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〈Research Paper〉

Improvement of Light Fastness of Berberine Colorant by Natural Antioxidants

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Abstract— In order to improve the light fastness of a natural colorant berberine, several natural antioxidants such as gallic acid, L-ascorbic acid, and α-tocopherol were applied by aftertreatment method. Even though the increase in light fastness of berberine colorant was not substantial, L-ascorbic acid was the most effective. It was considered that this improvement of the light fastness was due to high antioxidation action of L-ascorbic acid to colorant, which led very highly excited species of the colorant formed by photo-energy to return to the original stable state without being decomposed.

Keywords: *light fastness, berberine, Amur Cork tree, antioxidant, L-ascorbic acid*

1. Introduction

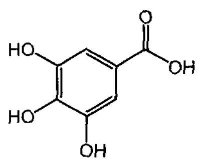
The interests in natural dyes are continuously being sustained for several reasons; non-toxicity, less negative effect of effluent, aesthetic aspect and the use of sustainable resource and so on[1-6]. Although the application of the natural dyes are not widely used in commercial purpose, they have attracted attention of many researchers mostly in Asian countries. Nevertheless, the natural dyes have several technical disadvantages such as stability, reproducibility, and fastness, not to mention of agricultural and economical problems. Especially among them, light fastness of natural dyes is one of most important requirements in their utilization for textile coloration.

Therefore, in this study the light fastness of berberine colorant, a major color component of Amur Cork tree, was studied to be improved by using several biological antioxidants such as α-tochopherol, L-ascorbic acid, and gallic acid.

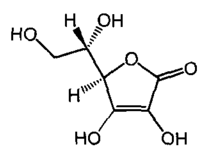
2. Experimental

2.1 Materials

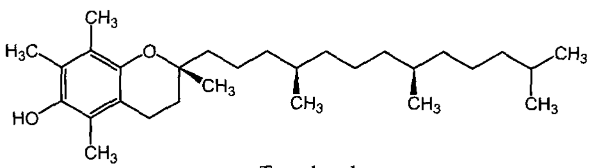
Substrate for dyeing was 100% silk fabric and the resource of a natural colorant was Amur Cork tree from which yellow colorant, berberine, was extracted. The antioxidants used for treatment of berberine-dyed silk fabric in order to improve light fastness were gallic acid, L-ascorbic acid, and α-tocopherol, which were purchased from Aldrich Co. of the highest purity and used without further purification.



Gallic acid



L-Ascorbic acid



α-Tocopherol

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2.2 Extraction of colorants

100g Amur Cork tree chopped mechanically was extracted with 400ml of distilled water at 70℃ for 2 h. The extracted solution was filtered to get 260ml of high concentration extracts under vacuum and then was used for dyeing at certain liquor ratios.

2.3 Dyeing

Silk fabrics were dyed in the extracts at appropriate temperatures for 2 h, and liquor ratio was 1:100. After dyeing, the fabrics were washed 3 times with water at room temperature and then dried in the air.

2.4 Antioxidants treatment

Dyed fabrics were padded with the solution of appropriate concentrations of antioxidants at room temperature and then dried under atmosphere without washing. The pick-up was around 90% on the average.

2.5 Light fastness

Dyed and treated fabrics were examined for light fastness by the same procedure of ISO 105-B02 test method except for different irradiation time which was only 1 h instead of 20 h. This was because most natural colorants were very vulnerable to light so that 20 hours-irradiation could not differentiate the positive effects of the antioxidants on the light fastness of the samples.

2.6 Color measurement

To measure color values, color strength and color difference of the fabrics, a color measuring devise(Konica Minolta spectrophotometer CM-3600d) was used. L*, a*, and b* values were obtained and K/S was calculated for color values and color strength. The color difference was calculated by the equation (1).

The difference of sum of reflectances obtained at every 10nm in the whole range of wavelength was used to compare color difference of the fabrics. The measurement was done by 2º observer under D_{65} light source.

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad \cdots \text{Eq.(1)}$$

2.7 UV-Visible spectrophotometry

To compare the blocking ability of UV energy of the antioxidants, UV-Visible spectrophotometer was used. The same weight of antioxidants were dissolved in ethanol and the absorbance was measured in the range of 200~400nm.

3. Results and discussion

To determine the optimum dyeing temperature, silk fabrics were dyed in the Amur Cork tree extract solutions, which contain berberine colorant, at 30, 50, 70, and 90℃ for 2 h and the result was shown in Fig. 1. Since the highest color strength was obtained at 50℃, that temperature was determined for optimum dyeing temperature of berberine colorant onto silk fabrics and in the following experiment dyeing was carried out at the temperature.

Fig. 2 is the color spectrum of silk fabric dyed with berberine extract showing strong reflectance in yellow color region, which means that the Amur Cork tree extract solution contains yellow berberine as a major color component[4].

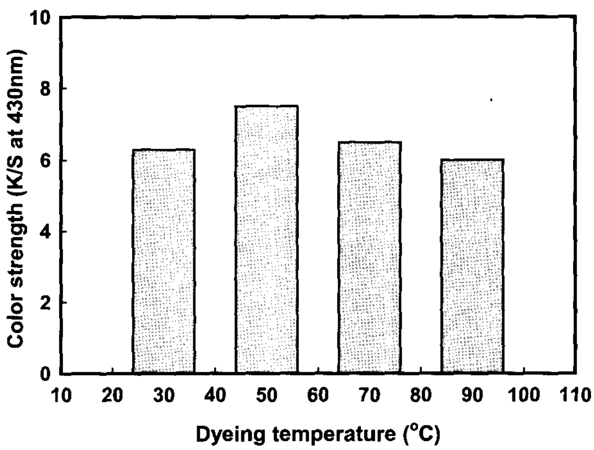


Fig. 1. Color strength of silk fabrics according to temperature.

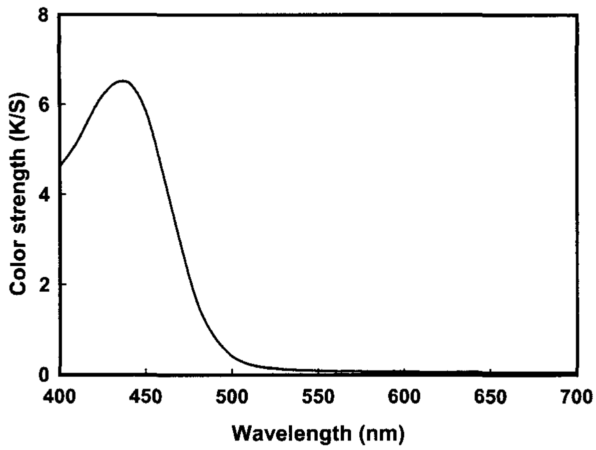


Fig. 2. Color strength spectrum of silk fabric dyed with berberine colorant.

The aim of this study was to investigate whether natural antioxidants improve the light fastness of natural colorants like berberine by scavenging photo-degrading action of various photo-active species, such as active oxygen, very highly excited state colorant, or radicals. It is well known that natural antioxidants like gallic acid, which is one of simple poly-phenols, L-ascorbic acid(vitamin C), and α-tocopherol(vitamin E) act as scavengers against active oxygen and hazardous radicals in living systems so that they could slow down aging of living cells[7-8]. The fading of colorants by light was understood as a very complicated process and could not be explained any single mechanism or factor.

However, what is generally accepted is that the colorants are in highly excited energy state by irradiation of light of high energy and by some reasons if the excited state could not return to the original stable state, the colorant decomposes irreversibly[9-10]. In this series of processes, sometimes a strong active species like active oxygen is thought to be related. In this study also, in order to figure out that those antioxidants could make a light-fading prevention effect on berberine colorants, silk fabrics were dyed with berberine extract and then treated with 1% antioxidants solutions of gallic acid, L-ascorbic acid, and α-tocopherol, respectively. Table 1 shows the color values and color differences of silk fabrics treated with the antioxidant solutions after dyed with berberine extracts, which also shows how much the color of the fabrics has changed by the antioxidant treatment itself compared with the untreated fabric. From the Table 1, it became clear that L-ascorbic acid made least color change to berberine-dyed silk fabric.

Table 2 is the results of fabrics after being exposure to light for 1 hour. For untreated fabric, the color has changed to a great extent showing the color difference 14.31.

However, L-ascorbic acid showed least color difference, 9.42, between unexposed and exposed to light and gave the most positive effect on improvement of light fastness of berberine colorant, even though the color difference was still great comparing with that of synthetic dyes. As for α-tocopherol, since the color difference became larger than that of the untreated, it made light fastness of berberine bad.

As one of investigations about the effect of antioxidants on improvement of light fastness, UV spectra of the antioxidants were obtained. According to Fig. 3, all of the antioxidants absorb ultraviolet rays in the range of 200~300nm.

Table 1. Color values and color differences of silk fabrics dyed with berberine colorant and then treated with 1% antioxidants aqueous solutions

Treatment	L*	a*	b*	ΔE
Untreated	81.76	-1.92	73.31	-
Gallic acid	82.42	-2.01	72.34	2.40
L-Ascorbic acid	81.84	2.46	71.80	2.17
α-Tocopherol	80.40	-0.09	78.10	5.41

Table 2. Color values and color differences of silk fabrics exposed to test light after dyed with berberine colorant and then treated with 1% antioxidants aqueous solutions

Treatment	L*	a*	b*	ΔE
Untreated	75.05	4.92	62.68	14.31
Gallic acid	77.78	2.86	64.97	9.98
L-Ascorbic acid	78.60	6.92	64.16	9.42
α-Tocopherol	73.12	7.27	67.69	14.68

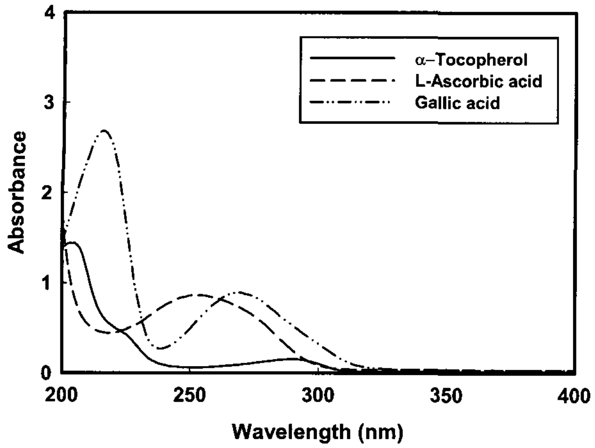


Fig. 3. UV spectra of 0.017g/L solutions of antioxidants in ethanol.

Table 3. Color values and color differences of silk fabrics exposed to test light after dyed with berberine colorant and then treated with different concentration of antioxidant solutions

Treatment		L*	a*	b*	⊿E
untreated	unexposed	77.86	-2.08	71.57	-
	exposed	72.49	3.9	63.21	11.59
0.5%	unexposed	77.03	2.12	67.46	-
	exposed	74.28	6.47	61.25	8.06
1.0%	unexposed	77.42	1.42	68.76	-
	exposed	75.04	5.73	62.71	7.08
2.0%	unexposed	79.22	-1.12	70.29	-
	exposed	78.04	1.88	62.32	8.06
3.0%	unexposed	80.56	-2.7	69.57	-
	exposed	79.37	-0.08	62.28	7.85

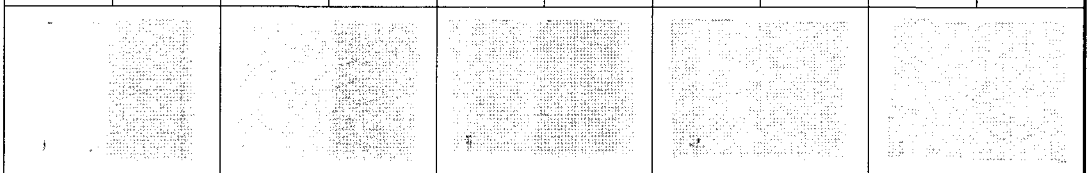
However, what absorbs the greatest amount of the highest energy was gallic acid, which is not coincident to the results of color difference of Table 2. Therefore, it can not be simply explained that the ability of L-ascorbic acid to improve the light fastness of berberine colorant is due to only absorptivity of ultraviolet energy of itself.

Table 3 shows the color values and color differences of silk fabrics after exposed to light, and the silk fabrics were dyed with berberine extracts and then treated with different concentration of L-ascorbic acid in advance to light exposure. In Table 3, the color difference values do not show any significant difference according to the concentration of L-ascorbic acid except for the untreated, which is entirely different results from those for visual observation of Table 4 where the color difference between the unexposed and the exposed is proportionally reduced according to the concentration of L-ascorbic acid.

Therefore, to make those results coincide each other, the difference, between the unexposed and the exposed, of sum of reflectance obtained in the whole wavelength range was calculated and showed in Fig. 4. From the results of Fig. 4, the optimum treatment concentration was obtained at around 2% L-ascorbic acid, which is well corresponds with the result for visual observation. This is because L*a*b* color coordination system is not perfect yet to represent visual sense of human especially in the yellow orange region.

As mentioned before, the photofading of colorants is very complicated and many kinds of factors are related. Therefore, since the photofading inhibition of L-ascorbic acid is also related to many factors, at this moment a decisive explanation could not be made.

Table 4. Pictures of silk fabrics exposed to test light after dyed with berberine colorant and then treated with different concentration of antioxidant solutions

Conc. of Antioxidant	Untreated		0.5%		1.0%		2.0%		3.0%	
	unexposed	exposed	unexposed	exposed	unexposed	exposed	unexposed	exposed	unexposed	exposed
Samples										
Color difference	11.59		8.06		7.08		8.06		7.85	

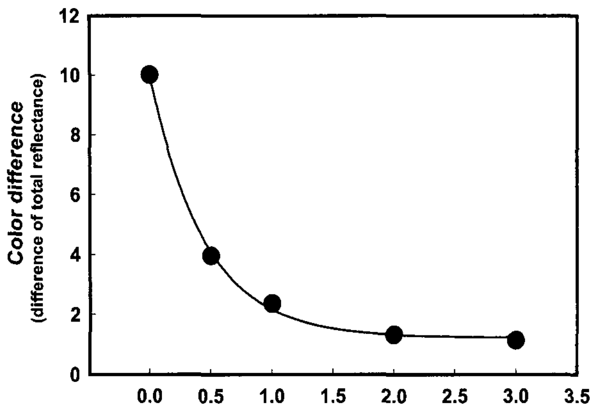


Fig. 4. The difference of sum of reflectance between the unexposed and the exposed silk fabrics to test light after dyed with berberine colorant and then treated with different concentration of antioxidant solutions.

However, a possible scavenging mechanism could be proposed as shown in Fig. 5. The ascorbate(AscH⁻) of L-ascorbic acid is converted to ascorbyl radical(Asc•⁻) by loss of one electron and one proton, and further converted to dehydroascorbic acid(DHA) by loss of additional one electron[7]. This conversion process is entirely reversible. Meanwhile by photo-energy a colorant is transferred to a higher energy state, namely very highly excited state(Dye*).

If the excited state is high enough, for example like a radical state, and photo-energy is supplied continuously, the colorant could be decomposed without returning to the original stable and low energy state.

However, if at this stage ascorbate acts as a scavenger toward the highly excited species like radical, the colorant could return to the original stable state of low energy without being decomposed. It is surely needed to mention that much more researches are necessary to make the proposed mechanism clear.

4. Conclusions

In order to improve light fastness of a natural colorant berberine, several natural antioxidants such as gallic acid, L-ascorbic acid, and α-tocopherol were applied by after-treatment method. Even though the light fastness was not good enough, it was improved considerably by L-ascorbic acid. It was thought that by antioxidation action of L-ascorbic acid very highly excited species of the colorant formed by photo-energy would return to the original stable state without being decomposed irreversibly. However, it is needed to make clear that much more researches are necessary to propose an exact mecahnism for this study.

References

1. H. I. Kim and S. M. Park, A Study on Natural Dyeing(2)-Dyeing of Modified Cotton Fabric with Amur Cork Tree, *J. Korean Soc. Dyers & Finishers*, **13**(3), 172-179(2001).

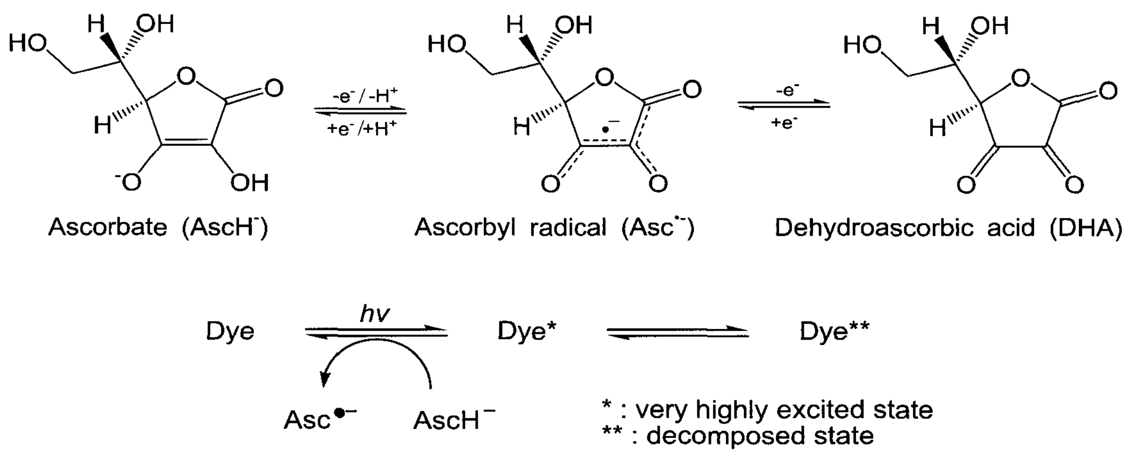


Fig. 5. A proposed scavenging mechanism of L-ascorbic acid against photo-fading of the colorant.

2. K. J. Yong, I. H. Kim, and S. W. Nam, Antibacterial and Deodrization Activities of Cotton Fabrics Dyed with Amur Cork Tree Extracts, *J. Korean Soc. Dyers & Finishers*, **11**(1), 9-15(1999).
3. S. Y. Han and S. C. Choi, Antibacterial Characteristics of the Extracts of Yellow Natural Dyes, *J. Korean Soc. Dyers & Finishers*, **12**(5), 315-322(2000).
4. T. K. Kim, S. H. Yoon, and Y. A. Son, Effect of Reactive Anionic Agent on Dyeing of Cellulosic Fibers with Berberine Colorant, *Dyes and Pigments*, **60**, 121-127(2004).
5. T. K. Kim and Y. A. Son, Effect of Reactive Anionic Agent on Dyeing of Cellulosic Fibers with Berberine Colorant - Part 2: Anionic Agent Treatment and Antimicrobial Activity of a Berberine Dyeing, *Dyes and Pigments*, **64**, 85-89(2005).
6. D. Cristea and G. Vilarem, Improving Light Fastness of Natural Dyes on Cotton Yarn, *Dyes and Pigments*, **70**, 238-245(2006).
7. A. Carr and B. Frei, Does Vitamin C Act as a Pro-oxidant Under Physiological Conditions, *The Journal of the Federation of American Societies for Experimental Biology*, **13**, 1007-1024(1999).
8. E. Burguieres, P. McCue, Y. I. Kwon, and K. Shetty, Effect of Vitamin C and Folic Acid on Seed Vigour Response and Phenolic-linked Antioxidant Activity, *Bioresource Technology*, **98**, 1393-1404(2007).
9. H. Zollinger, "*Color Chemistry*", Wiley-VCH, Zürich, Switzerland, pp.430-437, 2003.
10. S. H. Kim, Y. A. Son, and J. S. Bae, "*Dye Chemistry*", Green Publish Co. Seoul, Korea, pp.291-294, 2005.