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# Dyeing Properties of Vilangin Synthesized from *Embelin* on Cotton Fibre

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#### ABSTRACT

Semi synthesis involves the use of chemical compounds isolated from natural sources as the starting materials to produce other distinct compounds with added value and improved chemical properties. Most modified dyes have been synthesized through chemical modification to increase solubility and fastness properties of the dyes. A semi-synthetic dye (vilangin) has been obtained through chemical modification of embelin (a benzoquinone) isolated from Embelia schimperi berries crude extract, a plant-based dye. The vilangin dye was synthesized by condensation of embelin with formaldehyde in acetic acid solution., Their melting point and thin layer chromatography was done to determine purity. Characterization was done using Ultraviolet-Visible spectroscopy, Fourier Transform Infrared spectroscopy, Liquid chromatography Mass spectrometry and Nuclear Magnetic Resonance Spectroscopy. Embelin and the semi- synthesized dye were applied on cotton fabrics and colour fastness properties such as wash fastness, rubbing fastness, light fastness were evaluated. Embelin dye and vilangin dye exhibited similar colour strengths (K/S values) of 0.18 and 0.19 respectively. Use of mordants increased the colour strengths from 0.19 to 0.23 for the pre-mordanted cotton fibers ,the post-mordanted were in the range of 0.19-0.32 whereas the simultaneous mordanting showed better characteristics in the range of 0.27-0.52 for the vilangin dye. It has thus been established that the semi-synthetic dye possessed superior fastness properties compared to the parent embelin dye.

Keyword: colour strength, characterization, dyeing, embelin, vilangin

#### **INTRODUCTION**

Organic colorants and dyes obtained from natural sources such as plants and insects have been widely used since Pre-historic times for foods, textiles and other kind of paintings [1]. In mid- $19^{th}$  century, there was a transition from natural dyes [2] to synthetic dyes due to accidental discovery of 'mauvein', a synthetic dye that led to increased enormous advances in food sector by making them appealing ,appetizing and as an additive and was used in pharmaceutical industry as drug colourants and in drug identity and brand development[2-4]. However, the adverse harm caused to the environment by synthetic dyes as they are non-degradable were observed over a period of time [5, 6] and the strict environmental regulations that have been imposed globally has retarded the interest in synthetic dyes [7]. This has led researchers globally to venture back to the use of natural dyes because they are eco-friendly, non-hazardous and more sustainable. However, natural dyes have shown some limitations, which includes poor yield [8], poor colour quality and stability [9], limited shades [10], irreproducible results [11] and inadequate fastness properties [12]. Chemical modification of the natural dyes can overcome some of these inherent challenges [13].

*Embelia schimperi* belonging to the family Myrsinaceae, contains extensive amounts of phenolic compounds, tannins, flavonoids and saponins. Its extracts are useful antioxidants and have diverse health benefits [14].Studies done by Atlabachew on *Embelia schimperi* ethanolic crude extracts led to isolation of a new compound (2,5-dihydroxy-3-methyl-1,4-benzoquinone), commonly known as embelin [15]. Embelin is a naturally occurring alkyl substituted hydroxyl benzoquinone and a major constituent, orange coloured pigment isolated from *Embelia ribes* commonly used for dyeing hair[16]. However, the retention of its colour has been proven to be inferior due to its low solubility emanating from its crystalline and lipophillic nature. [17]. This

work therefore involved modification of embelin to improve fastness property and use as a textile dye. It involved semi –synthesis of a methylene bridged dimeric embelin derivative, vilangin and its dyeing qualities on cotton fibers compared to the parent compound (embelin) has been investigated for the first time. To ensure optimal color, reproducibility and attaining a specific range of colour hues, Premordanting-, post-mordanting and simultaneous mordanting was applied in the dyeing process.

#### **MATERIALS AND METHODS**

*Embelia schimperi* berries were collected from Western slopes of Mau ranges in Kericho County (0°20'13.3"S 35°22'43.4"E) which is 2400 m above mean sea level and 260 Km west of Nairobi. They were identified and authenticated in the Botanical Laboratory, Department of Biological Sciences in Moi University. Specimens were then deposited in the herbarium for future reference. The berries were air-dried for one week at room temperature and ground into fine powder using a grinder (Nutribullet, NB-101B model).

#### Preparation of crude extract

Dried powder (250 g) was accurately weighed using an analytical balance and extracted using the maceration method for 72 hours with periodical shaking using acetone .The extracts were filtered through cotton wool and then Whatman No. 1 filter paper. The extracts were concentrated under reduced pressure using a rotary evaporator (HAHNVAPOR Rotary evaporator, HS-2005S model, Korea) to obtain crude extracts [18].

#### Isolation of embelin

**Materials** 

A classical column was packed under n-hexane by slurry method using silica gel (60-120 mesh) for column chromatography. Acetonic crude sample (1 g) was introduced into the column and elution done with the solvent system established through TLC analysis (ethyl acetate: hexane; 6:4). The isolated embelin was confirmed by comparing with the embelin standard using Thin layer chromatography.

#### Chemical modification of embelin to vilangin

Vilangin was synthesized by condensation reaction of embelin with formaldehyde in presence of acetic acid solution as per the procedure of Balachandran et al [19]. Embelin (1 g) was weighed and dissolved in glacial acetic acid (30 mL) after which it was gently warmed at 30°C. This was followed by addition of 5 mL of 40 % formaldehyde. The resultant solution was then heated on a water bath at 40 – 45 °C with continuous stirring at a constant rate for a period of 10 minutes. The solution obtained was then allowed to stand at room temperature to cool.

#### Analytical techniques

UV- visible spectrophotometry was done, scanning was in the range from 200 to 700 nm wavelength using UV-2450 spectrophotometer (Beckham Coulter DU 720). FTIR spectroscopy done using ATR-FTIR spectrophotometer, NICOLET 6700 Thermo Scientific 2009-27701 Model, and scanning was done between 4000 and 500 cm<sup>-1</sup>. Liquid chromatography-mass spectrometry (LC-MS) analyses of samples were carried out using a Shimadzu (Noisiel, France) LC-20A ultra-HPLC (UHPLC) system equipped with an autosampler, interfaced to a PDA UV

detector SPD-20A and coupled with a LC-MS 8030 triple-quadrupole mass spectrometer). NMR analysis done using Avance DRX 400 NMR Spectrometer (Bruker, Germany).

# Physical characterization

The golden orange embelin crystals that were isolated were subjected to, TLC profiling on the isolated embelin and comparisons of purity was done using the embelin marker compound. Melting point determination was done using BUCHI Melting point apparatus, B-540.The solubility of vilangin was enhanced by varying its pH in solution and a chemical test was done by addition of dilute ammonia solution which resulted in a bluish-violet colouration an indication of the presence of embelin.

# Application of semi-synthetic dyes

Dyeing was done using the laboratory type dyeing machine (Paramount digi i) by exhaustion method. The modified dye and the cotton fabric material to liquor were in 1:50 ratio and the dyeing was carried out for 60 min at 85°C and the pH adjusted to 8.5 using 0.1 M HCl and 0.1 M NaOH. The adjustment of the pH to a basic solution aided in the solubility of the dye. A leveling agent, sodium sulphate, was added to help in dyeing exhaustion as it reduces the negative charges on fibers allowing the dyes to penetrate the textiles evenly and effectively [20]. Dyeing was also performed with alum, copper sulphate ,nickel and ferrous which acted as mordants, employing, pre-, post and simultaneous treatments of the cotton fabric. In the pre-treatment the cotton fabric was first soaked in aqueous solution of the mordants for 20 mins and then thoroughly rinsed with water prior to the dyeing process.For simultaneous dyeing,the cotton fabric was introduced to the dyebath containing vilagin and the mordant. In post mordanting, the cotton fabric was first dyed and then treated with the mordant thereafter [21]. Embelin and vilangin were used in dyeing cotton fabric without mordanting process. The cotton fabric underwent wetting with non-ionic detergent for 30 minutes before the dyeing began. This was done in order to allow a smother surface for dyeability following the protocol reported in literature [22]. After dyeing, the dye bath was allowed to cool then the dyed samples were removed and washed with cold water to remove the dyestuff that was unfixed. Non-ionic soapy solution was added to dyed cotton fabrics followed by washing with water and then airdrying [23]. The dyed cotton fabrics were then evaluated for color fastness properties.

# **Color Fastness Testing**

The dyed cotton fabrics were tested for wash, rubbing (dry and wet) and light fastness properties. The wash fastness test was carried out in a laboratory type machine for wet and dyeing processes and the procedure used was according to ISO 105-C02:1989, ISO 105 A02:1993, ISO 105-X12:2000 where the dyed cotton fabric is attached to blank cotton fabric and mechanically agitated in given time and temperature conditions,washed with soap and rinsed with water and dried,the change of colour of dyed faric relative to attached undyed fabric are assessed with the Grey scale. The Greyscale is used to evaluate the color fastness in the grading between one and five where five is the excellent grade [24].

# **Evaluation of color strength**

Color strength measurement of cotton fabric was done by employing SpectroFlash X-rite SP62 spectrophotometer using D65 [25]. The dyed cotton fabric was evaluated for their L\*, a\*, b\*, C\*,  $h^0$  values as per the CIELAB colour scale. L\* indicates luminosity or lightness, a\* is the

redness/greenness, and  $b^*$  is the yellowness/blueness coordinate,  $C^*$ ,  $h^0$  represents the chroma and hue angle respectively. The blank fabric was the undyed cotton fabric. The (K/S) ratio were determined using the Kubelka–Munk equation as shown in equation 1

 $\frac{K}{S} = \frac{(1 - 0.01R)^2}{2(0.01R)}$  (Equation 1)

Where (K) is given as respective absorption coefficient, scattering coefficient(S) and (R) is the minimum reflectance of complete capacity [26].

## **RESULTS AND DISCUSSION**

## Yield of embelin and the semi-synthetic dye and their characteristics

Embelin was isolated from the acetone extract of the berries of *Embelia schimperi*. The yield and melting point values, Table 1, shows embelin yield was at 40 % and the yield of Vilangin was at 47 %.

Source	% Yield	Melting point					
Embelin	40	142-145					
Embelin standard	-	140-144					
Vilangin	47	264-265					

#### Table 1: Physical properties of embelin and vilangin

Studies done by Shrrimali revealed the melting point of embelin isolated from the fruits of *Embelia ribes* to be in the range 142-144 °C [27] and the study by Kaur revealed melting point in the range of 142-145°C [28]. The values in literature agrees with the melting point of embelin isolated in this study ,which is in the range of 142-145°C.

## Characterization of embelin

The embelin crystals obtained were subjected to various tests characterization tests to establish their structural identity.

## UV/Visible spectroscopy

Ultra-Violet spectroscopic analysis of the isolated embelin was carried at a scanning frequency of 200-650 nm .Figure 1 shows the UV-visible spectrum of embelin and vilangin, Embelin exhibits an intense absorption band observed at 292 nm, the same is replicated by the embelin standard which revealed an intense peak at 292 nm, this transitions are due to  $\pi \rightarrow \pi *$  as previously reported by Ondee et al., [29]. The vilagin showed a similar absorption band at 292 nm and another weak band at 417 nm this was due to  $n \rightarrow \pi *$  transition . Upon formation of vilangin ,bathochromic shifts occur as a result of extended conjugation system [30].

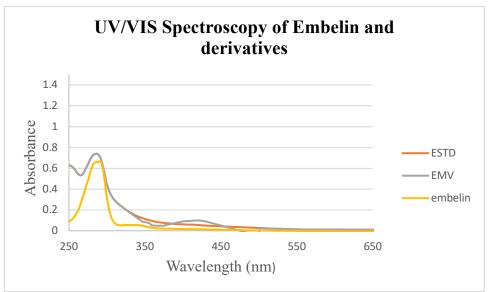


Figure 1: UV-Vis spectra of isolated embelin, embelin standard (ESTD) and Vilangin (EMV)

## **FTIR Characterization**

Embelin was subjected to Fourier Transform Infra-Red (FTIR) spectroscopy studies at a scanning frequency of 4000 cm<sup>-1</sup> and 500 cm<sup>-1</sup>, the spectra, Figure 2 (a), shows an intense absorption peak at 3301.84 cm<sup>-1</sup>, this is due to the –OH group, absorption at 2918.78 cm<sup>-1</sup> and 2851.01 cm<sup>-1</sup> is due to the C-H stretch. A peak at 1610.49 cm<sup>-1</sup> is due to C=O, whereas the absorptions at 1324.67 cm<sup>-1</sup> and 1188.13 cm<sup>-1</sup>were due to-C-O stretch of the alcohol groups. Similar results were observed in the embelin isolated from Embelia ribes [31]. FTIR Studies done by Badamaranahalli on embelin isolated from *embelia ribes* revealed an intense absorption peak at 3304 cm<sup>-1</sup> which was characteristic of -OH group and similar results for embelin isolated in this study, respectively[32].

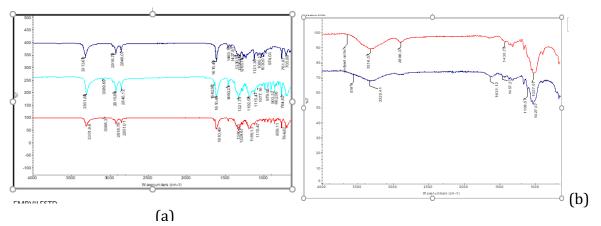


Figure 2: FTIR of embelin, embelin standard and Vilangin (b) Vilangin dyed cotton fabric

FTIR of vilangin, shows an intense absorption peak at 3313.63 cm<sup>-1</sup> which is due to -OH group, the other peaks shows, C-H stretch in the range of 2918.78–2848.07 cm<sup>-1</sup>, the peak at 1610.49 cm<sup>-1</sup> is due to C=O stretch (quinine carbonyl) and are similar with that of embelin . An absorption peak is observed at 1427 cm<sup>-1</sup>which is due to intensity of -C-O-H stretch, the

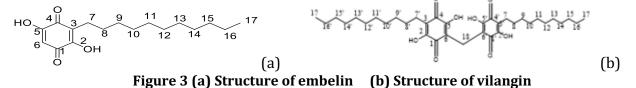
wavenumbers of -O-H group are further shifted left thus confirming formation of vilangin. Other characteristic peaks observed are similar to peaks in embelin. This results are consistent with similar results by Balachandran et al. [33]. FTIR of dyed cotton fabric Figure 2 (b),revealed a formation of a new peak at 1109.57 cm<sup>-1</sup>, this is due to possibly an interaction of the dye and cellulose polymer of cotton fabric.

## LC/MS Spectra

LC–ESI/MS analysis of embelin was carried out in order to confirm the structural identity .This was done in the negative mode and comparisons done with the analysis of embelin standard and values available in literature. The mass spectrum of embelin compound gave a pseudo molecular ion at m/z = 292.9 ([M-H]<sup>-</sup>), indicating a molecular formula of C<sub>17</sub>H<sub>26</sub>O<sub>4</sub> (calcd. 293.175285 [M-H]<sup>-</sup>). Analysis of vilangin showed that a product was formed with a measured pseudo molecular ion at m/z of 599.4 ([M - 1]<sup>-</sup>), in the negative mode consistent with the calculated molecular weight of 600.9. This corresponds to an addition of one embelin which was bridged by a methylene group to the starting material(embelin).

## **NMR Spectroscopy**

The embelin compound showed five signals in the <sup>1</sup>H NMR spectrum,a  $\delta$  0.8476 (3H,H17),  $\delta$  1.2450 ppm (18 H, 8H-16 H) corresponding to methylene groups of the side chain alkyl group ,  $\delta$  2.2780 ppm (2 H,H 7),  $\delta$  5.7878 ppm (1H,H 6) and  $\delta$  11.0326 ppm (2–0-H, H 2,H 5). Carbon -13 NMR for isolated embelin showed a C-3 peak at  $\delta$  118.0381 ppm,  $\delta$  104.4487 (C-6) quartenary carbon bearing the bridging carbon holding a methylene and a proton, C-15 at  $\delta$  40.1361 ppm, C-9-C-14 at  $\delta$  31.9193-22.7543 ppm and C-17  $\delta$  14.6955 ppm.



The <sup>1</sup>H NMR spectra of vilagin compound showed six resonance signals on formation of vilagin, the  $\delta$  5.7878 ppm signal observed in embelin was absent. This suggests that vilangin was formed by a reaction at C-6 ,revealing that the quinonoid ring was fully substituted. The spectrum also contained a peak at  $\delta$  2.5164 ppm (2H, s, *J*--Hz, H<sup>18</sup>) which is probably from the newly formed methylene protons in the vilangin compound. This has substituted the quinonoid proton in the embelin suggesting the formation of vilangin, These results are similar to those of Bouzeko et al. (2019) [34]. Other protons were observed at  $\delta$  10.6665 ppm (-O-H),  $\delta$  1.2450-1.3377 ppm (36 H),  $\delta$  0.8609 ppm (t,3H). The <sup>13</sup>C NMR showed a peak at  $\delta$  116.5014 ppm (C-6),which corresponds to a quartenary carbon bearing the bridging carbon holding a methylene proton .The carbon signals  $\delta$  104.4487 (C-6) observed in the embelin compound has disappeared confirming formation of Vilangin. This NMR data confirm the presence of two alkyldihydroxy-1, 4- benzoquinones formed as vilagin. The rest of the carbon signals are not observed as a result of fluxional effect characteristic of 2,5-dihydroxy-undecyl-benzoquinone compounds [35].

# Mordanting

Mordanting was done to increase the number of shades in the cotton vilagin dyed fabrics. The structure of ilangin present different functional groups present. The groups are in a position close enough to allow formation of a chelate complex. The Alum  $(Al_2K_2(SO_4)_4.24H_2O)$ mordanted cotton fabrics showed, light yellow shades in all the pre-,post and simultaneous mordanting. From Table 2 the value a\* are negative and the values of b\* , are positive this clearly displays a clear shift to yellowness according to CIELAB protocols and explains the yellowish colour achieved experimentally. The Iron (FeSO<sub>4</sub>.7H<sub>2</sub>O), mordants exhibits significant variations. The a\* for pre-mordanted cotton fabric is -1.13 and+14.74 for b\*. For post mordanted cotton fabric ,the a\* value is + 0.11 and+21,53 for b\* and for simultaneous mordanted cotton fabric ,the a\* value is + 1.54 and+ 30.24 for b\*. This shifts the shades to redness-yellowness, explaining formation of darker shades [36]. The copper mordanted copper fabrics for pre, simultaneous and post mordanting exhibits negative -a\* values and positive b\*, this places the dyed cotton fabrics in the green –yellow colour space. The same case applies to nickel mordanted cotton fabrics, they fall in the green –yellow colour space with lighter shades. The variability in mordants results in formation of different shades of colours [24].

# Colour strength analysis of embelin and Vilangin

Vilangin dyed cotton fabric ,reflectance capacity were measured and K/S values calculated from Kubelka–Munk equation .K/S of vilangin dyed fabric are shown in Table 2. Highest K/S values were measured in the ferrous mordanted cotton fabrics.

Table 2: Colour strength and shades of modified dye cotton fabrics									
Method	Morda nt	Ľ*	a*	b*	$\Delta E$	C*	Н°	K/ S	Shades
Embelin	NO	77.4	-	+18.3	12.6	18.4	7.68	0.1	
			2.47	0	6	7		8	
Vilangin	NO	77.8	-	+19.0	12.9	19.2	8.05	0.1	
-			2.69	2	9	1		9	
	Ferrous	79.9	-	+14.7	16.9	14.7	4.38	0.2	
Pre- mordanti ng			1.13	4	3	8		3	
	Copper	80.6	-	+13.0	15.4	13.2	10.3	0.1	
		2	2.38	2	7	4	5	9	
	Alum	80.1	-	+12.6	19.0	12.7	6.00	0.2	
		8	1.33	5	0	2		0	
	Nickel	80.2	-	+14.7	17.0	14.8	5.96	0.2	
		3	1.54	5	0	3		3	
POST	Ferrous	77.2	+0.1	+21.5	23.6	21.5	5.11	0.3	
		4	1	3	2	3		2	
	Copper	79.2	-	+17.4	19.6	17.5	4.45	0.2	
		3	1.36	8	3	3		6	~
	Nickel	80.2	-	+12.2	14.7	12.5	12.6	0.1	
		2	2.73	2	2	2		9	
	Alum	80.9	-	+12.1	14.5	12.2	7.63	0.2	and the second
		9	1.63	6	8	7		0	
SIMULT	Nickel	79.2	-	+18.3	20.4	13.3	0.19	0.2	
		2	0.06	8	9	8		7	
	Ferrous	75.2	+1.5	+30.2	32.4	30.2	2.92	0.5	
		3	4	4	7	8		2	
	Copper	78.3	-	+25.3	27.5	25.4	6.06	0.3	
		0	2.69	3	5	7		4	
	Alum	79.5	-	+17.5	19.6	17.5	4.60	0.2	
		6	1.41	1	7	7		8	

 Table 2: Colour strength and shades of modified dye cotton fabrics

The low colour strengths (K/S) values of pre- and post-mordanted cotton fabric dyed with vilangin dye, through pre- and post-mordanting methods showed significant variation in color strength this may be attributed to the fact of weak interactions between mordants and functional groups of dye molecules and cotton fabric [21]. This could be due to structural relationship between embelin and vilangin and the rate of diffusion of the dye to the molecule is almost similar under the given dyeing conditions. However vilangin has more water soluble groups and the interactions between dye-dye,dye-fibre and dye-Na+ ,observed that the main interactions in a dye molecule is as a result of  $\pi \rightarrow \pi *$  stacking interactions [37].

## Colour fastness properties of dyed cotton

The colour fastness properties were done according to ISO 105-C02:1989, ISO 105 A02:1993, ISO 105-X12:2000. The results obtained for washing, rubbing and light fastness are summarised in Table 3. The results shows excellent fastness properties for the vilangin dyes compared to embelin dye. The fastness tests suggests that vilangin dyes have good dyeability

for cotton fabrics. The colour fastness is improved by use of mordants , this may be due to formation of coordinate bonds which promotes the wash, rubbing and light fastness [38].

		Wash fastness		Rubbing fastness		
Method	Mordant	C.C	C.S	Dry	Wet	Light
				-		fastness
Vilangin	Without	2-3	2	3	3	4
Embelin	Without	2-3	2	2	2	1
Simultaneous	Alum	3-4	3	4	4	4
Mordanting	Copper	3	4	5	4	4
	Ferrous	4	4	5	4	5
	Nickel	3	3	4	4	4
Pre-	Alum	3	3	4	4	4
mordanting	Copper	3	3	4	4	4
	Ferrous	4	3-4	3	4	4
	Nickel	3	3-	3	3	4
Post-	Alum	4	4	3-4	4	5
mordanting	Copper	4	4	4	4	4
	Ferrous	5	4	4	4	5
	Nickel	4	4	4	4	5

Table 3. Colour fastness of the dyed fabric using different methods of mordanting

## C-C-Colour change, Colour stain. 1-Poor; 2-Fairly good 3- Good,4-Very good,5-Excellent

#### CONCLUSION

Chemical modification of embelin was successfully done by reaction of embelin with formaldehyde in acetic acid to obtain a semi-synthetic dye with appreciable yield for commercial exploitation. The modified dye was applied to cotton fabric with appreciable colour strengths and shades with excellent overall fastness properties compared to the embelin dye. The melting point of the modified dye and its characterization done using UV–Visible and FTIR spectroscopy ,LC-ESI/MS and NMR spectroscopy show that the obtained modified dye is a fairly pure compound which could be used in dyeing of textiles. Thus it can be concluded that modification of natural dye can be used to overcome the inherent limitations of natural dyes such as lack of reproducibility and inferior fastness properties for the bulk scale application.

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