre of distilled water for 48 h at ambient temperature. The mixture was allowed to settle and the supernatant decanted and filtered under vacuum. A 100 cm^3 portion of the supernatant was removed and placed in the dyepot; the volume of the dyebath was then made up to 200 cm^3 using distilled water, the pH of the dyebath being adjusted to 3, 4, 5 or 6 by the addition of aqueous (1 M) sulphuric acid, aqueous (30%) acetic acid, aqueous (5%) sodium acetate or aqueous (2%) sodium carbonate, respectively. A 4 g sample of wetted (distilled water) wool or nylon 6.6 fabric was placed in the dyebath and the sealed dyepot placed in the dyeing machine; dyeing was carried out using the method shown in Fig. 1.

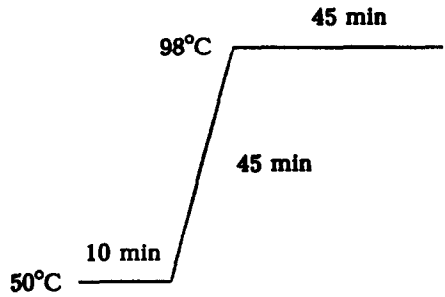


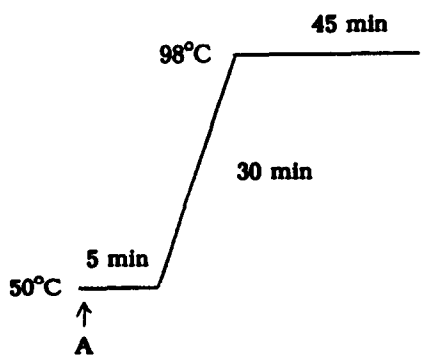
Fig. 1. Dyeing method.

Dyeing wool and nylon 6.6 with Lawsone

Lawsone (4 g) was dissolved in 1 litre of distilled water with stirring at ambient temperature. A 100 cm^3 portion of the ensuing solution was placed in the dyepot and the volume of the dyebath made up to 200 cm^3 using distilled water, the pH of the dyebath being adjusted to 3, 4, 5 or 6 using the method described above. A 4·0 g sample of wetted (distilled water) fabric was added and dyeing carried out using the method shown in Fig. 1.

Chroming of dyed samples

A 2·0 g portion of each of the dry samples of wool and nylon 6.6 which had been dyed with either Henna extract or Lawsone was wetted in distilled water and afterchromed using the method shown in Fig. 2; chroming was carried out in sealed, 300 cm^3 capacity glass dyepots housed in a Zeltex Vistacolor laboratory-scale dyeing machine employed a 50:1 liquor ratio.



A potassium dichromate 3% o.m.f
acetic acid (30%) 0.5% (pH 3.5)

Fig. 2. Chroming method.

The chromed, dyed samples were then rinsed in tap water and allowed to dry in the open air.

Colour measurement

The reflectance values of the dyed and also chromed samples were measured using a Macbeth 2020 Colour-Eye reflectance spectrophotometer interfaced to a Digital Rainbow PC under illuminant D_{65}, 10° standard observer with specular component excluded and UV component included. The samples were folded so as to present a total thickness of 4 layers of fabric and an average of two readings of each sample was taken. The CIELab values and also the K/S values at λ_{max} (400 nm for Henna extract and 460 nm for Lawsone on wool and nylon 6.6) were calculated from the reflectance values.

Wash fastness

Dyed and also chromed samples were submitted to the ISO CO6/C2 test method.[13]

Light fastness

The dyed and chromed samples were submitted to ISO B2 test method[13] using a Microscal fading lamp.

RESULTS AND DISCUSSION

Typical HPLC chromatograms of Lawsone and also of Henna extract are shown in Fig. 3, from which it is clear that the Henna extract contained a high proportion of a coloured species other than Lawsone which, in view of the findings of Mahmoud *et al.*,[12] may be Luteolin. The average Lawsone content of the henna leaves used in this work was found to be 0·57% (Table 1) which is in reasonable agreement with the values obtained by Cox[10] and Mahmoud *et al.*[12]

It was found (Tables 2–5) that the extent of uptake of both Henna extract and Lawsone on to wool and nylon 6.6 (in terms of K/S and L^* values of the dyeings) decreased with increasing pH of application. The finding that pH 3 yielded the highest K/S and lowest L^* values suggests that Lawsone, which is considered to be the major dye constituent of Henna, behaves as a levelling, non-metallised acid dye in its behaviour on both wool and nylon, from which it can be proposed that under the acidic dyeing conditions used, substantivity of the relatively small molecular size dye arises primarily by

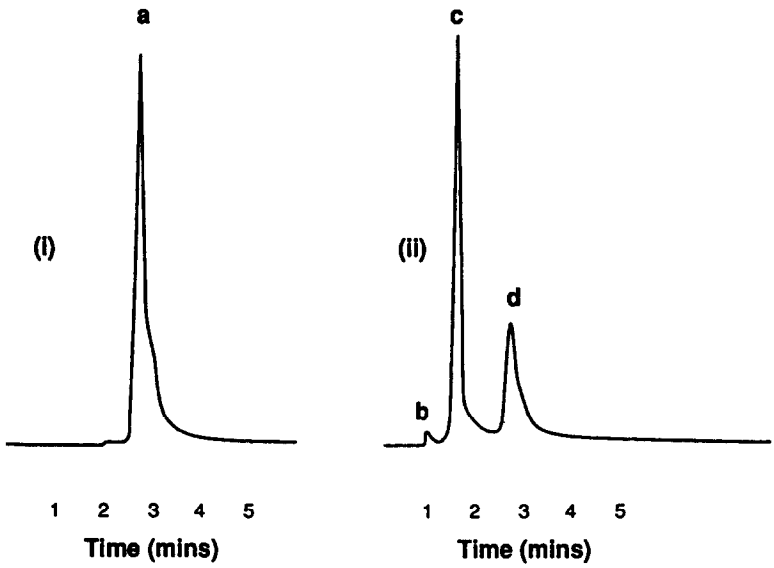


Fig. 3. HPLC analysis of (i) Lawsone and (ii) Henna extract: (a) 2·81 min; (b) 0·93 min; (c) 1·52 min; (d) 2·87 min.

virtue of ion-dipole forces of interaction operating between polar groups in the dye and protonated amino groups in the two substrates. The previously discussed HPLC results showed that the Henna extract used contained a high proportion of a coloured species other than Lawsone. If it considered that this coloured species was Luteolin, it seems reasonable, in view of the structural similarity of Luteolin and Lawsone, to propose that Luteolin would be substantive to both wool and nylon 6.6 and that its dyeing behaviour would resemble that of Lawsone. The finding (Tables 2–5) that the extent of uptake of both Henna extract and Lawsone was lower on nylon than on wool at each of the four pH values employed for dyeing can be attributed to the well-known lower amino group content of nylon 6.6. Tables 2–5 also show that the dyeings obtained using Henna extract were more

TABLE 1
Lawsone Content in Henna Leaves

Sample	*Lawsone* ($\times 10^{-3}$ g)	*Lawsone* (%)
1	12·0	0·60
2	11·0	0·55
3	11·0	0·55
Average	—	0·57

TABLE 2
Colorimetric and Fastness Data for Wool Dyed with Henna Extract

Sample	*pH*	*L**	*a**	*b**	*c**	*h*	*DE**	*K/S*	*Ch.*	*WO.*	*Co.*	*LF*
Unchromed[a]	3	32·1	13·6	23·8	27·4	60·3	—	21·1	—	—	—	—
							4·1					
Unchromed[b]	3	33·1	12·7	19·8	23·5	57·3		18·6	3	3–4	3–4	3
Chromed[a]	3	28·4	12·2	18·8	22·5	57·2		24·5	—	—	—	—
							1·9					
Chromed[b]	3	29·4	12·6	19·8	23·5	57·5		24·0	4	5	5	3–4
Uncromed[a]	4	33·4	12·9	22·9	26·3	60·4		19·6	—	—	—	—
							3·1					
Unchromed[b]	4	33·8	13·0	19·8	23·7	56·6		16·5	3–4	3–4	3–4	3
Chromed[a]	4	30·9	12·5	20·9	24·4	59·1		22·7	—	—	—	—
							1·1					
Chromed[b]	4	30·3	12·3	19·9	23·4	58·3		22·5	4–5	5	5	3–4
Unchromed[a]	5	36·0	13·2	23·1	26·6	60·1		15·9	—	—	—	—
							3·9					
Unchromed[b]	5	36·8	12·9	19·2	23·1	54·2		13·2	3	3–4	3–4	3
Chromed[a]	5	33·2	12·5	22·4	25·7	60·8		20·5	—	—	—	—
							0·5					
Chromed[b]	5	33·3	12·5	21·9	25·2	60·4		19·6	5	5	5	3–4
Unchromed[a]	6	40·3	12·7	22·2	25·6	60·3		11·3	—	—	—	—
							1·9					
Unchromed[b]	6	40·3	12·8	20·3	24·0	57·8		10·1	4	3–4	3–4	3
Chromed[a]	6	31·2	12·5	24·7	27·7	63·2		17·0	—	—	—	—
							1·1					
Chromed[b]	6	37·2	12·2	23·7	26·7	62·7		15·9	4–5	5	5	3–4

[a] Prior to ISO CO6/C2 wash test.
[b] After ISO CO6/C2 wash test.
* Colour difference between samples a and b.
Ch, change in colour of original sample; Wo., staining of wool adjacent; Co., staining of cotton adjacent.

yellow in hue than those secured using Lawsone (as demonstrated by the lower a^* and higher h values of the Henna extract dyeings); furthermore, the dyeings obtained on both nylon and wool using Henna extract were duller than those provided by Lawsone (as given by the lower c^* values of the henna dyeings). These findings may be attributed to the presence of the yellow flavone, Luteolin, in the Henna extract used in the work.

The afterchroming of mordant dyes on wool and nylon, by which a dye–metal complex is formed, characteristically imparts enhanced fastness to light and washing and also results in a dulling of the shade and a

TABLE 3
Colorimetric and Fastness Data for Nylon 6.6 Dyed with Henna Extract

Sample	*pH*	*L**	*a**	*b**	*c**	*h*	*DE**	*K/S*	*Ch.*	*Wo.*	*Co.*	*LF*
Unchromed[a]	3	46·3	8·9	23·9	25·5	69·5		8·3	—	—	—	—
							3.1					
Unchromed[b]	3	46·5	10·7	21·3	23·8	63·4		6·6	3–4	4	4	1
Chromed[a]	3	41·8	8·9	19·3	21·3	65·2		8·7	—	—	—	—
							0·6					
Chromed[b]	3	42·3	8·7	19·1	21·0	65·4		8·2	5	5	5	2
Unchromed[a]	4	47·4	9·1	22·8	24·5	68·5		7·2	—	—	—	—
							2·3					
Unchromed[b]	4	47·8	10·5	21·1	23·6	63·5		5·9	4	4	4	1
Chromed[b]	4	43·6	8·3	19·3	21·0	66·8		7·6	—	—	—	—
							0·2					
Chromed[b]	4	43·4	8·3	19·3	21·0	66·8		7·6	5	5	5	2
Unchromd[a]	5	49·1	9·7	21·7	23·8	66·0		5·9	—	—	—	—
							2·1					
Unchromed[b]	5	48·6	10·2	19·7	22·2	62·7		5·2	4	4	4	1
Chromed[a]	5	45·4	8·4	20·2	21·9	67·5		6·7	—	—	—	—
							0·6					
Chromed[b]	5	45·7	8·0	19·8	21·4	67·9		6·3	5	5	5	2
Unchromed[a]	6	51·7	9·6	18·8	21·1	62·8		4·3	—	—	—	—
							1·8					
Unchromed[b]	6	53·4	10·1	18·5	21·1	61·5		3·6	4	4	4	1
Chromed[a]	6	49·1	8·6	22·1	23·7	68·6		5·6	—	—	—	—
							0·6					
Chromed[b]	6	49·6	8·4	21·8	23·4	69·0		5·2	5	5	5	2

Legend as for Table 2.

bathochromic shift in the λ_{max} of the dyeing.[14] In view of the structure of Lawsone (**I**) and also of Luteolin (**II**) which may be present in the Henna extract used, it was considered that both colorants may chelate chromium and, therefore, that afterchroming might impart enhanced wash and light fastness to the dyes on the two fibres under consideration.

In this context, the wash and light fastness properties of both Henna extract and Lawsone on wool and nylon 6.6 were determined in order to assess the effects of afterchroming on fastness; since standard depth dyeings were not employed, the fastness results obtained cannot therefore be used as a comparison of the fastness characteristics of Henna extract and Lawsone on the two substrates. Tables 2–5 clearly demonstrate that afterchroming increased both the wash fastness of dyeings of both Henna extract and Lawsone on each of the two fibres by approximately one point in terms of

TABLE 4
Colorimetric and Fastness Data for Wool Dyed with Lawsone

Sample	*pH*	*L**	*a**	*b**	*c**	*h*	*DE**	*K/S*	*Ch.*	*Wo.*	*Co.*	*LF*
Unchromed[a]	3	30·2	25·6	26·2	36·6	45·6		25·2	—	—	—	—
							4·3					
Unchromed[b]	3	32·0	22·0	24·7	33·1	48·3		21·4	3	2–3	2–3	3
Chromed[a]	3	27·6	18·1	21·2	27·9	49·5		23·9	—	—	—	—
							3·7					
Chromed[b]	3	29·5	20·4	24·4	31·8	50·1		25·2	3	3–4	3–4	3–4
Unchromed[a]	4	31·2	26·2	27·4	37·9	46·2		25·9	—	—	—	—
							3·6					
Unchromed[b]	4	32·4	23·2	25·9	34·8	48·1		25·9	3	2–3	2–3	3
Chromed[a]	4	27·8	18·2	20·9	27·7	48·9		20·7	—	—	—	—
							4·5					
Chromed[b]	4	29·6	20·2	24·4	31·7	50·1		25·1	3	3–4	3–4	3–4
Unchromed[a]	5	32·4	25·9	29·0	39·0	48·1		24·4	—	—	—	—
							5·5					
Unchromed[b]	5	33·7	22·7	24·7	33·6	47·4		24·8	2–3	2–3	2–3	3
Chromed[a]	5	29·6	18·8	21·9	28·9	49·3		17·8	—	—	—	—
							4·1					
Chromed[b]	5	31·2	20·7	25·6	32·9	51·1		22·6	3	3–4	3–4	3–4
Unchromed[a]	6	36·1	25·4	30·2	39·5	49·9		21·6	—	—	—	—
							6·7					
Unchromed[b]	6	38·2	22·3	24·5	33·1	47·7		19·0	2–3	2–3	2–3	3
Chromed[a]	6	32·1	18·8	22·6	29·4	50·3		12·1	—	—	—	—
							6·1					
Chromed[b]	6	33·8	21·1	27·9	35·1	53·0		20·0	2–3	3–4	3–4	3–4

Legend as for Table 2.

colour change and staining; the DE values in Tables 2–5 show that the extent to which the wash fastness of both Henna extract and Lawsone were improved by afterchroming was greater on nylon 6.6 than on wool. Afterchroming also increased the light fastness of the two dyes on both substrates by between 0·5 and 1 unit, the improvement being greatest in the case of dyeings on nylon 6.6.

Afterchroming reduced the chroma of the dyeings of both Henna extract and Lawsone on each of the two fibres, this effect, which is characteristic of dye-metallisation,[14] being less marked when dyeing had been carried out at pH 5 and 6 (Tables 2–5). Tables 2–5 show that treatment with chromium altered the colour of the Henna extract and Lawsone dyeings on the two substrates, this being more marked for the two dyes on nylon 6.6 than on wool and also for dyeings of Lawsone on both fibres. In the case of Henna

TABLE 5
Colorimetric and Fastness Data for Nylon 6.6 Dyed with Lawsone

Sample	*pH*	*L**	*a**	*b**	*c**	*h*	*DE**	*K/S*	*Ch.*	*Wo.*	*Co.*	*LF*
Uncromed[a]	3	48·5	26·8	34·1	43·4	51·8		8·2	—	—	—	—
							17·5					
Unchromed[b]	3	52·9	17·4	19·9	26·5	48·9		3·8	1	3	3	1
Chromed[a]	3	51·2	18·1	26·2	31·8	55·3		4·9	—	—	—	—
							5·7					
Chromed[b]	3	51·6	14·9	21·5	26·2	55·1		3·9	2–3	4	4	2
Unchromed[a]	4	49·2	26·9	33·4	43·0	51·1		7·9	—	—	—	—
							18·3					
Unchromed[b]	4	54·6	16·7	19·3	23·5	49·0		2·9	1	3	3	1
Chromed[a]	4	52·5	18·6	26·6	32·5	55·0		4·5	—	—	—	—
							7·3					
Chromed[b]	4	53·5	14·0	20·8	25·1	56·1		3·3	2	4	4	2
Unchromed[a]	5	49·5	28·3	34·3	44·5	50·5		7·7	—	—	—	—
							20·9					
Unchromed[b]	5	54·1	17·8	17·9	25·2	45·2		2·9	1	3	3	1
Chromed[a]	5	52·9	18·4	25·9	31·8	54·6		4·2	—	—	—	—
							6·1					
Chromed[b]	5	53·9	15·4	20·6	25·7	53·2		3·2	2–3	4	4	2
Unchromed[a]	6	56·1	27·7	34·2	44·0	51·0		5·1	—	—	—	—
							24·1					
Unchromed[b]	6	62·9	15·5	14·6	21·3	43·3		1·4	1	3–4	3–4	1
Chromed[a]	6	57·7	18·2	25·8	31·6	54·8		3·1	—	—	—	—
							8·7					
Chromed[b]	6	59·6	13·9	18·5	23·1	53·0		2·0	2	4	4	2

Legend as for Table 2.

extract on both nylon 6.6 and wool, the afterchromed samples were deeper in depth than their unchromed counterparts (as given by the lower L^* and higher K/S values of the afterchromed dyeings); however, for the Lawsone dyeings on the two substrates, it was found that afterchroming did not always result in increased depth and colour strength.

The observed improvement in fastness to light and washing of the dyeings of Henna extract and Lawsone secured by afterchroming, together with the effects imparted by treatment with chromium to the shade of the dyeings, imply that for both dyes, afterchroming resulted in the formation of a dye–chromium complex. The findings that the unchromed dyeings obtained using Henna extract were more yellow in hue than those secured using Lawsone and that the extent of change in both the depth of shade and colour of the dyeings imparted by afterchroming differed for Henna extract and

Lawsone can be attributed to the presence of Luteolin in the Henna extract used in the work.

CONCLUSIONS

Henna can be used to dye both wool and nylon 6.6 fabrics; the dye appears to behave as an acid levelling, non-metallised acid dye with optimum uptake occurring at pH 3. Afterchroming improves both the wash and light fastness of the dye on both substrates and also alters the depth of shade, chroma and colour of the dyeings, this being attributable to the formation of a dye–chromium complex. Comparative dyeings obtained using Lawsone suggests that the sample of Henna used in the work probably contained Luteolin.

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