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Thermal degradation of natural dyes and their analysis using HPLC-DAD-MS

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Abstract

Berberine, palmatine, alizarin, purpurin, indigotin, and indirubin which were the major coloring compounds of *Phellodendron* bark, madder, and indigo plant were thermally degraded in 100°C oven in liquid dye form and also in silk dyed with five of these pigments. A mixed dye solution of six coloring compounds was prepared in DMSO solution and was thermally degraded for up to 7 days. Silk were dyed using either a mixed dye solution of five dyes or individual dye solutions and each were degraded for 7 and 14 days, respectively, and the dye was extracted from the samples for the HPLC analysis. The concentration of coloring compounds in the degraded samples were analyzed by HPLC-DAD-MS and the color difference (ΔE) of the degraded silk was examined using a spectro-colorimeter. Alizarin and purpurin were more resistance to degradation than other coloring compounds both when in solution form and in silk dyeings. And such result was verified by the color difference measurement of the degraded silk dyed with individual dye solution. The resistance of alizarin and purpurin to thermal degradation was highly likely due to the fomation of fiber-metal-dye chelated complex by alum or iron mordanting before dyeing.

Keywords: *Berberine*; *Palmatine*; *Alizarin*; *Purpurin*; *Indigotin*; Thermal degradation; *HPLC-DAD-MS*; Color difference

Introduction

Color fading is one of the major problems in the conservation and preservation of museum textiles dyed with natural dyes. Fading is more severe if museum textiles were those recovered from archaeological burials. Fading of a textile color is due to the degradation of dye which results in different degrees of loss of intact dye molecules. The more the intact dye molecules survive, the more the original color will be preserved. Museum textiles which were recovered from burial excavations of Korea, in most cases, look tan in color with complete loss of original hue (Ahn et al., 2012; Ahn et al., 2014; Park, 1996). It is highly probable that the tan color of these textiles were due to the loss of a great amount of dye molecules while the textiles were in burial and also after they were excavated. In order to provide complete documentation of exhumed textiles and to make proper cultural inference from them, it is necessary to examine the fading behavior of natural dyes with which these textiles were colored.

With this background, the purpose of this research was to investigate the degradation behaviors of the major coloring compounds of three different natural dye plants by thermally degrading them in 100°C oven and analyzing the concentration of dye

using a high performance liquid chromatography equipped with a diode array detector and a mass selective detector (HPLC-DAD-MS). The plant dyes of interest were *Phellodendron* bark (hwangbek), madder, and indigo, and the investigation was conducted on their major coloring compounds- berberine and palmatine of *Phellodendron* bark, alizarin and purpurin of madder, and indigotin and indirubin of indigo plant. Coloring compounds of these dye plants were selected since the three dye plants represent the major dyes of the past which dyed fabrics into yellow, red, and blue colors, respectively. The three dye plants differ also in their dyeing mechanisms. *Phellodendron* bark is the most representative basic dye among the natural plant dye, madder is the most representative mordant dye, and indigo is the most representative vat dye.

Fading of museum textiles has been investigated using different laboratory fading simulations and the results were analyzed using different instrumental techniques such as spectrocolorimetric measurements, chromatography, or mass spectrometry. Crews (1987) examined the fading rates of wool dyed with some of the natural dyes by artificially fading the samples with a weather-O-meter. Whitmore and Cass (1988) and Ye et al. (2000) investigated the fading of silk samples dyed with traditional Japanese or Chinese dyes by exposing the samples in ozone. Grosjean et al. (1987) examined the ozone fading of alizarin and Grosjean et al. (1988) of indigo deposited on Teflon membrane, the degradation product was analyzed using the mass spectrometry analysis. Colombini et al. (2007) examined the degradation of flavonoid yellow dyes such as weld, fustic, and dyer's broom using GC-MS and the degradation pathway was proposed.

Meanwhile, Needles et al. (1986) examined the burial induced degradation of wool and silk dyed with natural dyes by burying the samples in standard soil bed. They found that a significant darkening and a change of shades were examined in both wool and silk samples and the change was greater in the unmordanted samples. Peacock (1996) examined the color and physical change of undyed cotton, linen, wool, and silk fabrics by burying the samples in standard soil beds. Cotton and linen turned orange or red-brown and wool and silk turned yellow after 4 to 32 weeks of burial. Lee et al. (2001) examined the color change of cotton and silk dyed with brazilein, berberine, and shikonin after leaving them in air, water, and underground for one year. The results showed that cotton and silk stored underground exhibited the most color change toward achromic color.

Another common method which is used to examine the degradation of textiles is the thermal treatment. Brushwood (1988) reported the yellowing of cotton fabric after the fabric was treated in 200°C for 20 minutes. Needles and Nowak (1989) examined that linen dyed with synthetic dye became darker in color when the fabric was treated in 180°C for 10 hours. Ahn and Obendorf (2004) examined the degradation of alizarin dye using the gas chromatography mass spectrometry (GC-MS) after treating the dye with thermal degradation and peroxide/UV treatment. Different degradation products evolved after 100°C and peroxide/UV treatments and the latter proved to be the more accelerated method. Ahn (2011) examined the degradation of amur cork tree dye and its silk dyeings using the liquid chromatography mass spectrometry (HPLC-MS) after thermally degrading the samples in 100°C oven. The results suggested that there was a direct relationship between the color change of amur cork tree dyed silk and the berberine content in amur cork tree dye (Ahn, 2011).

While burying the textiles in soil is a way to examine the degradation in excavated textiles, it is difficult to simulate the actual burial since all burial conditions differ due

to the complexities in the soil micro-climate (Ahn et al., 2014). Thermal degradation in oven is based on the fact that high temperature accelerates the oxidation of organic materials (Ahn, 2011). The oxidation reaction in oven is said to accelerate two times by every 2°C increase in temperature (Ahn, 2011; Connors, 1990; Ramos et al., 1995). And since the textiles in burial context undergo oxidation by the soil organic environment during the long-term burial, thermal treatment can be an alternative to simulating the burial induced degradation of organic textiles (Ahn, 2011). In this research, the six major dyes- indigotin, indirubin, berberine, palmatine, alizarin, and purpurin- were thermally degraded in liquid dye form and also in silk dyed with five of these dyes (excluding indirubin) using alum mordanting or iron mordanting procedure. 100°C was chosen as the thermal degradation temperature since it was assumed that 100°C will give a better long-term degradation environment than higher temperature used in the previous research (Brushwood, 1988; Needles & Nowak, 1989), and that such long-term degradation would give oxidative degradation comparable to which is expected in the long-term burial degradation. This temperature was successfully used in the previous research in analyzing the results of thermal degradation of alizarin and *Phellodendron* bark using gas chromatography mass spectrometry (Ahn, 2011; Ahn & Obendorf, 2004). Indirubin was used in the degradation of liquid dye, but it was not used for dyeing the silk since its effect on color of dyed fabric is expected to be much less significant than indigotin considering the low composition of indirubin in indigo plant (Maugard et al., 2001). The color of degraded silk was also measured and the results were compared with those obtained from HPLC-DAD-MS analysis. This research focused on the analysis of degradation behavior of dyes in the form of liquid dye or as dye on fiber and not on the identification of specific degradation moieties.

Experimental

Materials

Indigotin, indirubin, alizarin, berberine chloride form (called berberine in the following), and palmatine chloride hydrate (called palmatine in the following) were purchased from Sigma-Aldrich. Purpurin was purchased from Tokyo Chemical Industry. Dimethyl sulfoxide (DMSO, HPLC grade), acetonitrile (HPLC grade), HPLC water (HPLC grade), and sodium hydrosulfite were purchased from Fisher Scientific. Formic acid (88%, ACS grade) was purchased from Macron Chemicals. Aluminium potassium sulfate [$AlK(SO_4)_2 \cdot 12\ H_2O$)] and iron sulfate ($FeSO_4 \cdot 7H_2O$) were purchased from Shinyo Pure Chemicals (Osaka, Japan). A glass vial with cap (Fisher Scientific, 25×95 mm) was used for preparing the liquid degradation samples. HPLC sample was filtered using a glass fiber enhanced 0.45 μm syringe filter by Alltech Associates (Deerfield, IL). Silk used for dyeing was the Standard Adjacent Fabrics for Colorfastness (KS K0905) purchased from KATRI (Seoul, Korea). Water used for dyeing was purified using Milli-Q Integral System by EMD MIllipore.

Method

Preparation of standard mixed dye solution and its thermal degradation

Six standard dyes were dissolved together in 300 mL DMSO with concentrations 0.016 g/L for indigotin and indirubin, 0.033 g/L for berberine, palmatine, alizarin, and purpurin to make a standard mixed dye solution, following Ahn et al. (2013).

For each 24 hours in 0 ~ 9 day degradation time, a 2 ml of mixed dye solution was added to each glass vial, loosely capped and put inside the 100°C oven. Each vial was taken out from the oven at the end of its designated degradation time. At this point, all the liquids in vials were evaporated with only the dye remaining on the inner surface of the vials. To these vials, 2 ml of fresh DMSO was added, rinsing the dye on the inner surface of the vials. The solvent was then filtered for the HPLC-DAD-MS analysis.

Preparation of silk dyeing and its thermal degradation

Silk fabric was dyed using two different modes. The first method used the mixed dye solution of five standard dyes and the second method used the separate dye solutions for each standard dye.

First, a mixed dye solution containing 0.025 g each of berberine, palmatine, alizarin, and purpurin was made in 370 mL of purified water, following Ahn et al. (2013). Approximately 2.45 g of silk fabric sample was mordanted with 0.49 g of aluminium potassium sulfate for 1 hour at 60°C (referred to as alum-mordanted silk in the following). The mordanted silk sample was dyed using the mixed dye solution prepared above for 1 hour at 60°C. Dyed silk was cut into approximately 1.7 g size, and dyed using indigotin dye solution by the reduction dyeing process. The indigotin dye solution was made with 0.017 g dye and sodium hydrosulfite in 250 mL purified water and the pH of the dyebath was adjusted to pH 11 using diluted NaOH solution. When the indigotin was dissolved, the silk sample was immersed and dyeing was carried out for 30 minutes at 60°C. Silk was then thoroughly rinsed with running cold water and air dried so that the leuco form of indigotin could freely oxidize to the insoluble indigotin within the silk. Another silk fabric of 2.45 g weight was mordanted using iron sulfate (referred to as iron-mordanted silk in the following) and then dyed with the mixed dye solution following the same procedure as above. The dyed silk samples were placed in 100°C oven for up to 7 days.

Second, individual dye solutions of berberine, palmatine, alizarin, purpurin, and indigotin were separately made by adding 0.025 g dye in 75 mL water. A silk sample weighing 2.45 g was alum mordanted (0.245 g) using the same procedure as above and dyed with berberine. The silk was alum mordanted again using a fresh mordant solution, and then dyed with palmatine. Following this procedure, the silk was dyed with alizarin and purpurin consecutively, with premordanting with fresh alum mordant solution before each dyeing. The silk was then dyed with indigotin using the reduction dyeing procedure, and the dyeing procedure was the same as above. A new silk sample weighing 2.45 g was iron mordanted, and dyed using the same procedure as above using individual dye solutions. The dyed silk samples were placed in 100°C oven for up to 14 days.

Extraction of dye from degraded silk sample

Approximately 0.5 cm × 0.5 cm size dyed silk specimen from each of the degraded sample was place in a small beaker with 0.4 mL of mixed solution of HCl/methanol/water (2:1:1 v/v/v) (Ahn et al., 2013). The beaker was placed in 100°C oven for 15 min so that the liquid can completely evaporate. An aliquot of 1.1 mL of DMSO was added to the dried out beaker. The solvent was then filtered for the HPLC-DAD-MS analysis.

Analysis

HPLC-DAD-MS analysis

An Agilent 1200 series binary HPLC-DAD-MS system (Foster City, CA) equipped with a diode-array detector (DAD) and a mass selective detector (MSD) consisting of a single quadrupole mass analyzer using the atmospheric pressure chemical ionization (APCI) source in the positive mode was utilized to detect the coloring compounds in the SIM (selected ion monitoring) mode. LC separation was achieved by 150 mm length, 4.6 mm i.d. stainless steel C18 column (Restek Corporation, Bellefonte, PA). The gradient elution applied in the analysis using solvent A (acetonitrile) and solvent B (1% formic acid in water) was: 0-5.7 min, 90-20% B; 5.7-10 min, 20-61% B, 10-15 min, 61% B. The flow rate was 1.0 mL/min, and the injection volume was 20 μL. Detection wavelength for the DAD was set for 288 nm with the spectrum detection range 190-700 nm. The column temperature of the MSD was 25°C and the ionization source was operated with drying gas (N_2) temperature 300°C, vaporizer temperature 100°C, nebulizer pressure 20 psi, capillary voltage of 5 kV in positive ion mode, fragmentor voltage 160 V, and mass range m/z 200-400.

Color measurement

For silk samples dyed with individual dye solutions, the color measurement was carried out using a JS-555 spectro-colorimeter (Color Techno System, Japan) under D_{65} illuminant and 10° standard observer at three spots and the average data were reported. The color difference ΔE relative to the undegraded silk was used as the measure of the extent of dye adsorption.

Results and discussion

Analysis of thermal degradation of mixed dye solution

HPLC-DAD-MS analysis was initially conducted on the untreated dye solution to find the retention time of the chromatogram peak, UV-visible absorption spectrum (λ_{max}), and major molecular ion of each coloring compound. The retention times of the peaks of berberine (1), palmatine (2), alizarin (3), purpurin (4), indigotin (5), and indirubin (6) in the chromatogram of the mixed dye solution were 6.2 ~ 6.9 min, 6.4 ~ 6.9 min, 8.8 ~ 9.0 min, 10.2 min, 9.8 ~ 10.2 min, and 10.7 ~ 11.4 min, respectively (Figure 1) (Ahn et al., 2014). The chromatogram peak of indigotin and purpurin overlapped and

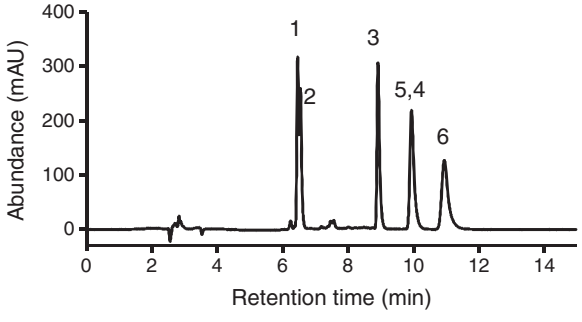

Figure 1 HPLC-DAD chromatogram of the mixed dye solution before degradation treatment. Numbers in the chromatogram indicate; 1 berberine, 2 palmatine, 3 alizarin, 4 purpurin, 5 indigotin, 6 indirubin (reproduced from Ahn et al., 2014).

the λ_{max} of both compounds appeared in the UV absorption band of each compound concomitantly (Figure 2). However the two compounds were distinguishable using the differences in major molecular ion typical of each compound which were m/z 263 for indigotin and m/z 257 for purpurin (Ahn et al., 2013; Ahn et al., 2014; Ren et al., 2007). The chromatogram peaks of berberine and palmatine also overlapped and their UV absorption bands were identical due to the fact that berberine and palmatine were both protoberberine alkaloids (Ahn et al., 2013; Ahn et al., 2014; Zhang et al., 2009). But the two compounds were distinguishable by the major molecular ions $[M + H_2]^+$ of each coloring compound which are m/z 338 and m/z 354 respectively (Ahn et al., 2014; Ren et al., 2007). The details of the λ_{max} of the UV-visible absorption bands and the major ion detected for each coloring compound follow the analytical results and discussion on the standard dyes reported previously (Ahn et al., 2013; Ahn et al., 2014).

The dye solution was thermally degraded in 100°C oven for 1 ~ 9 days and the degraded samples were analyzed using the HPLC-DAD-MS instrument. When the

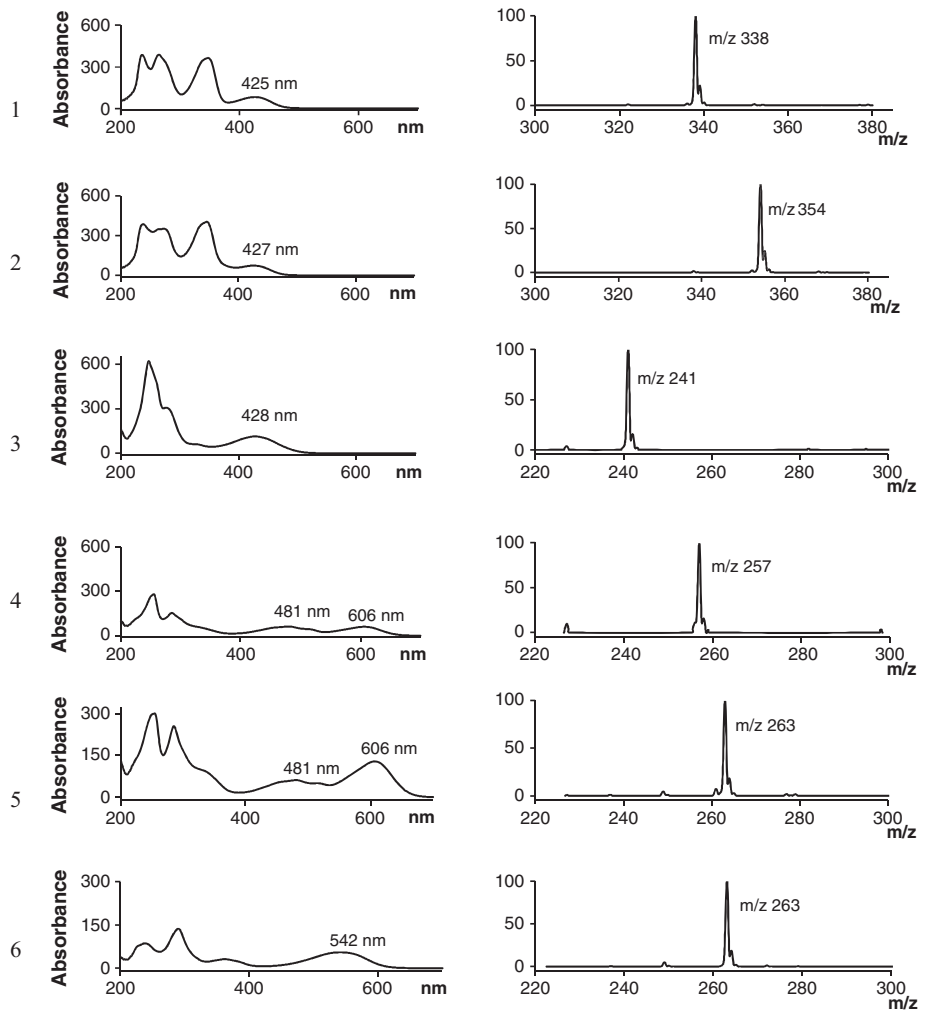

Figure 2 UV-Visible absorption spectra (left) and mass spectra (right) obtained through the HPLC-DAD-MS analysis on the mixed dye solution before degradation treatment. Numbers on the left indicate; 1 berberine, 2 palmatine, 3 alizarin, 4 purpurin, 5 indigotin, 6 indirubin.

HPLC chromatograms of the degraded samples were examined, there was a gradual lowering of the peaks of the six coloring compounds as treatment time progressed (Figure 3). The lowering of the peaks suggested decrease in relative abundance of each coloring compound, and visually, such decrease was most prominent in purpurin (4) and indigotin (5) peaks (Figure 3).

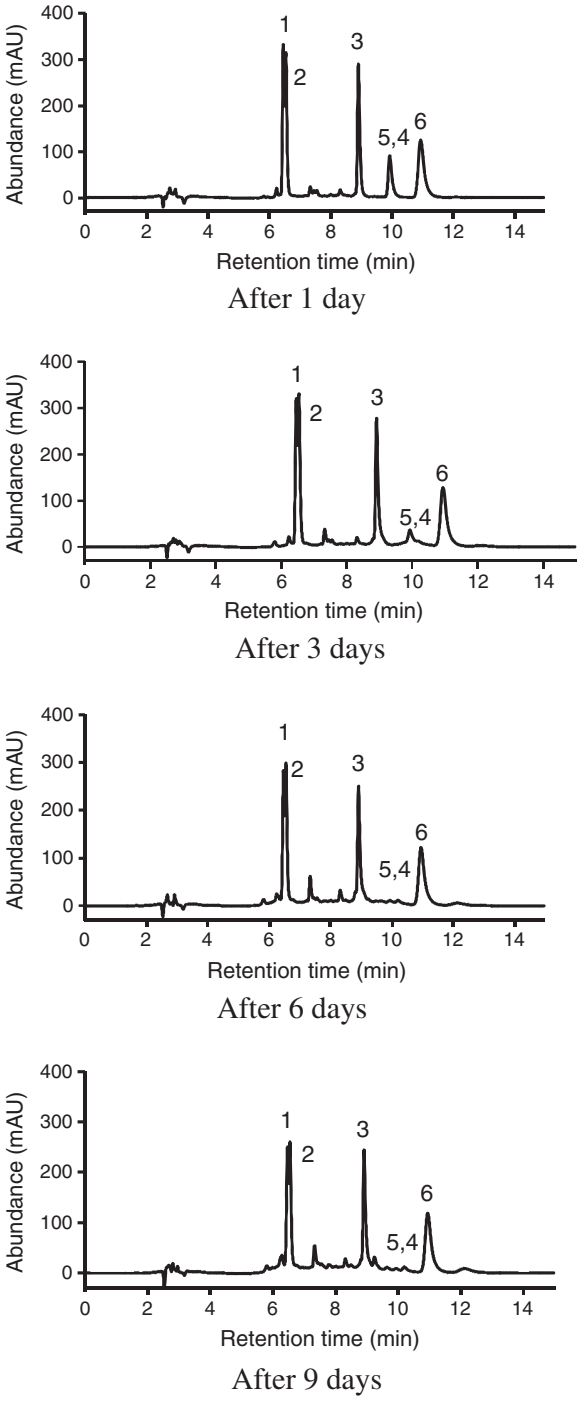

Figure 3 HPLC-DAD chromatograms of the mixed dye solution after 1 ~ 9 days of thermal degradation treatment. Numbers in the chromatograms indicate; 1 berberine, 2 palmatine, 3 alizarin, 4 purpurin, 5 indigotin, 6 indirubin.

In order to examine the change in relative concentration of six coloring compounds in the mixed dye solution by thermal degradation, ion chromatogram was generated from the mass spectrum of each ion m/z 338 (berberine), m/z 354 (palmatine), m/z 241 (alizarin), m/z 257 (purpurin), m/z 263 (indigotin), and m/z 263 (indirubin). The abundance of ion chromatogram was used as the measure of concentration of corresponding coloring compound detected in the HPLC-MS. Based on the abundance of the compound in untreated solution, the relative concentration of each coloring compound in the degraded dye solution was calculated in percentage, and the results were plotted in an Excel graph (Figure 4).

The result indicated that except for alizarin, the concentrations of all five dyes were close to zero % by 6 days of thermal treatment, meaning that most intact dye molecules were lost after 6 days of treatment (Figure 4). The decrease in concentration was more prominent in indigotin and purpurin. Purpurin in particular, lost most of its dye molecule by 2 days of thermal treatment. On the other hand, alizarin showed the least decrease in concentration and when the treatment was terminated, more than 30% of alizarin molecule survived in the dye solution. Degradation behaviors of berberine and palmatine were almost identical, and the two dyes were more resistant to degradation than indirubin, indigotin, and purpurin and less resistant than alizarin.

Analysis of silk dyed with mixed dye solution after thermal degradation

Two pieces of silk sample were dyed with berberine, palmatine, alizarin, purpurin, and indigotin consecutively, one treated with alum mordanting before each dyeing procedure and the other treated with iron sulfate mordanting before each dyeing procedure. After degrading the silk dyeings in 100°C oven up to 7 days, dye was extracted from each silk and the extracts were analyzed using the HPLC-DAD-MS analysis.

Figure 5 illustrates the HPLC chromatogram of the dye extracted from alum mordanted silk before and after the thermal degradation treatment. There was a noticeable change in the height of the peaks in HPLC chromatograms as the treatment progressed. After 7 days of thermal treatment the height of the peaks for all five dyes lowered. And such visual decrease was more dramatic in indigotin and purpurin since the peaks of these compounds almost disappeared after 7 days of thermal treatment.

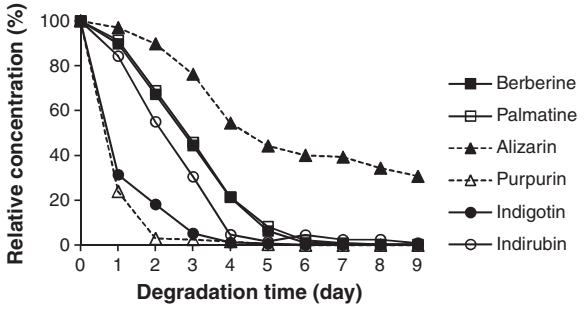

Figure 4 Relative decrease in the concentration of six pigments during 0 ~ 9 days of thermal degradation of mixed dye solution in 100°C oven.

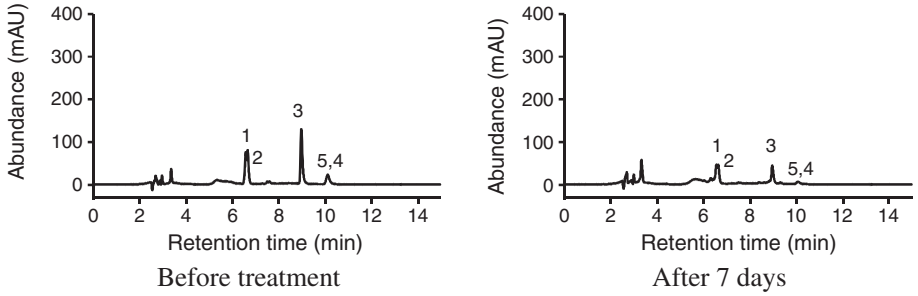

Figure 5 HPLC-DAD chromatograms of the dye extracted from alum mordanted silk dyeing before and after 7 days of thermal degradation. Numbers in the chromatograms indicate; 1 berberine, 2 palmatine, 3 alizarin, 4 purpurin, 5 indigotin.

Figure 6 illustrates the HPLC chromatogram of the dye extracted from iron mordanted silk before and after the thermal degradation treatment. Compare to the alum mordanted silk, there was more prominent lowering of the peaks of the five coloring compounds in iron mordanted silk. The HPLC chromatogram of alum (Figure 5) and iron (Figure 6) mordanted silk suggest that the concentration of the five dyes decreased in the silk dyeings after the thermal degradation treatment.

Figure 7 and Figure 8 illustrate the change in the relative concentration of five dyes in alum mordanted silk and iron mordanted silk, respectively. Both alum mordanted silk dyeing and iron mordanted silk dyeing showed decrease in the relative concentration of five dyes, and as expected from the HPLC chromatograms, there was a higher amount of decrease in iron mordanted silk sample. In both alum mordanted silk and iron mordanted silk, alizarin and purpurin showed lower amount of decrease compared to the other dyes. And indigotin showed a dramatic decrease during the 7 days of thermal treatment. And furthermore, the results indicated that in case of alizarin, iron mordanted silk showed a slightly lower decrease in dye concentration than the alum mordanted silk. This suggests that alizarin may be more resistant to degradation when the silk is mordanted with iron type mordant.

Effect of thermal degradation on the color values of silk dyed with individual dye

Color differences of alum mordanted silk and iron mordanted silk dyed with individual dye solution, after $0 \sim 14$ days of thermal degradation treatment are illustrated in

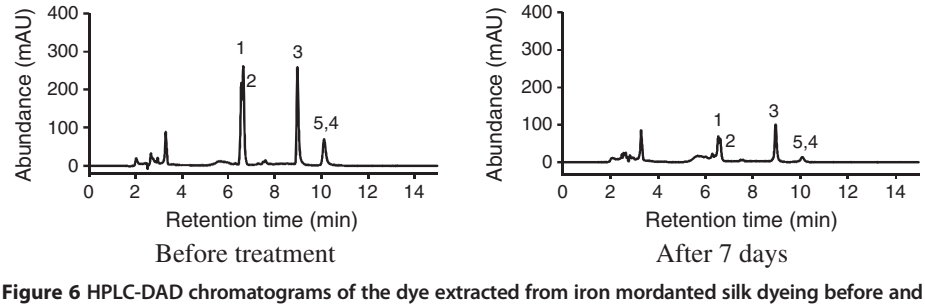

Figure 6 HPLC-DAD chromatograms of the dye extracted from iron mordanted silk dyeing before and after 7 days of thermal degradation. Numbers in the chromatograms indicate; 1 berberine, 2 palmatine, 3 alizarin, 4 purpurin, 5 indigotin.

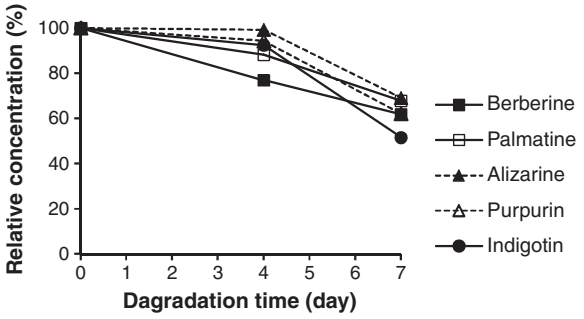

Figure 7 Relative decrease in the concentration of five pigments in alum mordanted silk dyeing after 0 ~ 7 days of thermal degradation treatment.

Figure 9 and Figure 10, respectively. In both alum mordanted silk and iron mordanted silk, the color different of the degraded sample relative to the untreated sample was most prominent in berberine and palmatine dyed silk and the least color difference was observed in alizarin and purpurin dyed silk. Such results were in agreement with the change in dye concentration analyzed by the HPLC-DAD-MS. However, in case of indigotin, there was a discrepancy between the two data. The color difference values indicated that indigotin dyed silk showed higher color difference in alum mordanted silk than in iron mordanted silk, whereas it was opposite when the change of dye concentration was examined using the HPLC analysis.

Alizarin and purpurin were more resistance to degradation than other coloring compounds both when in solution form and in silk dyeings. And such result was verified by the color difference measurement of the degraded silk dyed with individual dye solution. The resistance of alizarin and purpurin toward degradation treatment in silk dyeing was due to their dyeing mechanism. Being mordant dyes, alizarin and purpurin forms fiber-metal-dye chelated complex within the fiber by the metal compounds used in mordanting (Ahn et al., 2014; Khan et al., 2012; Samanta & Konar, 2011). Thus the aluminium and iron which were used in alum mordanting and iron mordanting, respectively, allow strong dye fixation by forming chelated structure (Ahn et al., 2014). Furthermore, alizarin and purpurin dye molecules will also form aggregates by the dye-metal-dye chelation (Ahn et al., 2014). And larger aggregates will

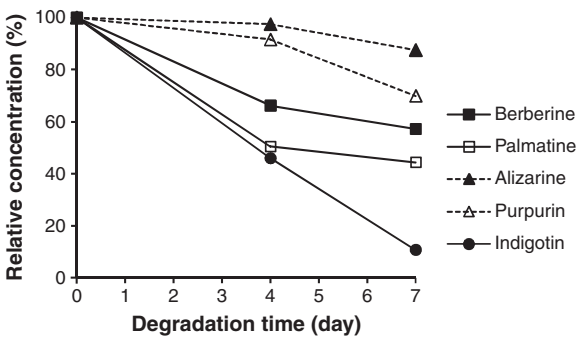

Figure 8 Relative decrease in the concentration of five pigments in iron mordanted silk dyeing after 0 ~ 7 days of thermal degradation treatment.

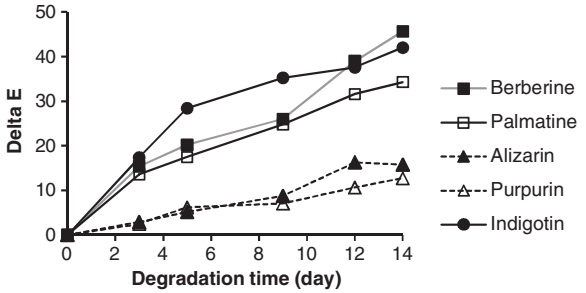

Figure 9 Color difference (ΔE) values of alum mordanted silk dyeings after 0 ~ 14 days of thermal degradation in 100°C oven.

allow the dye to be more resistant to degradation since the thermal oxidation will initially affect the peripheral structures of the dye molecules, possibly leaving the larger portion of dye to be unaffected (Ahn et al., 2014; Crews, 1987; Giles & Mckay, 1963).

Berberine and palmatine showed a larger degree of color difference in silk dyeings relative to the untreated samples. They are affixed to silk fibers by the ionic bond which forms between the cationic nitrogen in the dye molecule and the anionic sites of acidic amino acids in silk protein (Ahn et al., 2014). However, the size of berberine and palmatine dye particles within the fiber would be smaller since their structure do not enable the dye to form hydrogen bonding which allow the formation of larger aggregates (Ahn et al., 2014). Therefore, berberine and palmatine would be more susceptible to oxidative degradation by high temperature since larger surface area is exposed by the smaller particle size of dye molecules.

Indigotin is known to be one of the most fast natural dye since dyeing with indigo involves vat dyeing process which forms insoluble indigotin dye molecules within the fiber (Crews, 1987; Padfield & Landi, 1996). However, in a recent study on the degradation of indigotin in solution it was found that indigotin was highly susceptible to degradation by H_2O_2 treatment with UV radiation forming isatin as main degradation product (Ahn et al., 2014). Similar oxidative degradation would have occurred by the thermal treatment of this study. It is interesting that indigotin in silk dyeing also showed a high degree of degradation by thermal treatment when the dye is known to be one of the most fast natural dye. Although indigo dye forms insoluble indigotin

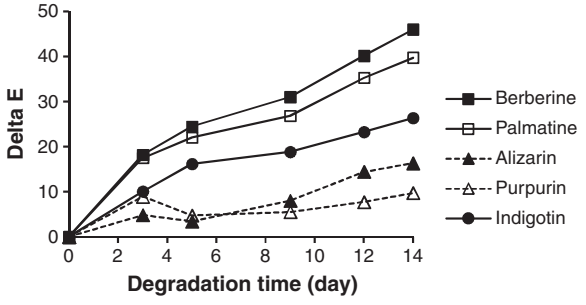

Figure 10 Color differemnce (ΔE) values of iron mordanted silk dyeings after 0 ~ 14 days of thermal degradation in 100°C oven.

molecules within the fiber, the dye molecules do not have any chemical bonding sites with fiber nor it has possible sites for forming aggregates within themselves (Ahn et al., 2014). Therefore small indigotin particles are merely trapped in the amorphous area of the fiber (Ahn et al., 2014) which enable easy attack from external oxidative degradation forces.

Conclusion

The purpose of this research was to investigate the degradation behaviors of major coloring compounds of three different natural dyes by thermally degrading them in 100°C oven. The results indicated that alizarin and purpurin were more resistance to degradation than other coloring compounds both when in solution form and in silk dyeings. And such result was verified by the color difference measurement of the degraded silk dyed with individual dye solution. It is highly likely that the resistance of alizarin and purpurin toward degradation treatment in silk dyeing was due to the formation of fiber-metal-dye chelated complex within the fiber by the metal compounds used in mordanting. The higher degree of survival of alizarin and purpurin dye molecules were also due to the probable formation of large aggregates of dye by the dye-metal-dye chelation. Berberine, palmatine, and indigotin were less resistant to degradation by the thermal treatment possibly due to the fact that these dyes do not have active chemical sites which allow the formation of large aggregates of dye. And larger aggregates will allow the dye to be more resistant to degradation since any type of degradation force will initially attack the surface of dye particles, possibly leaving the larger portion of dye within to be less affected. It is suggested that same type of degradation behavior would occur in the archaeological textiles which were in the long-term burial environment. The method and the results of the present investigation can be applied in the identification of badly faded museum textiles which were recovered from burials. Future study is needed in the examination of specific degradation moieties of each dye for a more in-depth results of degradation of six natural dyes studied in this research.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
CA participated in the research design and carried out major experiments and writing. XZ participated in setting up the HPLC protocol and the data collection, and LL participated in the color analysis of degraded textiles. SKO participated in the collaboration of research design and the interpretation of data. All authors read and approved the final manuscript.

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