Research Article

Dyeing of Silk with Anthocyanins Dyes Extract from *Liriope platyphylla* Fruits

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A new source of natural anthocyanins dyes, from *Liriope platyphylla* fruit, is proposed. This paper analyzes the dye extracts, the primary color components of the extracts, the color features of the extracts under different pH conditions, and their application in silk dyeing. The research shows that, nine anthocyanins are found in *L. platyphylla* fruits by analyzing the results of the HPLC/DAD, MS, and MS/MS spectra. The five major anthocyanins related to delphinidin, petunidin, and malvidin derivatives take up 91.72% of total anthocyanin contents. The color of the solution is red under acidic condition ($\text{pH} < 3.0$) and stays in yellow under alkaline condition with pH values above 7.0. The dye extracts applied to silk fabric with mordant free dyeing show different color under different pH conditions, changing between purple, blue, green, and yellow. However, the dyed colors is light and the dyeing rate is low. Metal mordant such as Sn in chelation enhances the dye depth and improves the fastness of the dyed silk fabrics, especially in silk fabrics dyed by premordanting and metamordanting.

1. Introduction

Natural dyes are generally environment friendly and have many advantages over synthetic dyes. In recent years, the applications of natural dyes are researched due to their biodegradability and higher compatibility with the environment [1–3]. Anthocyanins, with their common structure shown in Figure 1, are flavonoids commonly found in flower petals, fruits, and leaves and produce orange, red, violet, and blue colours [4, 5]. Earlier studies show that anthocyanins are especially abundant in bilberry, strawberry, raspberry, grape skin, blackberry, and so on [6–10]. Interests in these water-soluble pigments have been increased substantially during the last decade because of the increasing evidence demonstrating potential therapeutic effects. Researches also show that anthocyanins have strong oxidation resistance, inhibit the growth of cancerous cells, inhibit inflammation, and have antiobesity effects. The therapeutic properties of anthocyanins have been reviewed and proved [11–14]. Despite the great application potentials that anthocyanins represent for food, pharmaceutical, and cosmetic industries, their

application in textile is limited as the pigments lack affinity for the fiber and cannot be sustained during washing and therefore requires further investigation.

In general, anthocyanins show colour variation caused by pH or metal chelation changes. As natural dye used in textile, it is important to study the color coordinates of anthocyanin dye extracts and the dyed fabrics influenced by the pH values of dyeing bath, the metal mordant, and the mordanting processes, which would help to understand the basic color effects of the dyed fabrics using anthocyanin extracts as natural dyes.

L. platyphylla is an evergreen perennial, widely distributed in China, India, Japan, and Korea. Its dried tubers have been commonly used as traditional herbal medicine to cure acute and chronic inflammation and cardiovascular diseases including thrombotic diseases [15, 16]. Various phytochemical and biochemical investigations on tubers of *L. platyphylla* have been reported [17–19]. However, up to now, few reports can be found on analysis and applications of the fruits of *L. platyphylla*. In this work, the analysis of the anthocyanin components of the *L. platyphylla* fruit extracts was

R ₁	R ₂	Anthocyanin	Aglycon
H	H	Pelargonin	Pelargonidin
OH	H	Cyanin	Cyanidin
OCH ₃	H	Peonin	Peonidin
OH	OH	Delphin	Delphinidin
OCH ₃	H	Petunin	Petunidin
OCH ₃	OCH ₃	Malvin	Malvidin

FIGURE 1: Structure of common anthocyanins.

FIGURE 2: Fruits used for extraction.

FIGURE 3: HPLC separation of anthocyanins in the fruits of *L. platyphylla*.

performed with HPLC/DAD, MS, and MS/MS spectra. The color coordinates of the extracts and silk fabrics dyed by the extracts were analyzed with CIE1964-XYZ and CIE1976LAB of the Commission Internationale de L'Éclairage.

2. Experiments

2.1. Chemicals. The methanol, SnCl_2 , and hydrochloric acid were analytical-grade reagents obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. (China). Trifluoroacetic acid (TFA) was analytical-grade reagent obtained from Aladdin Chemistry Co., Ltd. (China).

2.2. Plant Material. Fruits of *L. platyphylla* were harvested in Zhejiang Sci-Tech University, Hangzhou, Zhejiang, China, in January 2013 and the samples (Figure 2) were packed immediately and stored in a freezer at -20°C until processed.

One criterion of the fruit is its moisture content, which is evaluated first for the fresh fruits. Moisture content is the percentage of water contained in a material. 100 g of the fresh fruits was taken and kept in an oven at 100°C for 24 h and weighted afterward. Triplicate assays were applied. The moisture content (%) of the fresh fruits is $50.2 \pm 8.6\%$.

2.3. Extraction of Anthocyanin Dyes. The fruits were crushed with a mortar and weighed for preparation. Three typical methods are used in this paper, which are mainly differentiated by the solvents used. All the three methods extracted anthocyanins by putting the fruits into a curtain solvent, stirring them for 10 min, and keeping them 24 h at room

temperature in darkness without stirring [30, 31]. The mixture was then filtered through a Buchner funnel under vacuum. The solid residue was washed with the same solvent until a clear solution was obtained. The combined filtrates were dried using a rotary evaporator at 55°C or 60°C , which was chosen individually for each solvent for the best extraction results. The concentrate was dissolved in distill water and the solution obtained was used for dyeing. The first method uses methanol containing 0.1% (V/V) of concentrated hydrochloric acid with 55°C for drying and the second method uses solvent $\text{CH}_3\text{OH}/\text{TFA}/\text{H}_2\text{O}$ 49.5/0.5/50 v/v/v with 60°C for drying, while the third method uses methanol containing 5.0% (W/V) of concentrated citric acid with 55°C for drying.

2.4. Total Anthocyanins Content Measurement. Total anthocyanins content (TAC) was normally determined using pH differential method and expressed as cyanidin-3-glucoside (Cy-3-glc) equivalents, according to the following formula [32, 33]:

$$c [\text{mg/L}] = \frac{A \times M_w \times \text{DF} \times 1000}{\epsilon_M \times d}, \quad (1)$$

where A is the absorbance value in visible region, equaling $(A_{\lambda_{\text{max}}} - A_{700})_{\text{pH}1.0} - (A_{\lambda_{\text{max}}} - A_{700})_{\text{pH}4.5}$, which corresponds to sodium acetate-acetic acid buffer solution when $\text{pH} = 4.5$ and potassium chloride-hydrochloric acid buffer solution when $\text{pH} = 1.0$ to dilute the anthocyanin extracts; M_w is the molecular weight (g/mol) of Cy-3-glc (449.2 g/mol in the analysis); DF is the dilution factor; ϵ_M is the molar extinction coefficient (26,900 for Cy-3-glc); and d is the path length of the cuvette (1 cm in the analysis). The experiments were performed in triplicate assays.

FIGURE 4: Structure change of anthocyanin with pH in aqueous solution.

FIGURE 5: Visible spectra of *L. platyphylla* fruit extracts at several pH values.TABLE 1: Total anthocyanin contents by different acids (mg/100 g fresh weight; mean $\pm$ SD of triplicate assays).

Extracting acid	TAC
0.1% HCl	474.45 $\pm$ 25.67
5% citric acid	615.84 $\pm$ 34.21
0.5% TFA	535.37 $\pm$ 28.75

2.5. HPLC/DAD Analysis. HPLC/DAD experiments were performed using the HPLC machine (1260 Infinity, Agilent Technologies, CA, USA). For analysis, the separations of anthocyanins were carried out on Agilent Zorbax SB-C18 column (4.6 $\times$ 250 mm, 5 μ m) (Agilent Technologies, CA, USA)

FIGURE 6: Visible spectra of Sn chelated anthocyanins extracts in buffer solutions at pH 1.0.

equipped with a C18 guard column (Agilent Technologies, CA, USA). The column oven temperatures were set to 35°C. The mobile phase consisted of 5% formic acid (solvent A) and 100% CH₃CN (solvent B). For the separation of anthocyanin extracts on SB-C18 column (4.6 $\times$ 250 mm, 5 μ m), the elution conditions were set as follows: isocratic elution 0% B, 0–10 min; linear gradient from 0% B to 10% B, 10–20 min; 14% B, 20–60 min; 100% B, 60–80 min; flow rate 0.5 mL min⁻¹; and injection volumes 10 μ L. The detected wavelength was 520 nm and all spectra peaks from 250 nm to 640 nm were recorded.

2.6. HPLC/MS and HPLC/MS/MS Analysis. HPLC/MS and HPLC/MS/MS experiments were performed using the same HPLC machine (Agilent Technologies) equipped with a mass

TABLE 2: Identification of anthocyanins in *L. platyphylla* fruit extracts.

Peak	RT (min)	MS	MS ²	UV-Vis data				Tentative identification	References
				$\lambda_{vis,max}$	$\lambda_{acyl,max}$	$A_{440}/A_{vis,max}$	$A_{acyl,max}/A_{vis,max}$		
1	31.330	465	303	524	346	28.74	9.51	Dp 3-glu	[20–22]
2	32.217	611	465/303	525	347	28.18	9.51	Dp 3-rut	[23]
3	35.882	479	317	515	332	32.47	6.84	Pt 3-gal	[21, 24]
4	37.867	595	449/287	517	325	31.13	18.13	Cy 3-rut	[21, 23, 25–27]
5	39.807	479	317	525	345	27.99	11.19	Pt 3-glu	[21, 22, 26, 28]
6	41.460	625	479/317	527	347	27.38	9.97	Pt 3-rut	[23]
7	50.835	609	463/301	518	331	31.97	8.77	Pn 3-rut	[23, 24, 29]
8	52.762	493	331	527	348	27.96	11.48	Mv 3-glu	[20–22]
9	55.024	639	493/331	528	348	26.86	10.57	Mv 3-rut	[23]

RT: retention time; Dp: delphinidin; Cy: cyanidin; Pt: petunidin; Pn: peonidin; Mv: malvidin; glu: glucoside; rut: rutinoside; gal: galactoside.

spectrometer (LCQ FLEET, Thermo Fisher Scientific, PA, USA) and electrospray ionization (ESI). The HPLC column and HPLC conditions for the mobile gradient were the same as those in HPLC/DAD experiments. The MS analytical parameters were as follows: polarity, positive; ion source, turbo spray (ESI); capillary temperature, 350°C; capillary voltage, 60 V; spray voltage, 4.5 KV; and full-scan range, from m/z 400–1200. MS² scan of the most abundant ion uses relative collision energy of 20%.

2.7. Mordanting. The weighed silk fabrics were treated with tin metal salts for premordanting, metamordanting, and postmordanting. The amount of mordant used was 5% (o.w.f.). The fabrics were mordanted at liquor ratio of 50:1. In premordanting, fabrics were immersed in the mordant solution at 60°C for 30 min. In metamordanting, fabrics were immersed in a dyeing bath containing both mordant and extracted dyes for 120 min. In postmordanting, fabrics were immersed in a dyeing bath containing only extracted dyes for 120 min and only mordant at 60°C for 30 min, separately. Due to the light sensitivity of the mordants, fabrics after mordanting should be dyed immediately.

2.8. Dyeing. The weighted silk fabric was dyed at a liquor ratio of 50:1. 20 g of dye concentrates was dissolved in 1000 mL deionized water for a piece of fabric weighing 20 g. The fabric was kept in dye bath for 120 min at 60°C. The pH value of the dyeing solution was adjusted with dilute solutions of hydrochloric acid or sodium hydroxide. The dyed fabric was rinsed with cold water and finally dried at room temperature in shade.

2.9. Color Analysis. Colorimetric methods are very useful in characterizing the color properties of pigments. Tristimulus colorimetry has been widely applied. An absorbance spectrum ($\Delta\lambda = 1$ nm) of anthocyanin dye solutions was recorded with a UV-VIS double-beam Spectrophotometers TU-1950 (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). D65 standard illuminant and 10° standard observer

TABLE 3: Color coordinates of the *L. platyphylla* fruit extract at several pH values.

pH	L^*	a^*	b^*	C^*	h
1.0	62.21	45.84	0.80	45.84	1.00
3.0	65.82	33.99	3.69	34.19	6.20
5.0	67.56	12.06	7.09	13.99	30.47
7.0	64.10	4.29	21.13	21.56	78.53
9.0	63.04	4.74	21.47	21.99	77.54
11.0	58.10	3.49	29.67	29.87	83.29
13.0	58.59	4.79	32.04	32.39	81.50

were considered in the calculation. Reference blank measurements were made with the cuvette filled with distilled water. The whole visible spectrum (380–780 nm) was recorded. The CIELAB parameters (L^* , a^* , b^* , C^* , and h) were determined following the CIE1964-XYZ and CIE1976LAB of the Commission Internationale de l'Éclairage.

Color values of dyed fabrics were evaluated by means of color strength (K/S), color differences (ΔE_{cmc}), and other CIELAB values (L^* , a^* , b^* , C^* , and h). With 10 mm sample diameter (geometry $d/10^\circ$), CIELAB values were calculated for illuminant D65 on Datacolor SF600 spectrophotometer with software data match Color Tools 3.1 (Datacolor International, NJ, USA). Five measurements were made on each sample and variations in the percentage reflectance values over range of 400–700 nm were recorded.

In the uniform space CIELAB, L^* corresponds to the brightness (100 = white, 0 = black), a^* to the red-green coordinate (positive sign = red, negative sign = green), and b^* to the yellow-blue coordinate (positive sign = yellow, negative sign = blue). Chroma (C^*) is the quantitative attribute of colourfulness. Hue (h) is the attribute according to which colors are defined as reddish, greenish, and so forth. The total colour difference (ΔE^*) between two samples is estimated using the following expression:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}, \quad (2)$$

FIGURE 7: Some colour samples obtained by metamordanting dyeing and control (without mordant) dyeing.

TABLE 4: Color coordinates of the Sn chelated anthocyanins extracts in buffer solutions at pH 1.0.

No.	Concentration of Sn^{2+} (mol/L)	λ_{max} (nm)	L^*	a^*	b^*	C^*	h
1	0	526	46.90	69.19	24.84	73.52	19.75
2	0.005	531	29.72	56.47	-2.30	56.52	357.66
3	0.010	532	20.74	46.53	-5.05	46.80	353.80
4	0.015	534	16.91	42.43	-6.83	42.97	350.85

TABLE 5: Silk dyeing with *L. platyphylla* fruit extracts at several pH.

pH	L^*	a^*	b^*	C^*	h^*	ΔE^*
1.0	58.76	16.79	-7.59	18.43	335.66	40.21
3.0	69.26	8.88	0.41	8.89	2.65	26.14
5.0	70.68	0.25	1.95	1.97	82.64	22.94
7.0	71.93	-0.66	7.65	7.68	94.93	22.17
9.0	74.66	-0.17	12.73	12.73	90.76	21.29
11.0	74.34	1.13	13.42	13.47	85.19	21.95
13.0	80.92	2.94	18.76	18.99	81.08	20.48

TABLE 6: Silk dyeing with *L. platyphylla* fruit extracts with tin mordanting at several pH by premordanting.

pH	L^*	a^*	b^*	C^*	h^*	ΔE^*
1.0	45.1	15.24	-15.57	21.79	314.39	54.2
3.0	43.76	11.92	-23.95	26.75	296.47	57.96
5.0	36.62	10.41	-24.43	26.56	293.08	64.13
7.0	42.49	5.81	-19.41	20.26	286.65	56.14
9.0	51.61	2.01	-12.77	12.93	278.93	44.91
11.0	64.14	2.14	4.82	5.28	66.07	29.62
13.0	72.98	0.17	9.57	9.57	88.98	21.65

where ΔE^* indicates the total color differences between dyed fabric and undyed original silk fabric. The color indicators of the undyed silk fabric are L^* (93.6), a^* (-0.28), b^* (3.00), C^* (3.01), and h^* (95.42).

2.10. Fastness Testing of Dyed Fabrics. The dyed silk fabrics were tested according to AATCC standard methods. The specific tests were color fastness to light, AATCC 16-2004;

TABLE 7: Silk dyeing with *L. platyphylla* fruit extracts with tin mordanting at several pH by metamordanting.

pH	L^*	a^*	b^*	C^*	h^*	ΔE^*
1.0	55.5	13.29	-16.16	20.92	309.42	44.75
3.0	55.7	8.19	-15.93	17.91	297.2	43.2
5.0	55.52	6.34	-17.93	19.05	289.44	43.97
7.0	43.73	6.4	-22.01	22.92	286.2	56.19
9.0	52.84	-0.72	-18.32	18.34	267.76	46
11.0	56.7	4.41	-5.91	7.37	306.72	38.24
13.0	63.02	2.61	2.43	3.57	42.98	30.72

color fastness to crocking, AATCC 8-2007; color fastness to washing, AATCC 61-2009; and color fastness to perspiration, AATCC 15-2009. The colors of the specimens were rated by referencing to the Gray Scale for Color Change. The staining on each undyed original fabric was rated by means of the Gray Scale for Staining.

3. Results and Discussion

3.1. Effect of Acids on Total Anthocyanin Content. Anthocyanin from the fruits was extracted using 0.1% HCl, 5% citric acid, or 0.5% TFA. The total anthocyanin contents extracted from the fruits using different acids are shown in Table 1. The results show that the citric acid gives better yield and deeper color, which produce 29.8% and 15.0% more anthocyanins than 0.1% HCl and 0.5% TFA, respectively.

3.2. Characterization of Anthocyanins in the Fruit Extracts. Figure 3 shows the HPLC chromatograms of anthocyanin extracts carried on C18 columns. In Figure 3, nine different anthocyanins from the fruits are identified. Peaks 1, 2, 5, 6, and 9, eluted at 31.330 min, 32.220 min, 39.807 min, 41.460 min, and 55.024 min, indicate the major anthocyanins and take up 9.32%, 8.06%, 9.51%, 36.54%, and 28.29% of the total anthocyanin content, respectively. The four others (peaks 3, 4, 7, and 8) take up total 8.28%, each accounting for 0.5% to 4% of the total anthocyanin content.

By combining the results of DAD, MS, and MS/MS spectra, the nine different anthocyanins extracted from the fruit of *L. platyphylla* are summarized in Table 2. Among the nine different anthocyanins, delphinidin 3-glucoside (Dp 3-glu), delphinidin 3-rutinoside (Dp 3-rut), cyanidin-3-glucoside (Cy-3-glu), petunidin 3-glucoside (Pt 3-glu), petunidin 3-rutinoside (Pt 3-rut), malvidin 3-glucoside (Mv 3-glu), and malvidin 3-rutinoside (Mv 3-rut) were confirmed by previous reported NMR spectroscopy data [34].

3.3. Effect of pH Values on Anthocyanin Dye Colors. Anthocyanins show great susceptibility toward pH variation, being more stable in acidic media at low pH values than in alkaline solutions at high pH value. The ionic nature of anthocyanins enables the changes of the molecule structures according to the prevailing pH values and results in different colors and hues at different pH values. In acidic aqueous solution, anthocyanins exist in the form of four main equilibrium species

TABLE 8: Silk dyeing with *L. platyphylla* fruit extracts with tin mordanting at several pH by postmordanting.

pH	L^*	a^*	b^*	C^*	h^*	ΔE^*
1.0	67.46	1.07	-1.93	2.21	299.03	26.63
3.0	71.78	-4.92	0.24	4.92	177.21	22.47
5.0	72.86	-5.22	0.36	5.24	176.01	21.47
7.0	73.49	-5.3	5.91	9.01	99.46	19.85
9.0	78.72	-0.62	11.19	11.21	93.18	16.98
11.0	76.84	-0.66	11.89	11.91	93.19	18.97
13.0	85.93	-0.86	16.75	16.77	92.95	15.76

(Figure 4) [35]: red flavylium cation, blue quinoidal base, colorless carbinol or pseudobase, and yellowish chalcone. Under acidic conditions ($\text{pH} < 2.0$), the anthocyanins exist primarily in the form of red flavylium cation. Increasing the pH value causes fast loss of the proton and produces quinoidal base forms, blue or violet. At the same time hydration of flavylium cation occurs and the carbinol or pseudobase is generated, which slowly reaches equilibrium and produces the chalcone in faint yellow. The relative amounts of above four forms of anthocyanins at the equilibrium condition vary according to pH values.

The visible spectra of *L. platyphylla* fruit extracts at different pH values are shown in Figure 5. The values of the color indexes are described in Table 3. Figure 5 shows that, with the increasing of pH value, the maximum visible absorption peak moves towards the long wavelength. The absorbance decreases first and then increases. Table 3 shows that the color of the solution is red under strong acidic condition ($\text{pH} < 3.0$) and stays in yellow under alkaline condition with pH value above 7.0.

As seen in Table 3, the lightness index L^* is inversely correlated to the color contents in the solution. When under acidic condition ($\text{pH} < 3.0$), the index L^* of the *L. platyphylla* fruit dye solution is stable, the pigment mainly presents in the form of red anthocyanin molten salt, and the a^* is positive and relatively high. When pH increases to above 3.0, the pigment gradually transforms from colored substances into colorless substances, which are mainly colorless methanol false alkali. When pH increases to above 5.0, the value of L^* starts to increase and the solution color becomes deepened, transforming from red anthocyanin molten salt to blue quinone alkali. With the further increasing of the pH value, the solution color becomes lighter, since the blue quinone alkali or colorless methanol false base structure transforms to light yellow chalcone structure. A similar conclusion can be obtained from the analysis of a^* and b^* values. The C^* value reflects the singularity of each pigment structure in the solution. The more complex the pigment structure is, the lower the value of C^* is. Based on the data in Table 3, the C^* value is higher under strong acid ($\text{pH} < 3.0$) or strong base ($\text{pH} > 11.0$), which suggests the chemical structures of pigments in these two solutions are simple. They are mainly in the form of anthocyanin molten salt at $\text{pH} < 3.0$ and chalcone structure at $\text{pH} > 11.0$, which is consistent with the previous analysis.

TABLE 9: Fastness properties of dyed silk fabrics with *L. platyphylla* fruit extracts.

Dyeing methods	pH value of dyeing liquor	WF ^a	Perspiration CC ^b	Staining	Crock _{dry}	Crock _{wet}	LF ^c
Control (without mordant)	1.0	2	2	1.5	2.5	2	1.5
	3.0	2.5	2	1.5	2.5	2	1.5
	5.0	2.5	2	1.5	2.5	2.5	1.5
	7.0	2.5	2	1.5	2.5	2.5	1.5
	9.0	2	2	2	2.5	2.5	1.5
	11.0	2.5	2.5	2	2.5	2.5	1.5
	13.0	2.5	2.5	2	2.5	2.5	2
Premordanting	1.0	3.5	3	3.5	3.5	3.5	2.5
	3.0	3.5	3	3.5	3.5	3.5	4
	5.0	4	3.5	4	4	4	3.5
	7.0	4	3.5	3.5	4	3.5	3.5
	9.0	3.5	3.5	3.5	4	3.5	3.5
	11.0	4	3.5	3.5	4.5	3.5	3.5
	13.0	4.5	3.5	4	4.5	3.5	3.5
Metamordanting	1.0	3.5	3	3	3.5	3.5	3.5
	3.0	3.5	3.5	3.5	3.5	3.5	3.5
	5.0	4	3.5	3.5	3.5	4	4
	7.0	4	4	3.5	3.5	3.5	3.5
	9.0	3.5	3.5	4	3.5	3.5	4
	11.0	4	3.5	3.5	4	3.5	4
	13.0	4	3.5	4	4	3.5	3.5
Postmordanting	1.0	3.5	3.5	3.5	3.5	3.5	3.5
	3.0	3.5	3.5	3.5	3.5	3.5	4
	5.0	4	3.5	3.5	4	4	4
	7.0	4	4	3.5	4	3.5	4
	9.0	4	3.5	3.5	4	3.5	3.5
	11.0	4	4	4	4	3.5	3.5
	13.0	4	4	4	4	3.5	3.5

^aWashing fastness, ^b color change, and ^clight fastness.

3.4. Metal and Anthocyanin Chelation. Metals have been commonly used to stabilize the color of cyanidin, delphinidin, and petunidin, which have more than one free hydroxyl group in the chromane ring and are capable of metal chelation [36, 37]. The most common metals in anthocyanin complexes are tin (Sn), copper (Cu), iron (Fe), aluminum (Al), and magnesium (Mg) [38]. The main characteristic of anthocyanins and anthocyanindins with *o*-di-hydroxyl groups in the B ring (Cy, Dp, and Pt) is their ability to form metal-anthocyanin complexes [35, 39]. The resultant formations of metal-anthocyanin complexes were suggested by the sample colors as shown by L^* , a^* , b^* , C^* , and h . Visible spectra of Sn chelated *L. platyphylla* fruits extracts at pH 1.0 are shown in Figure 6. The color coordinates are shown in Table 4. As shown in Figure 6, with the increasing of the concentrations of Sn^{2+} , the bathochromic maximum absorption wavelength of the *L. platyphylla* fruits shifts with $\Delta\lambda = 5\text{--}8\text{ nm}$, the absorbance increases significantly, and the hyperchromic change is obvious.

Based on the CIELAB color system in Table 4, with the increasing of the Sn^{2+} concentration, the color indicators such as L^* , a^* , b^* , and C^* of the solution show a decreasing trend. The color of the solution changes from red to blue

violet as shown in Table 4, which suggests that the Sn^{2+} forms a violet complex with the red flavylum cation.

3.5. Dyeing of Silk by the Extracts. The silk was dyed using the *L. platyphylla* fruit extracts without mordanting, with tin premordanting, metamordanting or postmordanting at different pH values. The corresponding CIELAB values of dyed silk are shown in Tables 5, 6, 7, and 8, respectively. Some colour samples are shown in Figure 7. As concluded from the pigment color indicators, the dyed silk fabric without mordant dyeing shows different color results under different pH conditions, such as purple, blue, green, and yellow. The dyed color is light and the dyeing rate is low. The color is comparable deep with pH = 1.0 and becomes lighter with the increasing of the pH values.

Compared to silk fabrics dyed without mordanting in Table 5, silk fabrics dyed with stannous chloride mordant has deeper dyed color as shown in Table 6 to Table 8. The total color difference ΔE^* is increased obviously. The color of the fabric dyed with mordants appears to be red-purple, blue-purple, blue, green, yellow, and so forth.

Different pH values of dyeing solutions cause differences not only in hue color and ΔE^* values but also in L^* , a^* , b^* ,

C^* , and h^* values. In case of mordant dyeing, the color depth of dyed silk fabric with stannous chloride postmordanting is low and the dyeing results are not satisfactory. When the dyed fabric is under postmordant processing, part of the anthocyanins transfers from fabric to the dyeing bath.

The washing fastness, perspiration fastness, crocking fastness, and light fastness were investigated with the results shown in Table 9. The results are satisfactory for SnCl_2 mordanted fabrics due to the special chelation of anthocyanin color moieties and stannous.

4. Conclusion

The anthocyanin extracted from *L. platyphylla* fruits as a source of natural dyes has been utilized for the first time for silk fabrics dyeing to my best knowledge. In principal components analysis, nine anthocyanins from the fruits were identified by analyzing the results of the HPLC/DAD, MS, and MS/MS spectra. The five major anthocyanins related to delphinidin, petunidin, and malvidin derivatives take up 91.72% of total anthocyanin contents. In terms of acids used for extraction, 5% citric acid gave better yield and deeper color compared with 0.1% HCl and 0.5% TFA. In silk fabrics dyeing, the fruit pigment under mordant free condition presents different color results, changing between purple, blue, green, and yellow. However, from the point of the dyed color, the color is light and the dyed rate is low. The metal mordant such as tin in chelation with the extracts greatly enhances the dye depth and improves the fastness properties of the dyed silk fabrics, especially for silk fabrics dyed with premordanting and metamordanting.

Conflict of Interests

The authors have declared that they have no conflict of interests.

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