Chromatographic and colorimetric characterizations of brominated indigoid dyeings

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ABSTRACT

The major indigoids constituting modern and archaeological purple pigments produced from molluskan species include, in varying compositions, indigo, 6-bromoindigo, and 6,6'-dibromoindigo. Though woolen Tyrian Purple dyeings produced from these pigments were the most prized and precious of all dyeings in antiquity, a full chromatographic and colorimetric analysis of multi-fibered textiles dyed with these indigoids has not been previously performed. This current study reports on high-performance liquid chromatographic (HPLC) analyses conducted on the indigoid pigments and on woolen dyeings individually produced from them. In addition, comparative colorimetric analyses via reflectance spectrophotometry were performed on standard multifiber fabric swatches, each consisting of 13 different synthetic and natural fibrous materials. Each swatch was dyed with one of the cited indigoids. These colorimetric properties included the Kubelka-Munk spectral curves, color strengths at the wavelengths of maximum absorptions, color coordinates of the CIE L*a*b* and L*C*h* color spaces, and the color differences. Excellent functional correlations were observed among these properties and these relationships should be applicable to similar dyeings on other fabric materials. The results show that filament triacetate and nylon-66 possess the most remarkable color strengths of all the fiber materials investigated in all the dyeings, and of the natural fibers studied, wool possessed the highest color strength and cotton the poorest with all three dyes. Such chromatographic and colorimetric analyses would further our understanding of the colors produced from ancient, and modern, purple-dyed textiles.

1. Introduction

Purple and violet brominated indigoid pigments are exclusively produced in nature from the colorless precursors extracted from the hypobranchial glandular fluids of certain mollusks. These colorants are spontaneously formed via complex biochemical pathways involving enzymatic hydrolysis followed by photochemical and oxidative reactions when these chromogens are exposed to air and light [1]. The ancients of the Near East, especially the inhabitants along the Mediterranean basin, utilized these pigments to produce majestic woolen dyeings historically known as Royal Purple, Imperial Purple, or Tyrian Purple, for sovereigns, high officials, and military generals. Red-purple Argaman and blue-purple Tekhelet woolen dyeings were also mentioned in the Bible for textile furnishings in the First and Second Temples in Jerusalem as well as for the ritual vestments of the High Priest.

The chemical constitution of the raw purple and violet pigments produced from purple-producing sea snails has been studied chromatographically and spectrometrically [1–7]. The malaco-logical pigments consist of brominated and un-brominated colorants, which can include isatinoids, indigoids, and indirubinoids [5]. The indigoids are the major dyes found in archaeological pigments and in pigments from the historically important Muricidae snail species inhabiting the waters of the Mediterranean, Hexaplex trunculus (also known as Murex trunculus), Bolinus brandaris and Stramonita haemastoma. The indigoid pigments produced from molluskan sources consist of, in varying quantities, indigo (C.I. Vat Blue 1, 73000) and abbreviated as IND, violet 6-bromoindigo (also known as monobromoindigo, MBI), and purple 6,6'-dibromoindigo (C.I. Natural Violet 1, 75800) denoted as DBI, whose molecular structures are shown in Fig. 1A. Thus, depending on the relative compositions of these dyes in the pigment, sea snails from this species can produce either reddish-purple or bluish-purple (i.e., violet) pigments, and consequently dyeings produced from them will also have these varying colors. Though the common denomi-nator of all purple-producing sea snails from all parts of the world is...
DBI, it is the presence of significant quantities of MBI in a pigment — modern or ancient — that attests to the malacological provenance of the pigment as the *H. trunculus* snail [5].

In antiquity, perhaps dating four millennia ago, purple and violet dyings from molluskan indigoidal pigments were produced in a reduction-oxidation process, chemically similar to dyings with indigo itself. Natural reduction of the colorants in the raw pigments to their soluble yellowish leuco ("whiter" or less-colored) forms was performed via a fermentation vat, which was actuated by the bacteria present in the snail with the animal’s flesh as their nutrient [8]. The textile was then introduced into the dye bath and subsequently removed so that the reduced indigoid in the woolen fleece would be air-oxidized back to its original insoluble pigment. This reduction-oxidation dyeing procedure associated with the three indigos is summarized in Fig. 1 [9]. Etters [10] estimated the pKₐ’s of the leuco-indigos from the literature data for pK₁ and pK₂ found for the related tetra-, tri-, di-, and mono-sulphonic acid forms of indigo species as 7.97 (±0.78) and 12.68 (±0.45), respectively. Similarly, Baig [11,12] found that the unionized leuco indigo converts to the mono-anion between pH values of 5.5–11. Thus, since in the current study the pH of the vat is reduced to a lower alkaline value before dyeing the fabric, the species adsorbed on the fabric are most likely the neutral leuco-indigoid molecule as well as the mono-anion. The general overall chemistry is identical to the classical method of indigo vat dyeing via the alkaline dithionite (also known as hydrosulphite) method dating from the early 1900’s [13], which was soon after the commercial production of synthetic indigo. This dithionite vatting method has also been used for dyeing wool with brominated indigoids [3,14,15].

The oldest molluskan purple dyeing yet found was reported to be from about the middle of the 2nd millennium BCE from a royal palace of ancient Qatna, Syria [16]. Purple-dyed textiles were discovered at the Siberian desert site of Pazyryk and dates from about the 4th century BCE [17,18], and from later eras a number of 2000-year old Roman Period purple-dyed textiles have also been reported [19–22] as well as a 3rd — 5th century CE purple-dyed Coptic textile [23,24]. A beautiful example of an archaeological Royal Purple dyeing is from a late 1st century BCE fragment (see Fig. 2) reportedly from the mantle or cloak belonging to King Herod the Great of ancient Israel, which was found atop the palatial fortress at Masada in the Judean Desert [19,20,25]. Residual pigments from Phoenician dye vats along the Eastern Mediterranean have also been found, as for example, at 13th century BCE Sarepta (present day Lebanon) [26,27] and at 7th century BCE Tel Kabri in northern Israel [9]. The use of the molluskan purple pigment as a paint pigment, and not as a textile dye, is rare but three important examples were found. These include the oldest example of purple on Late Bronze Age (17th century BCE) Minoan wall paintings at Akrotiri in Thera (Santorini), Greece [28–30]; a purple paint pigment on a 5th century BCE King Darius the Great marble jar [5]; and a brown paint pigment from a 12th century CE church in France [31].

There has been considerable recent interest in indigoidal and related components as is evident from the literature, especially in this journal [32–37]. Further, in modern times, brominated indigoid pigments have been used to dye wool by means of the alkaline-dithionite reduction vat, though on a very limited scale. These include dyeings with a modern *H. trunculus* pigment [14], with synthetic DBI [3,15,38], and with synthetic MBI [3]. Natural purple dyeings were also performed using *H. trunculus* pigments via a natural fermentative reduction vat [8,39,40].

Previously, some colorimetric properties of purple dyeings were determined for wool that was dyed naturally with the molluskan...
pigment [8] as well as with synthetic DBI [3,15,38] and with MBI [3]. A similar analysis was also performed on a limited number of synthetic textiles dyed with DBI [38]. In addition, direct dyeing and vat dyeing using the pigment (mainly DBI) from the Ocenebra inornata sea snail has been published [41]. However, a full comparative chromatographic and colorimetric investigation of all three indigoid dyeings on natural and synthetic textiles has not been performed prior to this study. This article reports on the results of the dye-purity analyses performed via high-performance liquid chromatography (HPLC) on the three raw indigoid pigments and compares them with those performed on the woolen dyeings produced from them. Further, colorimetric analyses were performed on standard multifiber fabric swatches individually dyed with an indigoid. The determined properties include the Kubelka-Munk $K/S$ spectral curves, the color strengths at the wavelengths of maximum absorptions, $\lambda_{\text{max}}$, the coordinates of the CIE 1976 $L^*a^*b^*$ and $L^*C^*h^*$ color spaces, and the color differences within each indigoid set. Comparative analyses and functional correlations among these properties were performed.

2. Materials and methods

2.1. Chemicals and materials

For the dye extractions, HPLC-grade (99.9%) dimethyl sulfoxide (DMSO) from Aldrich (Milwaukee, WI, USA) was used. The mobile phase solvents, methanol and water, were HPLC-grade and acquired from J. T. Baker (USA). The dyes analyzed were IND from Aldrich (USA) with a reported 95% purity, and of the brominated indigoids, MBI was obtained from K. Ramig and O. Lavinda (Baruch College, NY, USA) and DBI from S. Karimi (Queens College, NY, USA), who synthesized them according to previously published procedures for MBI [3,42] and for DBI [33,43]. The multifiber fabric (labeled as "Warp Stripe 13 Fiber Fabric, Style #43"), consisting of the 13 fiber materials listed in Table 1, was obtained from Testfabrics (Pittston, PA, USA).

2.2. Dyeings

Each multifiber Testfabric swatch was individually dyed with one of the three indigoids (IND, MBI, and DBI) according to the previously published alkaline-dithionite vatting method [3], and obtained from K. Ramig and O. Lavinda.

2.3. Chromatographic system

A Waters High-Performance Liquid Chromatography (HPLC) system was used for the reverse-phase chromatographic analyses, which included a 600E Controller and 996 Photodiode array (PDA) detector. Two Waters 3.0 x 150 mm stationary phase C-18 columns were utilized in this study: XBridge 3.5 μm particle size (Part No. 186003028) and Symmetry 5 μm particles (Part No. WAT054200). The linear gradient elution method consisted of a binary methanol/water mobile phase with a constant flow rate of 0.6 mL/min according to the following times and increasing methanol percentages:

- 0 min, 20%; 3 min, 70%; 6 min, 70%; 20 min, 84%; 30 min, 100%.

2.4. Dye extraction and filtration

For the chromatographic analyses, a micro-sample from each raw pigment (~50 μg) and from each dyed textile (~5 mg) was placed in a 2-mL glass vial with 400 μL of DMSO and placed in a dry block heater set at 150 °C for 5 min. The residual textile and pigment samples were then re-extracted with a fresh sample of DMSO and combined with the first extraction. The hot solution was immediately placed in a micro-centrifuge tube filter assembly consisting of a polypropylene body and a 0.45-μm nylon filter membrane (Grace Davison Discovery Science, Catalog No. 24139) and centrifuged for a few minutes. This filtered dye solution was then immediately injected into the 20-μL sample loop of the HPLC. All these steps were performed under subdued light.

2.5. Colorimetric reflectance spectrophotometer

For the determination of the spectral curves as well as of the CIE $L^*a^*b^*$ and $L^*C^*h^*$ color spaces, a portable Datacolor Check II Plus Reflectance Spectrophotometer was used with a pulsed Xe light source and an Extra-Ultra Small Area View (XUSAV) aperture size consisting of a 3.0 mm illuminated diameter with data measured from a reflected 2.5 mm diameter. Data was collected from 400 to 700 nm at 10 nm intervals for the standard D65 daylight illuminant and 10° observer angle with specular reflectance included. Each dyed textile material was measured at least at 6 locations on that fabric and the results were averaged and showed good uniformity.

<table>
<thead>
<tr>
<th>Dyeing</th>
<th>Fabric</th>
<th>No.</th>
<th>Material Abbrev.</th>
<th>IND</th>
<th>MBI</th>
<th>DBI</th>
</tr>
</thead>
<tbody>
<tr>
<td>IND</td>
<td>MBI</td>
<td>DBI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Filament Acetate (Diacetate)</td>
<td>1-FA</td>
<td>612</td>
<td>600</td>
<td>527</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 SEF (Modacrylic)</td>
<td>2-SE</td>
<td>625</td>
<td>600</td>
<td>536</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Filament Triacetate</td>
<td>3-FT</td>
<td>607</td>
<td>591</td>
<td>597</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Cotton, bleached</td>
<td>4-C</td>
<td>656</td>
<td>627</td>
<td>533</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Creslan 61 (Acrylic)</td>
<td>5-C6</td>
<td>655</td>
<td>625</td>
<td>525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Dacron 54 (Polyester)</td>
<td>6-DS</td>
<td>620</td>
<td>604</td>
<td>598</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 Dacron 64 (Polyester)</td>
<td>7-D6</td>
<td>612</td>
<td>606</td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 Nylon 66 (Polyamide)</td>
<td>8-N6</td>
<td>617</td>
<td>609</td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 Orlon 75 (Acrylic)</td>
<td>9-O7</td>
<td>655</td>
<td>625</td>
<td>530</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Silk, spun</td>
<td>10-S</td>
<td>627</td>
<td>590</td>
<td>532</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 Polypropylene (Polyolefin)</td>
<td>11-PP</td>
<td>655</td>
<td>324</td>
<td>527</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 Rayon (Viscose)</td>
<td>12-RV</td>
<td>657</td>
<td>625</td>
<td>524</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 Wool, worsted</td>
<td>13-W</td>
<td>655</td>
<td>533</td>
<td>527</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Dyeings

Optimal dyeing conditions, which include temperature-time gradients and concentrations, generally vary from one fiber material to another. However, the dyeing method used for the current study was the one that has been optimized for wool as this proteinic fiber was historically dyed with the purple molluskan pigment. Additionally, the dyeing procedure utilizes mild temperatures as thermal debromination of the indigoidal pigment can occur. In order to eliminate any possible photo-debromination of the dissolved leuco-MBI or -DBI, a well-known phenomenon \([1,8,38,44\text{--}47]\), the entire reduction-oxidation dyeing procedure was performed under subdued light conditions.

The three sets of indigoid dyeings are shown in Table 1, which also shows the respective wavelength at maximum light absorption, \(\lambda_{\text{max}}\), for each dyed fabric material, as described in Section 3.3.1 below.

3.2. Chromatographic analyses

In order to be able to ascribe the color determined from a colorimetric analysis of a dyeing to that produced from a single dye, it was necessary to first determine the purity of the raw pigment that was used for that dyeing. Subsequent to that, the dye was extracted from each woolen dyeing and chromatographed in order to determine whether the original purity of the dye was maintained throughout the dyeing process, as the indigoid dyes can undergo degradation, as mentioned in Section 3.1 above.

The chromatograms obtained from the HPLC method for the DMSO-extracted solutions of each of the three raw pigments (IND, MBI, and DBI) and of the corresponding dyeings produced from them are shown in Figs. 3\text{--}5. In order to detect all the possible colorants present in each sample, the relevant visible wavelengths from 400 to 700 nm were scanned. Each chromatogram is shown at 5 different wavelengths (400, 450, 500, 540, and 600 nm), with the major component peak increasing with increasing wavelength. The 540 nm value was chosen as dissolved indirubinoids absorb near that value, and 600 nm is the wavelength at which all the indigoidal solutions exhibit strong absorptions [5].

From even a visual inspection of these chromatograms it can be seen that the major dye in each sample is relatively pure, with the minor components showing only small peaks. The composition and purity of each dye is related to the relative integrated area of that dye’s peak, and was calculated at a standard wavelength of 288 nm. At this wavelength, all the major and minor colorants that may be present in the dyeing can be detected.

Fig. 3. HPLC chromatograms of DMSO-solutions at increasing wavelengths (and peak heights) of 400, 450, 500, 540, and 600 nm of IND in (A) the raw pigment using XBridge column, and in (B) the woolen dyeing using Symmetry column.
present have significant absorptions and this wavelength was also previously used in other HPLC studies of these components [5,48]. The peak area of each indigoid relative to the total peak areas of all the detected colorants, expressed as a percentage, is given in Table 2. The table shows the peak area of each major dye, both as a pigment before the dyeing and as a dye after the dyeing. In the MBI sample, the two main impurities were, as expected, DBI (5.0%) and IND (2.0%) in the raw pigment, and these were also present in the dyeing at 3.8% and 6.1%, respectively. From the table it is apparent that indigo is virtually unaffected by the dyeing and maintains its high purity. Although MBI and DBI undergo some decomposition, nevertheless, they are still at very high levels in their respective dyeings. Thus, all the subsequent colorimetric properties of all the dyed fabrics can be ascribed to a single dye on that material.

3.3. Colorimetric analyses

3.3.1. Kubelka-Munk spectral curves

The percent reflectance (\%R) values determined spectrophotometrically were transformed into the Kubelka-Munk \(K/S\) values according to

\[
K/S = (1 - R)^2 / 2R
\]

where \(K\) and \(S\) are the Absorption and Scattering Coefficients, respectively, and \(R\) is expressed as a fraction [49–51]. These transformed spectral curves produce absorption-type data and are shown in Fig. 6. The maximum \(K/S\) value at the corresponding wavelength \(\lambda_{\text{max}}\) is known as the color strength at a single wavelength (SWL) of a dyeing [52], and, among other factors, is related to the composition of the dye on the textile.

The values for the wavelengths at maximum absorptions evaluated from Fig. 6 are given in Table 1. These values are not to be taken as the sole indicators of the observed color as the spectral curves show that there is significant shouldering in the curves for a considerable number of fabric materials. This is true for fabrics dyed with DBI (Fig. 6C) and in the curves for MBI dyeings (Fig. 6B), and to a lesser degree also with IND (Fig. 6A). This is due to the complex colorimetric nature of the brominated dyes as they exhibit both red and blue components, as described in section 3.3.2 below.

From Fig. 6, the highest \(K/S\) value for IND-dyeings is observed for nylon-66 (abbreviated as 8-N6) at 617 nm. In MBI dyeings, the color strength of nylon at 609 nm is again nearly the highest, only to be minimally surpassed by that of filament triacetate (3-FT) at 591 nm, and triacetate also has the highest \(K/S\) value at 597 nm of all the DBI dyeings.

Fig. 4. HPLC chromatograms of DMSO-solutions at increasing wavelengths (and peak heights) of 400, 450, 500, 540, and 600 nm of MBI in (A) the raw pigment using Symmetry column, and in (B) the woolen dyeing using XBridge column.
Wool had the greatest color strength of all the natural fibers investigated in all three indigoid dyeings. The color strengths of the woolen dyeings of this study can be compared with those measurements that have been previously performed on related dyeings. A colorimetric measurement on a red-purple wool naturally dyed via fermentative reduction with the pigment from the *H. trunculus* sea snail, which consists of a number of colorants [5], shows that the $\lambda_{\text{max}}$ value in the naturally dyed wool was approximately 530 nm (see Fig. 15.2 of reference [8]). From Table 1, it can be seen that the spectral curves for wool dyed solely with DBI (Fig. 6C) or only with MBI (Fig. 6B) have $\lambda_{\text{max}}$ values of 527 and 533 nm, respectively, which are nearly identical with the value for the naturally dyed wool. The shape of the spectral curve for the naturally dyed wool exhibits a prominent right-shoulder between 600–650 nm. A comparison of that profile with that of the three indigoids of this current study shows that the naturally dyed wool closely resembles that of an MBI dyeing, which indicates that the naturally dyed wool has a significant quantity of MBI.

Another study reported on the spectral absorption curves for wool samples that were individually dyed with each of the three indigoids (Fig. 3 of reference [3]). Those $\lambda_{\text{max}}$ values are in agreement with the ones of this current study. The main difference is in the shape of the spectrum of DBI-dyed wool, in which the previous study shows it with the prominent right-shoulder, a feature that is missing in the DBI-dyed wool of the current study. In the present work, this shoulder was present in wool dyed only with MBI. Hence, this disparity in the spectral curves of DBI dyeings from both studies may be due to the possible partial photo-debromination of the DBI to MBI that may have occurred during the dyeing process in the other study.

### 3.3.2. Blue and green-to-red values

In the CIE 1976 $L^*a^*b^*$ color space [53], $L^*$ represents the lightness of the dyeing, and the $a^*$ coordinate ranges from green ($-a^*$) to red ($+a^*$), whereas the $b^*$ component ranges from blue ($-b^*$) to yellow ($+b^*$). The $L^*$ values for the naturally dyed wool in this study are in the range of 98.8–99.7, indicating a very light dyeing. The $a^*$ and $b^*$ values are also very close to zero, indicating a nearly neutral coloration. The HPLC chromatograms of DMSO-solutions at increasing wavelengths (and peak heights) of 400, 450, 500, 540, and 600 nm of DBI in (A) the raw pigment using XBridge column, and in (B) the woolen dyeing using Symmetry column.

![HPLC chromatograms of DMSO-solutions at increasing wavelengths (and peak heights) of 400, 450, 500, 540, and 600 nm of DBI in (A) the raw pigment using XBridge column, and in (B) the woolen dyeing using Symmetry column.](image)

**Table 2**

<table>
<thead>
<tr>
<th>Dye</th>
<th>$t_R$ (min)</th>
<th>Pigment</th>
<th>Dyeing</th>
</tr>
</thead>
<tbody>
<tr>
<td>IND</td>
<td>13.50</td>
<td>99.7</td>
<td>98.8</td>
</tr>
<tr>
<td>MBI</td>
<td>17.37</td>
<td>92.5</td>
<td>87.6</td>
</tr>
<tr>
<td>DBI</td>
<td>21.92</td>
<td>97.6</td>
<td>86.8</td>
</tr>
</tbody>
</table>

In the CIE 1976 $L^*a^*b^*$ color space [53], $L^*$ represents the lightness of the dyeing, and the $a^*$ coordinate ranges from green ($-a^*$) to red ($+a^*$), whereas the $b^*$ component ranges from blue ($-b^*$) to yellow ($+b^*$).
yellow (\(+b^*\)). (For simplicity, these properties will henceforth be denoted without the asterisks.) The blue and red characters of the observed colors of all the dyeings are shown in Fig. 7. In general, for all the dyeings, the red component increases with the degree of bromination. None of the dyeings exhibited a yellow component. In addition to the obvious blue component of IND dyeings (Fig. 7A), only a green value is present in all these dyeings. With few exceptions, the relatively low green value is fairly constant in these dyeings, and thus, the relatively high blue values produce absorptions above 600 nm, with wavelength values of 632 \(\pm 25\) nm (see Table 1). For MBI dyeings (Fig. 7B), the blue character \((-b)\) is also considerably greater than its absolute \(a\) value, with some dyeings showing a green character and others red. For DBI dyeings (Fig. 7C), the pattern of blue-to-red ratio is more complex, with many dyed fabrics exhibiting approximately equal values. In these DBI dyeings, the fiber with the redest component is wool (13-W), and the fabric with the greatest blueness is filament triacetate (3-FT), which produces the highest \(K/S\) value as seen in Fig. 6C. The color strengths found in the spectral curves of Fig. 6 can be understood in light of the relative blue and red characteristics of the colors depicted in Fig. 7. In IND dyeings, the fabric with the highest \(K/S\) value was nylon-66 (8-N6), with a very large blue character. For DBI dyeings, the greatest color strength was exhibited by filament triacetate (3-FT), which had the bluest character. For MBI dyeings, filament triacetate and nylon-66 had the highest, nearly identical,
color strengths, partially due to their nearly identical blue character, which were the highest of all such dyeings.

3.3.3. Wavelength groupings

The seemingly random wavelength values shown in Table 1 for MBI and DBI dyeings can be organized to show group clustering about certain regions according to their relative a and b color values. Fig. 7 shows that as far as the b coordinate is concerned, all the dyeings exhibit only a blue component (−b values), whereas some show green (−a) and others red (+a) character. Thus, the algebraic sum of a and b represents either the total negative sum of the green and blue components, or the difference between the red and blue values. Most of the values for a+b are negative, and thus the negative sum, −(a+b), is used in plotting it against the corresponding \( \lambda_{\text{max}} \) value.

Fig. 8 shows the plots of the comparative sums of a and b for MBI and DBI dyeings as a function of the corresponding observed wavelength at maximum absorption, \( \lambda_{\text{max}} \). For the MBI dyeings with relatively high absolute sums of a and b, all the wavelengths are clustered within a region centered at around 610 nm. Of these MBI dyeings, only one fabric, wool, which has a relatively lower absolute sum of a+b, exhibits a much lower wavelength of close to 530 nm. This wavelength for wool is indicative of an observed reddish-purple hue in its dyeing and is due to its relatively high red value (+a), which is about 3–4 times larger than the other closest values as seen from Fig. 7B. For DBI dyeings, a similar clustering pattern is again exhibited. For higher values of −(a+b), the wavelengths are grouped in a thin vertical oval strip centered at about 600 nm, whereas for lower values the wavelengths are clustered in a small elliptical region centered at about 530 nm.

The two regions for each set of dyeings are very similar. These two clustered groupings can be explained on the basis of the relative values of a and b. For higher values of −b, and thus for −(a+b), the observed color would be bluish with wavelengths from about 600 nm and higher. Dyeings exhibiting the lower wavelengths of about 530 nm possess a considerable observed reddish character, which is due to a relatively higher +a value and a lower algebraic value of −(a+b).

3.3.4. Color strengths vs. lightness

For all the dyeings, the color strength (K/S) is inversely related to its lightness (L), as both are indicative of the relative concentration of the dye in the fiber. Fig. 9 shows the plot of the maximum Kubelka-Munk K/S value for each dyed fabric as a function of its lightness (L) property. A simple exponential decay function can be

Fig. 8. Group clustering of the \( \lambda_{\text{max}} \) values for the indigoid dyeings: (A) MBI, (B) DBI.

Fig. 9. Color strength (K/S) as an exponential decay function of the lightness (L) for the indigoid dyeings: (A) IND, (B) MBI, (C) DBI.
employed for all the dyeings, which produces excellent correlation between these two properties. An even higher match exists between these two properties for relatively high $L$ values from about 50 and up for all three dyeing sets.

### 3.3.5. Color differences

The color difference between two dyeing samples, $\Delta E$, is defined as the Euclidean distance between these two sets of color coordinates, according to [54]:

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

For each set of dyeings with a particular indigoid, the color difference between the color of any fabric and the one with the highest $K/S$ value for that set was calculated and plotted in Fig. 10 as a function of the lightness ($L$). For IND dyeings, the fabric material with the highest $K/S$ value was nylon-66 (8-N6), whereas for both MBI and DBI dyeings, filament triacetate (3-FT) had the highest color strength. Though the color difference is dependent on all three coordinates, it can be seen from Fig. 10 that the dominant term is the lightness $L$. Excellent linear correlations between the color differences and the lightness values for all the dyeings were found. Hence, dyeings with low lightness values exhibit color values that are close to that displayed by the fabric with the highest color strength.

### 3.3.6. Chromas vs. blueness

The Chroma ($C$) value expresses the purity of the color and is dependent on both the $a$ and $b$ color coordinates as $C$ is the vector magnitude corresponding to the color point $(a,b)$ [46]:

$$C = \left( a^2 + b^2 \right)^{1/2}.$$

However, as can be seen from Fig. 7, the blueness values ($-b$) for IND and MBI are, in general, considerably greater than the corresponding $a$ values, though this is not the case with DBI dyeings, which show in many cases nearly identical absolute values for $a$ and $b$. Thus, for IND and MBI dyeings an excellent linear correlation exists between $C$ and $-b$ alone for these two sets of dyeings, as can be seen from Fig. 11, where $C$ is approximately equal to $-b$. For these dyeings the chroma increases linearly with increasing blueness.

### 4. Conclusions

This is the first time that a full comparative colorimetric analysis is reported on natural and synthetic textiles dyed with the three indigoids that are the most dominant in molluskan purple. Z.C. Koren / Dyes and Pigments 95 (2012) 491–501

![Fig. 10. Color difference, $\Delta E$, of a dyeing with respect to the fabric with the highest color strength in each indigoid set: (A) IND, (B) MBI, (C) DBI.](image)

![Fig. 11. Chroma ($C$) of a dyeing as a linear function of its blueness ($-b$): (A) IND, (B) MBI.](image)
pigments. The relative abundances of these colorants in the pigment will thus affect the colors of the dyings produced from these pigments.

This study found that four fabric materials—filmament tricetate, nylon-66, wool, and filament acetate—generally had the highest color strengths in all the indigoid dyeings. Of these fabric materials, filmament tricetate and nylon-66 showed the most remarkable color strengths in all the dyeings. Of the natural fibers investigated, wool had consistently the most noteworthy colorimetric properties.

Filmament tricetate had the greatest color strength in MB1 and DBl dyeings, and in IND its color strength was near to the highest. It had the bluest character in IND and DBl dyeings and nearly equal to that of nylon-66 in MB1 dyeings. The $\varepsilon_{\text{max}}$ value for tricetate was nearly constant in all three indigoid dyeings with values close to 600 nm.

Nylon-66 had the highest color strength in IND dyeings and was nearly equal to that of tricetate for the highest value in MB1 dyeings. In DBl dyeings, the color strength of nylon-66 was near the top.

Excellent functional correlations were made among the various colorimetric properties, which may predict similar properties for indigoid dyes on other fabrics. Such colorimetric analyses performance. Journal of the Society of Dyers and Colourists 1993;109:251–5.

The color strengths in all the indigoid dyeings. Of these fabric materials, filmament tricetate and nylon-66 showed the most remarkable color strengths in all the dyeings. Of the natural fibers investigated, wool had consistently the most noteworthy colorimetric properties.

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