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The influence of the main elemental constituents of thousand year old barai mud extension of shades of natural dyed silk from marigold flowers

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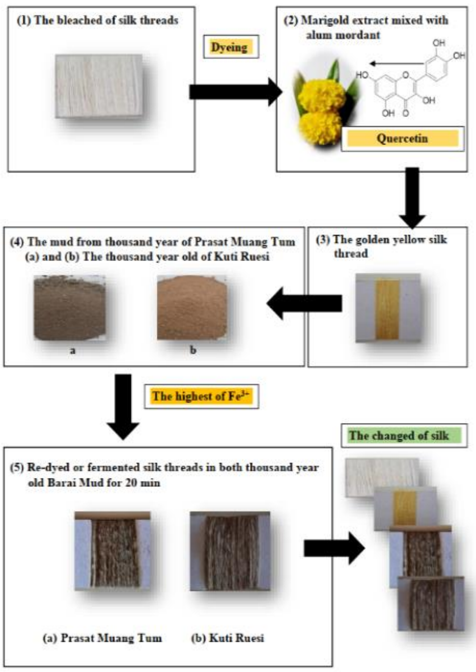
Abstract

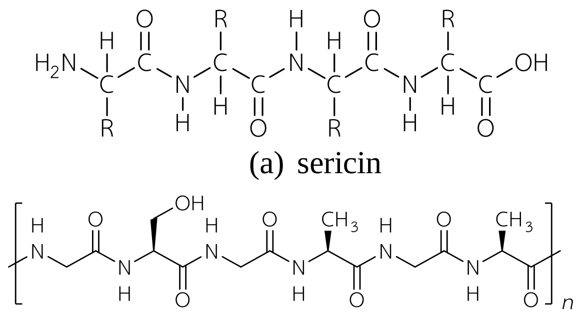
This research aimed (1) to study the main element of thousand year old mud and types of color-giving substances from marigold flowers and (2) to study the causes of silk color change from dark yellow to dark green at Bankhokmuang, Chorakhemark Sub-district, Prakhonchai District, Buriram Province. Firstly, the researcher studied the element of the mud from Barai Prasat Muang Tam and Barai Kuti Ruesi, using EDXRF. Secondly, the researcher studied types of phytochemicals in marigold extract using HCl solution and NaOH solution. Finally, the researcher dyed the silk with marigold flower extract mixed with alum and dyed it with iron ion solution and the mud solution from both sources. The results showed that both muds had the highest amount of Fe_2O_3, 64.03% of Barai Prasat Muang Tam mud and 44.22% of Barai Kuti Ruesi mud. The coloring substance of marigold extract was flavonoids and had good water solubility. Then the researcher dyed the silk with marigold flower extract mixed with alum because alum contained Al^{3+}ions. The silk was dark yellow. The silk was divided into three groups to be dyed again. The first group was dyed with 1,000 ppm iron ion solution. The second group was dyed with a solution of Barai Prasat Muang Tam mud. The third group was dyed with a solution of Barai Kuti Ruesi mud. All group color changed from dark yellow to dark green. Thus, iron ion solution and both of Barai mud solution were rich in iron ion. This complex compound could form with flavonoids which made golden yellow color turns dark green and sticks to silk threads. It was also water insolubility. The color was not faded. All groups had different shade values at the significance level of 0.05.



Keyword: Flavonoids; Bankhokmuang; Natural dyes; Prasat Muang Tam; Kuti Ruesi

1. Introduction

Natural silk is composed of two structural proteins: fibroin (72 – 81 weight%) and sericin (19 – 28 weight%), and a small amount of fat or wax (0.8 – 1%) and ash (1 – 1.4%). Fibroin is the main component of silk fibroin. It acts as the inner core and provides mechanical strength. While serine is an outer coating similar to adhesive [1]. Sericin is a polar amino acid that is insoluble in cold water, but it dissolves in hot water because long protein molecules decompose into smaller fractions under extremely hot conditions and are easy to decompose [2]. It has the ability to prevent uv light, moisture and high oxidation [3]. Fibroin is an amino acid with low polarity or insoluble in water, which is easily soluble in organic solvents [4] and has exceptional mechanical strength and toughness properties [3]. Silk has been used in many fields such as textile, medical treatment, industry and cosmetics. And silk manufacturing of Thailand focuses on utilization of silk fiber (fibroin) especially to fabricate the silk cloth [24]. Nowadays, there are many different techniques to do the research of silk structure research, such as ultraviolet spectrophotometer, Fourier transform infrared (FTIR), and thermogravimetric analysis (TGA) and X-ray diffraction (XRD) [2]. The structural characteristics of fibroin and sericin are typically as shown in the Fig. 1.


(a) sericin

(b) fibroin

Fig. 1 The structural characteristics of a sericin (a) and a fibroin (b)

Mud cloth dyeing [5] is an important method of producing grays and blacks on fabric that can be quickly achieved by soaking plant tannins and dipping them in the mud from a still pond river or field. It is one of the earliest dyeing techniques in Southeast Asia [5]. This dyeing method can be found in southwestern China, Taiwan, Philippines, Thailand, Cambodia, Vietnam, Malaysia, Borneo and Sulawesi. Borah *et al.* [6] investigated the chemistry of the bogolan or mud dyeing process in Mali using tannin-rich plant extracts to dye and ferment the iron-containing mud using infrared spectroscopy, scanning electron microscopy (SEM) and X–ray absorption spectroscopy (XANES) in probing cotton fibers impregnated with tannin and iron salt solutions. It was found that iron was transferred electrons from the mud iron-bearing mud to the cloth. This conclusively demonstrated and confirmed that the dyeing of local fabrics by fermentation mud has actually been around for a long time.

At present, the extensive use of synthetic coatings can produce a large amount of waste, and unstable coatings can cause serious harm to health and destroy the ecosystem. Further research is needed to select potential sources of natural dyes and to study the appropriate yield of dyes extracted from natural dyes. Most natural dyes are environmentally friendly and are substitutes for synthetic dyes, which is not only harmful to the environment, but also dangerous to people with skin allergies and other diseases. Most natural dyes come from natural plants, minerals, animals and bacteria, and they have been used for textile coloring since ancient times [7], unlike synthetic dyes [8]. Today, natural dyes are still used with mordant. Surprisingly, they can provide bright and dark colors [9]. Satpathy *et al.* [10] also increased the absorption of dyes and improved the color fastness. It has been determined and proved that the effectiveness of reducing agent helps to prevent color peeling and washing. According to Nur Fadzli *et al.* [11], *Tagetes erecta* L. (Mexican variety) was used as the source of natural dyes. According to Lohar and Jayoti [12], marigold is one of the main sources of carotenoids that can produce high color output, namely lutein pigment, which contains the vertical antennae of carotenoids and can create unique colors, such as yellow to orange [13]. According to previous studies, it was found that the extract from tagetes erecta is non-toxic and harmful to the environment [12, 13].

Bankhokmuang is a large traditional community with the foundation of cultural prosperity in the past. One important evidence is Prasat Muang Tam which has a history of more than 1,400 years. The villagers of Khok Muang used to work in agriculture and mixed agriculture because the soil in this area is rich in minerals. Thousands of years ago, the soil here was an elemental-rich volcanic region.

At present, Bankhokmuang is another important cultural tourism village in Thailand because it is an ancient village with a history of hundreds of years. The most important thing is that this village is connected with the "Prasat Muang Tum" which is lower than Khao Phanom Rung Castle. Prasat Muang Tum is the castle with five heads, bareheaded, without decorations like other Nagas in the Khmer castles. There is a curved pool in each of the corner of Prasat Muang Tum [14].

Kuti Ruesi or hermit's cloister Bankhokmuang is a religious place for the hospital or "Arokaya Shrine". Based on the stone inscription found at Ta Phrom Prasat, it was said that King Jayavarman VII of Cambodia 1724 – 1762 B.E. ordered to build 102 hospitals around his kingdom and assumed that many small sanctuaries in the Northeast of Thailand was built by laterite and surrounded by walls. This buildings was called Kuti Ruesi or the hermit cloister. However, the real medical facility was probably built of wood in the same area. So, it was already damaged. One of them was a hermit's residence located in front of the castle at Bankhokmuang [15]. There is also a large barai located about 1,000 years ago.

Recently, there has also been the emergence of the thounsand year old barai mud weaving group, which dyes local fabrics (cotton and silk) with natural colors from marigold flowers together with barai mud, Prasat Muang Tam and Kuti Ruesi. There is a story telling about the history as follows: The villagers of Bankhokmuang regularly caught fishes around Barai at Kuti Ruesi and braai at Prasat Muang Tam. This caused a lot of mud sticking to clothes and could not be washed off. Therefore, the villagers were interested in using the Barai mud from both sources to apply in dyeing clothes using natural dyes that were readily available in the local area (marigold). This resulted in a new community products from the wisdom of local people. The weaving group of the community was led by Ms. Piyaphat Srichana, a member of Huay Chorakhemark Sub-district Administrative Organization, Prakhonchai District, Buriram Province. Together with the villagers and the group members of the weaving group, they had a vision and would like to study the properties of dyeable soil and the cause of the change in color when repeated the use of the dyed soil from golden yellow to sage green.

For this reason, the researcher cooperated with the community leaders to study the elemental constituents of the Barai mud and the types of extracts that offers color from marigold flowers for dyeing native silk. The main staining steps was from local wisdom and made some adjustments for convenience and suitability in scientifically proven, and this can create a body of knowledge for Bankhokmuang community. It is highly expected that the results of this research are able to create a sense of love for the homeland to the next generation of the Ban Khok Muang community and be able to pass on this wisdom to other people who are interested in silk dyeing and they also can learn the research results as academic knowledge.

2. Materials and Methods

Preparation of Solution

The weight of ferrous sulfate ($FeSO_4 \cdot 7H_2O$, AR grade, Ajax Finechem, Australia) about 0.5 g. was dissolved in 0.5% nitric acid, adjusted the volume with distilled water in a 100 mL volumetric flask. The final concentration was 1,000 ppm. Poured into the bottle for further use.

The weight of alum ($KAl(SO_4)_2 \cdot 12H_2O$) about 10 g was added 100 mL distilled water. Then poured the solution into the container and boiled it at 80 °C. Let it cool at room temperature, and then poured the solution into a 1,000 mL volumetric flask (adjusted the volume with distilled water). Poured into the bottle for further use.

The weight of sodium hydroxide (NaOH, AR grade, Ajax Finechem, Australia) about 4 g. was added 25 mL of distilled water to dissolve. The resulting solution was poured into a 100 mL volumetric flask. The final concentration was 1 N.

The stock solution of 1M HCl (HCl, Analysis GR, Merck, Germany) was prepared. Then 1 M HCI solution was pipetted 8.2 mL and adjusted volume by distilled, poured the solution into a 100 mL volumetric flask. The final concentration was 0.1 M.

The Extraction of Dyeing from Marigold

Marigold was collected from the night bazar market in Buriram. Washed it with clean water, and then washed it with distilled water three times. Took out marigold and unfolded it on a stainless steel tray. Dried it at 50 °C for 24 hr. in oven. Then ground thoroughly with a mortar, and put the fine powder of marigold into a zipper bag before use. The weight 5 g of dry powder marigold was added 100 mL of distilled water and left to boil for 10 min. Then it was filtered by suction, and kept at 4 – 5 °C before dyeing the silk sample.

The Scouring of Silk

Chemicals that were used included soap, soda ash, multi-purpose liquid (colorless and odorless detergent). The weight of 180 g soap solution was dissolved in 30 – 40 L of water. Added 50 g of soda ash and 1 tablespoon of multi-functional liquid. Then the substances were stirred together. Used 30 L of degumming agent for each silk * 1 Yellow silk 40 L liquid.*It can be adjusted according to the weight of the silk thread to be dyed.

The Phytochemicals of Marigold Extract

Weighed the marigold powder into 10 g, added 10 mL distilled water, stood for 1 hr. and then filtered with filtered paper no. 1, poured 2 mL of marigold extract into the test tube. Then 1 – 2 drops of sodium hydroxide solution was added in order to observe the color changing from clear yellow to dark brown. When diluted hydrochloric acid solution was added again, it was as mentioned earlier, transparent yellow indicated that the extract sample contains flavonoids [16].

The Study on Main Elemental Constituents in Mud, Barai Prasat Muang Tum and Kuti Ruesi

Dried the mud samples of barai Prasat Muang Tam and barai Kuti Ruesi. Then ground them thoroughly with mortar and put them into zipper bags as shown in Fig. 2. Analyzed the elemental compositions in the samples by non-standard machine at room temperature, Method/X-ray fluorescence energy dispersion spectrophotometer model XGT-5200, room temperature 25 °C, humidity not more than 60 °C under the following conditions: X-ray tube: 50 kV maximum, 1 mA, Rh target fluorescent X-ray detector: Peltier cold silicon drift detector (SDD) element Detection: Na to U (sampling under normal pressure) Energy range: 0 – 40 kV Non Filter.

(a) Prasat Muang Tum (b) Kuti Ruesi

Fig. 2 The color characteristics of mud from thousand year old of Prasat Muang Tum (a) and (b) The thousand year old of Kuti Ruesi

Comparison of Three Groups of Silk Thread Tones

The traditional dyeing process of local wisdom was as follows: used calendula extract and alum to heat and bleach silk at 70 – 90 °C. This was a combination of dye (alum) and dye (marigold extract), also known as simulation dyeing about 40 min. Then dyed the auxiliaries again after dyeing with Barai mud solution, or wet mud fermentation. This was called post-dyeing, which lasted about 20 min. The duration required for the whole dyeing process was one hour.

Therefore, in this experiment, the CRD (completely random design) was redesigned. This is an experimental plan. There was only one research factor, but there were many levels or treatments. According to the traditional dyeing wisdom of the local community, the silk dyeing experiment was divided into three groups. Each group prepared and carried three bales of bleached silk thread for three repeated tests, and the weight of each bale was about 1 g and 20 cm long.

Group 1: Iron Ion Solution or Ferrous Sulfate Solution ($FeSO_4 \cdot 7H_2O$)

The silk was dyed with marigold extract and alum for 40 min, and then fermented in 1,000 ppm concentrated iron solution for 20 min. The color change was observed. Then the silk was rinsed with water and dried. Then it was sealed for further color measurement. (3 times repeated experiment)

Group 2: Mud of Barai Thousand Year Old from Prasat Muang Tum

The weight of 60 g of dried weight of the thousand year old barai mud from Prasat Muang Tum was weighed and prepared. 300 ml of distilled water was mixed and added to ferment the silk. After that, the silk threads that were dyed with dyeing marigold extract were soaked in the prepared thousand year old barai mud from Kuti Ruesi for 20 min before being washed with water and dried to prepare for further color measurement (3 times repeated experiment).

Group 3: Mud of Barai Thousand Year Old from Kuti Ruesi

The weight of 60 g of dried weight of the thousand year old barai mud from Kuti Ruesi was weighed and prepared. 300 ml of distilled water was mixed and added to ferment the silk. After that, the silk threads that were dyed with dyeing marigold extract were soaked in the prepared thousand year old barai mud from Kuti Ruesi for 20 min. Then the silk was washed with water and dried to prepare for further color measurement (3 times repeated experiment).

Color Measurement of Silk Thread

The main objective of this research was to study the color change of silk thread after being fermented by the mud from both sites and iron ion solutions ($FeSO_4 \cdot 7H_2O$). Sometimes the color was unable to be classified by human eye vision. Therefore, in order to gain the accurate and credible experimental results and to identify numerically color variations, the CR-400 KONICA MINOLTA colorimeter was used with the CIELAB L* colorimetric system with a value of 0 – 100, ie. a value used to indicate brightness was of 100. White 0 was black, a* values were (+) red, (–) green and b* values are (+) yellow (–) blue, compared to the shade of bleached silk.

Statistical Analysis

This research designed a completely randomized experiment (CRD) to study the color gamut values from Experiment 2.6, and to analyze the obtained values for one-way analysis of variance: (One way ANOVA) of silk threads dyed with iron ferrous sulfate solution. The barai mud solution, Prasat Muang Tam, and Kuti Ruesi, whether there was a difference or not. The statistic used for testing the significance was the F-test.

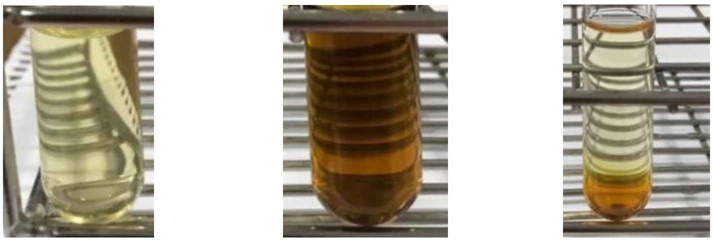
The Characterization Structure of Silk Thread by FTIR

The structural characterization and identification of important functional groups of silk threads used for binding to the structure of dyes or mordants in this study was Fourier transform spectroscopy (Fourier Transform Infrared Spectroscopy (FT-IR)) Make/Model: Bruker/Tensor 27 Condition: Check Signal (Amplitude) – 1753 Resolution 4 Sample scan time 64 Background scan time 64.

3. Results and Discussion

Physical Characteristics and Types of Phytochemicals in Marigold Extract

Marigold extract was transparent yellow with pH value of 7.89. It was neutral. During this experiment, the type of phytochemicals extracted from marigold extract was tested. According to the method of Panchal and Parvez [16], it was found that when dropping sodium hydroxide (NaOH)1 N, it was normally dark brown, but when adding hydrochloric acid (HCl) solution, then it turned transparent yellow again as shown in Fig. 3. Therefore, it was concluded that marigold extract was a flavonoids. According to Kurkina *et al.* [17], it was reported that the type of flavonoids in Marigold flower was a yellow quercetin as shown in Fig. 4.



(a) Marigold extract (b) NaOH 1 N (c) HCl 0.1 M

Fig. 3 The physical characteristics and types of phytochemicals in Marigold extract (a) Marigold extract (b) NaOH 1N in Marigold extract and (c) HCl 1M in Marigold extract

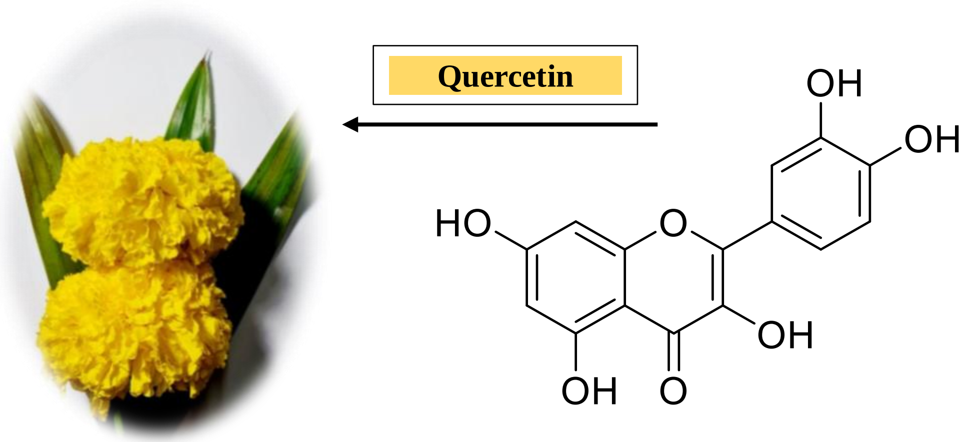


Fig. 4 The type of flavonoids in Marigold flowers

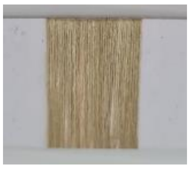
When alum or potassium sulfate ($KAl(SO_4)_2 \cdot 12H_2O$ solution was added to the marigold extract, it was found that it gave more golden yellow. When ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$) was added, it changed from golden yellow to dark green with a pH of 4.5. It was slightly different. As flavonoid was a kind of polyphenol compound, it contained water-soluble carbon and hydroxyl, and it could also combine with metals (Al^{3+}, $Fe^{2+, 3+}$, and Cu^{2+}) and binding complexes [18]. Therefore, the properties of Al^{3+} were from alum solution and ferrous sulfate ion solution ($FeSO_4$, Fe^{2+}). It was metallic. So, it caused the dye to appear darker yellow and turn dark green. This phenomenon also caused the color to adhere to the silk and to prevent the dye from being not sticking. The modified dye solution was as shown in Fig. 5.

(a) Marigold extract (b) $KAl(SO_4)_2$ $12H_2O$ (c) $FeSO_4 \cdot 7H_2O$

Fig. 5 (a) The color changes of Marigold extract (b) add $KAl(SO_4)_2 \cdot 12H_2O$ solution (c) add $FeSO_4 \cdot 7H_2O$ 1,000 ppm

The marigold extract was used to dye the silk by mixing alum into the boiled extract at a temperature controlled range of 70 – 90 °C. Then nine sets of prepared silk threads were divided into three groups to be soaked and dyed for 40 minutes in three repetitions. The results were shown as follows: Table 1 it was found that the color of the silk thread was golden yellow dyeing with alum mordanting and marigold extract) giving the average L*, a* and b* values of 77.67, 5.14 and 35.90, which showed a darker shade or a decreasing in brightness and a yellow value (b*). When compared with bleached or undyed silk (L* a* and b* averaged 87.27, 5.09 and - 1.29) and silk dyed with marigold extract (L* a* and b* mean 64.19 8.85 and 19.81), it was very noticeable that at this stage, the difference in the color of the silk was clearly seen, especially the silk threads dyed with marigold flower extract mixed with alum. It had brighter color than the dyed silk threads with marigold flower extract due to the influence of aluminum heavy metal solution from alum solution. This was in line with the research conducted by Deveoglu *et al.* [19] who explained that alum was a natural-friendly pigment that gave darker shades and was brighter and could prevent color fading of fibers dyed with natural dyes as shown in table 1.

Table 1 The silk thread dyeing at different conditions with marigold flower extract

Type of Dyeing	Dyeing Conditions	Average Shade		
		L^*	a^*	b^*
Silk Bleached		87.27 ± 0.04	5.09 ± 0.57	-1.29 ± 0.06
Marigold Flower Extract		64.19 ± 0.02	8.85 ± 0.63	19.81 ± 0.90
Marigold Extract Mixed with Alum Mordant		77.67 ± 0.04	5.14 ± 0.43	35.90 ± 0.45

The Main Elemental Constituents of Thousand Year Old Barai Mud

In this step, the quantification of the main elemental constituents in the thousand year old barai mud from Prasat Muang Tum and Kuti Ruesi that influenced the shade of silk was investigated by EDXRF. It was found that the iron oxide (Fe_2O_3) content of the two barai mud (Fe_2O_3) was the highest at 64.103% and 44.222 %, respectively, followed by silica (SiO_2), alumina (Al_2O_3) and titanium dioxide (TiO_2). As shown in Table 2, it was reported that iron ion solution or ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$) was actually the main cause of color change due to the difference in charge type in the iron ion (+2) solution and the iron oxide (+3) ion in the thousand year old barai mud. Hence, it is interesting to see the shade of silk thread refermented in iron ion solution or ferrous sulfate ($FeSO_4 \cdot 7H_2O$) solution compared to silk thread refermentation in thousand year old barai mud from both sites for 20 minutes and then observed with the naked eye how the color shade looked. When measuring the shade with the CR-400 KONICA MINOLTA colorimeter with the CIELAB colorimetric system, there was a value that corresponds to the naked eye or not. So, the next step of comparison of three groups of silk thread tones had been carried out.

Comparison of three groups of silk thread tones

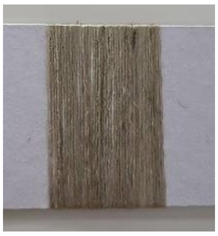
When alum (Al^{3+}) and iron ions (Fe^{2+}) was added, the yellow color of the silk became darker and clearer. It actually affected the tone and color changes of the silk. In the thousand year old barai mud, both types of mud contained the highest levels of iron oxide ions (Fe_2O_3) and Fe^{3+}charges. Therefore, at this stage, the bleached silk threads were divided into three groups with three bundles per group. All of which were dyed with marigold flower extract mixed with alum coloring agent in the first stage for 40 minutes at a temperature of 70-90 °C. Then, the first set of silk threads was fermented and soaked in a solution of iron ions or a solution of ferrous sulfate ($FeSO_4 \cdot 7H_2O$). The second and third silk groups were further fermented and soaked in the Prasat Mueang Tam thousand-year-old Barai mud and the thousand-year-old Barai Kuti Ruesi mud solution in order to study color shades. The results showed that all three groups of silk turned green when observed with eyes, but it was observed that the color tone of the two groups of silk dyed with mud of thousand year old barai was darker than that of silk fermented with ferrous sulfate solution. In addition, silk threads fermented with Prasat Muang Tum barai mud solution had a darker shade than silk threads fermented with mud of Kuti Ruesi. This is because in the mud of thousand year old barai, Prasat Muang Tum is rich in iron ions (Fe^{3+}) in larger quantities and more concentrated.

From Table 3, when measuring the average shade values (L* a* and b*) of the 3 types of dyed silk, it was found that the lightness decreased as observed from the L* value of the dyed silk thread. The extract from marigold flowers mixed with alum was 77.67 (Table 1) decreasing by 66.06, 43.00 and 49.03, respectively, and the b* value or the yellowness from 35.90 (Table 1) decreased to 14.35, 14.15 and 18.57. It clearly showed that the yellowness actually decreases and the greenness increased instead, as observed from the a* shade value in Table 3, which decreases from 5.14 (Table 1) to 3.53 3.23. and 3.39. Thus it clearly confirms that the shade of silk thread changed color from yellow to grayish green indeed, which was caused by the influence of iron ion (Fe^{3+}) in both barai mud solution and the ferrous sulfate (Fe^{2+}) solution. This is consistent with the research of Manyim *et al.* [20] who reported that he dyed silk with natural dyes from red onion peels using a coloring agent, iron ion solution, ferrous sulfate, and alum solution, and found that the silk shades were colored in grey-green. It was further noteworthy that different types of iron ion solutions produce shades in the same direction. As reported by Hutakamol *et al.* [21], it was described that iron ion-type pigments typically gave darker shades in black or gray tones. For this reason, when dyed over the original shade, which was yellow, it produced a grayish green color mixture depending on the concentration and density or abundance of iron ions. However, there was a caution that if too much iron ion solution was used, it might cause the fibers to become brittle and easily broken. The study also found that mud cured silk thread to be softer and shinier than silk thread fermented with ferrous sulfate ion solution. The reason is because in the thousand year old barai mud has various minerals that can be precipitated. Most of them are iron oxide (Fe^{3+}), also known as akaganeite, which have strong metal properties that adhere to fabric well. It also contains secondary minerals such as silica (SiO_2), alumina (Al_2O_3) and titanium dioxide (TiO_2) that enhance the properties of fabric fibers to make them soft and shiny.

Table 2 The Main Elemental Constituents of Thousand Year Old Barai Mud from Both Sites

Order	Type of Elements	Result	
		Prasat Muang Tum	Kuti Ruesi
1	Al_2O_3	6.663%	7.522%
2	SiO_2	16.476%	36.018%
3	SO_3	0.432%	N.D.
4	K_2O	0.368%	2.944%
5	CaO	3.206%	1.151%
6	TiO_2	7.517%	6.280%
7	Cr_2O_3	0.133%	0.068%
8	MnO_2	0.449%	0.626%
9	Fe_2O_3	64.103%	44.222%
10	NiO	N.D.	0.095%

Table 3 Re-dyed or Fermented Silk Threads in Both Thousand Year old Barai Mud for 20 Minutes

Type Of Mordant	Conditions	Shadow value (Average)		
		L^*	a^*	b^*
Ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$)		66.06 ± 0.72	3.53 ± 0.04	14.35 ± 0.02
Mud slurry, barai thousand years old, Prasat Muang Tum		43.00 ± 0.66	3.23 ± 0.02	14.15 ± 0.03
Mud slurry, barai thousand years old, Kuti Ruesi		49.03 ± 0.47	3.39 ± 0.04	18.57 ± 0.15

Statistical Analysis

One way analysis of variance (One way ANOVA) was performed using SPSS program to compare the pairwise shade mean of the three staining methods. The within-group and between-group discrepancies of the data were analyzed using the F statistic (F-test) first because it was a comparison of the means of two or more population groups. The test results showed that all three staining types passed preliminary agreement since the value was higher than the significance level 0.05, where the luminance shade (L*) was 0.361, the green shade (a*) was 0.056, and the yellow shade (b*) was 0.885. This means that the variance of each sample was equal. Pairwise comparisons were then performed using Turkey and Scheffe's methods. The differences between the three staining methods were found at a significance level of 0.05.

Structural Characteristics of the Binding of Silk Threads with Dyes and Colorants

In this step, the main objective was to study the important functional groups of pure silk (not dyed) to confirm the formation of complex compounds when bound with various heavy metals and natural colorants. As shown in Fig. 6. it was found that the wave number position between 3600-3400 cm^{-1} was the hydroxyl group –OH stretching band. Next, the wave number position between 3200-3300 cm^{-1} was the amine group N–H stretching band. Both groups had overlapping vibrations of the molecules of both types. In addition, a slight peak appeared at wave numbers between 1700 – 1600 cm^{-1} (1612 cm^{-1}). This further confirmed the existence of C=O stretching vibrations of the carbonyl group [22]. The wave number position between 1300 – 1000 cm^{-1} was the vibration of the C–H bending (1366 cm-3) C-N and C-C stretching (Amide III, 1228 cm^{-1}) groups. Finally, the wave number position of 1036 cm^{-1} was the vibration of the C–C stretch (β-sheet) [19].

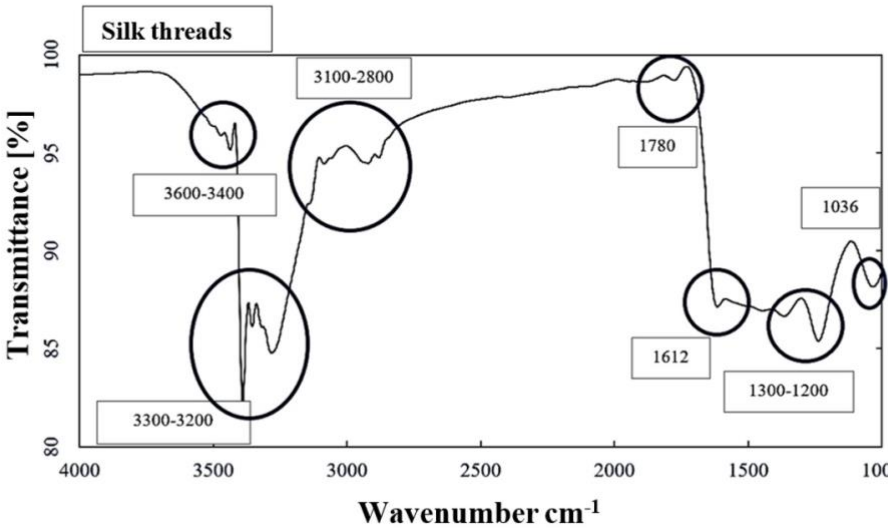


Fig. 6 The characteristics of functional groups of silk threads

Therefore, As shown in Fig. 6., it clearly confirmed that silk contained important functional groups that could actually form complex compounds with silk and natural dyes. This is in line with the research of Rodríguez-Arce and Saldías [18]. Most of which were found in nature contain quercetin as shown in Fig. 7. The structure of quercetin could bind heavy metals in 3 positions, which were the oxo group (–O) and the hydroxyl group (–OH) in the neutral solution or in the condition that negative ions.

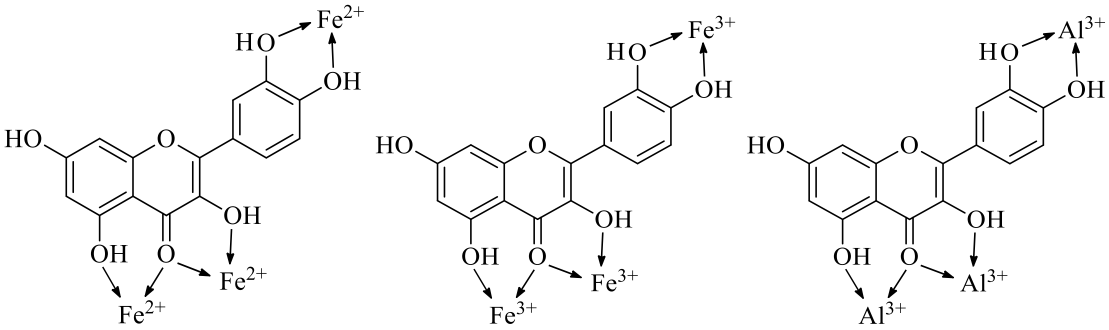


Fig. 7 The flavonoid with different metals complex

Therefore, it is possible that the alum ion or potassium aluminum sulfate solution and ferrous sulfate ion solution due to the electron exchange reaction occurring could capture flavonoids from marigold flowers. It was a stable complex. This was the reason for changing the pH value. According to Zhou *et al.* [23] study, the formation of complexes between three flavonoids, baicalin, quercetin, and rutin, was investigated with two metal salts, including ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and titanium sulfate ($Ti(SO_4)_2$). It was found that when the silk was dyed with all three flavonoid extracts, the silk had a greenish yellow color. When repeated dyeing with colorants or salts of iron ferrous sulfate, ion solution, it showed dark green. Titanium sulfate gave orange-yellow color. Therefore, it could be confirmed that flavonoid extracts from marigold flowers could form complexes with 3 heavy metal ions, Al^{2+}, Fe^{2+}, and Fe^{3+} that were attached to silk threads. This made silk threads had non-fading properties. The model of the structure of the silk thread and the metal salt ions was as shown in Fig. 8.

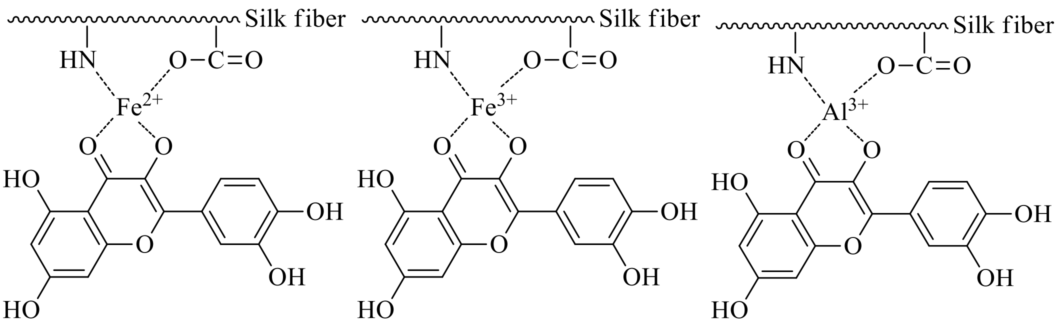


Fig. 8 The structure model of silk thread with metal ions and flavonoid extract from natural dyes

4. Conclusion

The extracts from marigold flowers were flavonoids, which could form color complexes with heavy metals such as aluminum (Al^{+3}) and iron (Fe^{2+}) and Fe^{3+}). The reason why the dyed silk had a darker shade and changes from the original is because in the thousand year old barai mud from both sources was rich and dense with iron ions (Fe^{3+}). Thus it causes the color of the silk thread to change from yellow to dark green. With the above reasons and conclusions, this research has created a new body of knowledge in Bankhokmuang community. The people in the community can pass on this knowledge to the future generations who are interested in the silk dyeing. This could make the local people proud of their hometown in the present and the future.

5. Suggestions

Because this research is a study of the main elemental constituent of the soil in the ancient site, everyone should dress modestly before going in for activities and should have permission from the local community leaders at all times. Moreover, after completing the research, researchers should apply the knowledge gained to other types of mordant instead of using mud in sacred places to preserve and conserve such places for future generations to study further, and continue to tell stories to everyone.

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