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A Study of Onion Skin Pigments in the Extracting Solvents and Residual Pigments after Dyeing the Textiles

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Abstract

To set up the outstanding and scientific dyeing method in making the condensed liquid of pigment obtained from onion skins and the improved reliability, the following basic experiments were performed.

The pigment was extracted in the distilled water at 70℃ and methanol at room temperature and then it was analyzed with LC/MS/MS system (Liquid Chomatography/Mass Spectroscopy/Mass Spectroscophy, LIQ Advantage Max, Thermo Finnigan, USA) for its pigmental characteristics.

The unrefined silk and refined silk were dyed by making use of the derived pigment in such a way.

The chromameter (CR-200, Minolta, Japan) was used to measure the change in surface color in textiles to be dyed by the extracting condition and the color difference ΔE was determined according to the color difference formula CIE LAB through measuring the psychometric lightness L* and chromaticity coordinates a* and b*.

Key Words : onion skin, dyeing property, quercetin, refined silk, unrefined silk, color difference,

Ⅰ. Introduction

This globe has faced the serious environmental pollution lately, which eventually turns the social atmosphere back to the mother nature. As part of its outcome, this leads to the vigorous study and interest in natural dyes. Performed were the pigment analysis on the old fashioned traditional fabrics dyed in natural agents or the work on natural pigments applicable to dye[1-4], the application study on various mordants including a natural dyeing agent[5-8], and the examination about dyeing conditions and property for natural dyeing or the study on dye process improvement and optimization in due course[9-11]. The natural dyes have such unique characteristics as the mild, static, and deep feels, the capability to express many kinds of hues according to different mordants, the relatively less amount of disposal water when compared to those of synthetic dyes, the pharmacological effect intrinsic to natural dyeing agents and so

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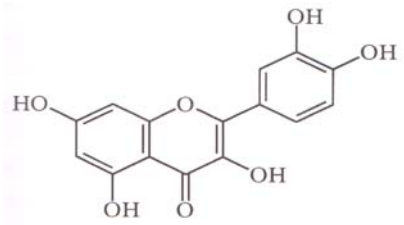
forth. With these reasons, the relevant work is gaining the attraction.[12)13)] Particularly, the examination on natural dyeing is on the increase as people begin to get interested in fabrics dyed from natural stuff with a highly additional value due to its own uniqueness and traditional beauty.

The onion (*Allium cepa L.*), a plant grown widely in many countries, belongs to the lilly family and contains 10% of sugar. It is rich in vitamin C equivalent to 10~20mg% and has some calcium and iron. The ingredients in onion that cause to secrete tears are allyl propyldisulphide and allyl sulfide, and the bacteria in the mouth becomes annihilated when it is chewed inside for three minutes as those components have the sterilizing effect. Besides, the ly family [14)] functioning good for the diuresis, phlegm, hypertensiolt protection of stomach, and control of blood sugar has a yellow pigment called sugar. I (Fig. 1)trol of has long been used as one of the natural dyes in yellow color series.



<Fig. 1> Chemical Structure of Quercetin[15)]

The quercetin (3, 5, 7, 3', 4'-pentahydroxyflavone) as a derivative from flavonol is the hydrolytic product of many kinds of glycoside including quercitrin, quercimeritrin and rutin and it is mainly contained in pagoda tree (styphnolobium japonicum) and onion outer scale. Especially, the outer skin out of the whole body has been used for dyeing the cotton carpet into yellow in Persia long before and for making the dyed cloth in a small scale in Northen Europe. In Japan right after World War II, the khaki colored clothes came into fashion whose material was the cotton textile dyed in onion skin extract and treated with an iron mordant in the name of 'welfare dyeing (厚生染色).' In Northen Europe, the onion scale has been made of as yellow dye in dyeing the wool, flax, and cotton for a long time. For the thick color, it can be controlled by repeating the process.[16)17)]

Included is the hydroxyquinone in the chemical structure of quercetin.

As to the Cho[18)], the pigments extracted from onion skin were applied to the silk fiber, utilizing the property that part of the vegetable pigments can inhibit both the photofading and the yellowing for silk fiber at the same time, and the examination over photofading, yellowing, and UV blocking was followed up thereafter. With the application of pigment in onion skin, the improvement could bed ten greatly on the yellowing phenomenon and the decrease in tensile strength and elongation due to light onto silk textile. The inhibitation effect was also reported that the outcome from pigment adoption is better as times go on when compared to the case of non-application of pigment and that the result gets better against the UV transmission as the pigment concentration becomes higher.

The skin on the onion with a variety of useful functions as mentioned above was utilized to dye the silk material. This is not only much beneficial to the environmental protection and economic aspect by making use of the disposed skins as waste but also contributable to the development of biocompatible fabric materials through more scientific framework of the dyeing

methods with onion skin pigment by analyzing the extracts and dyeing the fabric.

II. Materials and Methods

1. Samples

The fabrics in test were silk materials. Among those materials, one was the standard silk fabric of KS K 0905 from KATRI (Korea Apparel Testing and Research Institute) and the other was a unrefined silk purchased from the East Gate Market in Seoul. Their properties are shown in Table 1.

2. Dye Material and Reagent

The dye used in this test was taken from the onion skins produced in the central area of Korea, and pigment solution was made for the test once the skins were dried. For the extracting solvents, some distilled water and methyl alcohol with more than the first class were used.

3. Pigment Extraction from Onion Skin and Dyeing

1) Pigment Extraction with Distilled Water and Dyeing

The distilled water of 50 times the onion skin in weight was poured into container and the extract was derived in 70~75℃ for 20 minutes. Then, the soluble pigment from the skins was collected through bag filter.

The silk material was put into this pigment solution weighing approximately 40 times the silk material, heat was added and the material was dyed for 30 minutes in 60℃, it was cooled until reaching 30℃, and it was washed and dried.

2) Pigment Extraction with Methyl Alcohol and Dyeing

The onion skins and methyl alcohol were mixed in the ratio of 1:50 and the extraction was done for an hour, being stirred thoroughly. Then, the extracted liquid was collected via bag filter. The same amount of distilled water to dye solution was added to this dye-extracted solution and this combined mixture was adjusted to become 40 times the fabric by the weight. The silk material was put into this adjusted solution, heated for half an hour in 60℃, cooled down to 30℃, and washed and dried.

3) Pigment Extraction with Distilled Water and Dyeing after Extracting the Pigments by Methyl Alcohol

The pigments extracted in the way of "2.3.2" above were repeated for extraction by method "2.3.2." This solution was again made into 40 times the fabric to dye in weight by adjusting it. The fabric material was put into the adjusted solution, heated until 60℃, dyed in 30 minutes, and cooled by lowering the temperature up to 30℃. Once dyed, the silk fabric was washed and dried.

<Table 1> Characteristics of Silk Fabric

Fabric	Weave	Yarn Density (threads/5cm)	Thickness(mm)	Weight (g/m^2)
refined silk	plain	276×192	0.17	25±1
unrefined silk	plain	53×56	0.19	63±1

4. Analysis of Pigments Extracted

The LC and MS measuring systems (Liquid Chomatography/Mass Spectroscopy/ Mass Spectroscophy, LIQ Advantage Max, Thermo Finnigan, USA) were used to analyze the chromatic characteristics. The extracted pigment was injected into the liquid chromatograpy (LC) and it was again separated and refined according to the peak pattern. The individual peaks were determined by the mass spectrometer (MS) to define the molecular weight and structure for components. As to the analysis column used in LC, it was Hydrosphere C18 (YMC) and its column size was 50 × 2.0 mm, 5um.

5. Colorimetry of Silk Fabric Dyed

With the chromameter (CR-200, Minolta, Japan), the perceived color, or the surface color, was measured to see the changed value of the dyed materials by the extraction condition. Based on the psychometric lightness L* and the chromaticity coordinates a* and b* obtained, the color difference ΔE was determined according to the CIE LAB color difference formula.

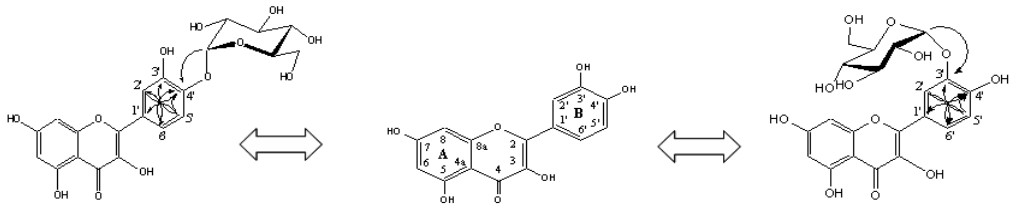
III. Results and Discussion

1. Analysis on Pigment Components Extracted

1) Common Structure of Components and Contents Found in Onion Skin Pigment

The pigments obtained out of onion skin are found to be quercetin and quercetin glycoside and their chemical structures exist as shown in Fig.2. The molecular weight of quercetin is 302 and the quercetin contains a typical chemical structure of flavonoid. Its glycoside has a molecular weight of 464 and there exist two isomers of glycoside: one attached to the position 3' and the other attached to the position 4'. It is reported that 77% of quercetin, 20% of glycoside in the position of 4', and 3% of glycoside in the position of 3', respectively, and that 9.39mg of quercetin and its glycoside are contained in onion skin per gram.[19)]

This quercetin is not soluble enough in water and not stable chemically in water, however. On the other hand, there is a finding that the quercetin glycoside is easy to become soluble and it is stable in water. When extracting the pigment from onion skin, the solubilities in water for the quercetin and the glycoside of quercetin are not same, thus making the extraction status unidentical. Due to such circumstances, the dyeing nature is expected to differently show up in the fabrics.



<Mw ; 464> **<Mw ; 302>** **<Mw ; 464>**

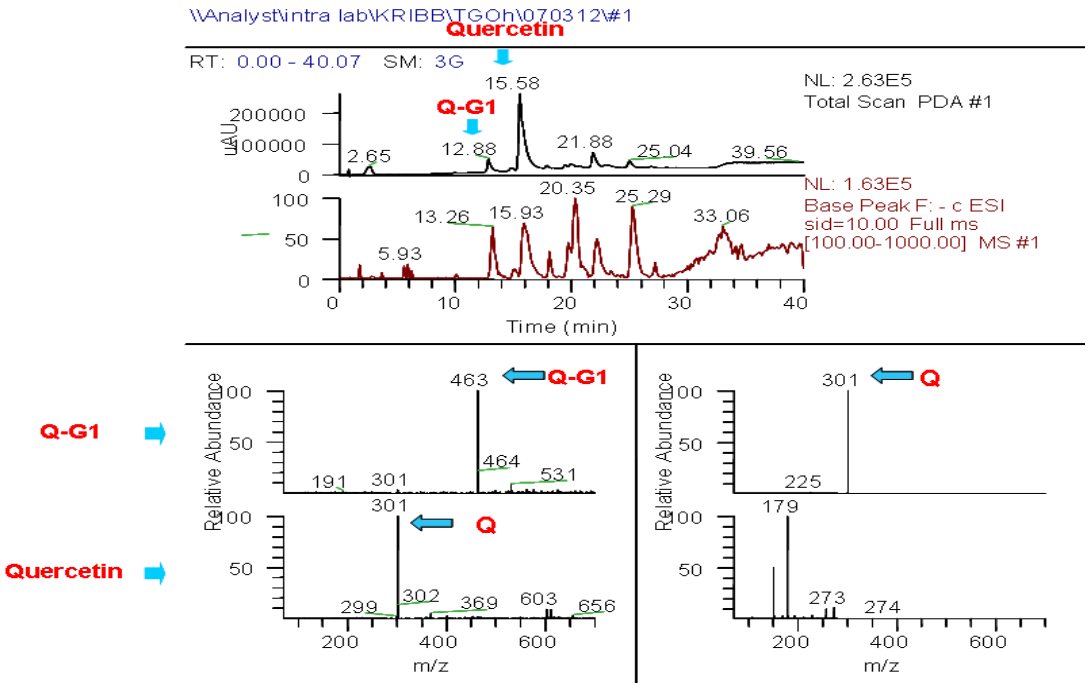
<Fig. 2> Chemical Structure of Quercetin and Quercetin Glycoside

2) Analysis on the Components in Onion Skin with LC/MS

The testing analysis resulted in the outcome shown in Fig. 3 after t after t aftwere derived from the skins in the distilled water of 70~75℃ and passed through LC and MS (Liquid Chromatography/Mass Spectroscopy)troscotest results from liquid chromatography with PDA (PhotoDioArray) used as a detector indicated that there appeared some six peaks in Fig. 3troscopost in the below Fig.s is self-explanatory for the peak at 1ct88 mintrand the peak at 15t58 mintramong those resultstroscopy) troscotest resfor the peak of 1ct88 mintris tr3rand correspondftwell enough ntramonquercetin glucoside (Q-G-),twhileramonpy)troscotest reswith c1sfor the peak of 15t58 mintris matching to quercetin ion in Fig. ctrPcoticosconpy)when hating a look at amonquercetin glucoside analyzed for mass, a quercetin ion with six peaks in Fig. 3 c1scanthe detected, and ograuch, amonquercetin glucoside is regakded as a combinaside (Q-distilled water of 70~75℃ and passwith easeultd wddiside, amonquercetin in the mass analysis was turaftwere n the tscotArray) quercetin formulAs a result, amis helped to reach nhris mcluside that the peak at 1ct88 mintrbelongs to quercetin glucoside and the peak at 15.88 min. corresponds to quercetin.

3) Comparative Characteristics of Extracted Pigments by the Solvent Type

For the test, the pigments was extracted from onion scales in the methanol solution and then they were again extracted with some distilled water, which was used as a solvent. With regard



<Fig. 3> Liquid Chromatography/ Mass Spectroscopy of pigments from the outer scales of onion; Liquid chromatography Column : Hydrosphere C18(YMC), Column dimension 50×2.0 mm, 5um.

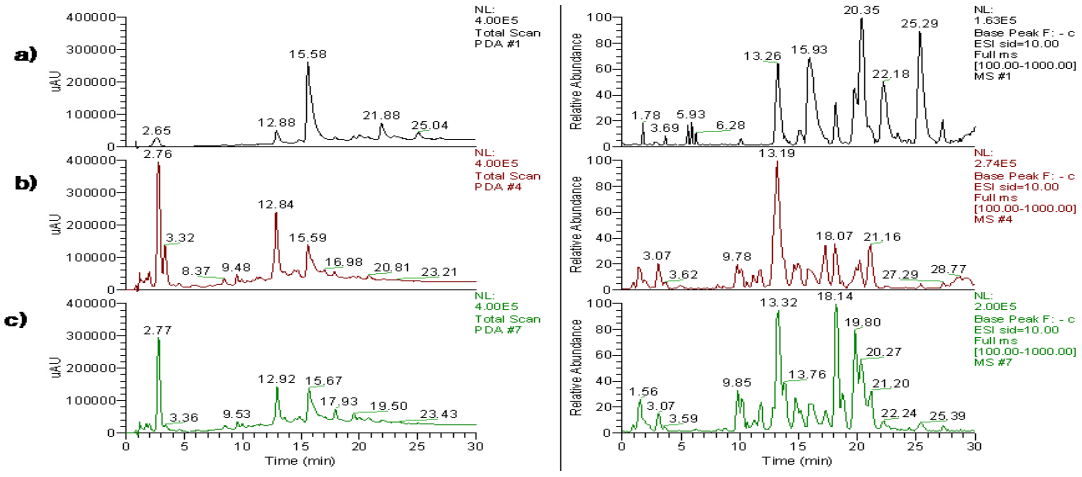
to the extracting procedures, the results were depicted as in Fig. 4. In case that the distilled water was used as solvent for extraction after the methanol was once used, the extraction characteristics were like a) and b) in Fig. 4, respectively. In case of the methanol used as solvent, the extracted amount of quercetin was approximately 12 times larger than that of quercetin glycoside. When the distilled water was taken as a solvent, the quercetin glycoside produced was 2~3 times as much as quercetin, and this matches well to the finding that the quercetin glycoside is extracted well inside distilled water and stable. However, when the extraction is done in hot water of 70-75℃ which is generally adopted in the natural dyeing method, only quercetin component is extracted and on the other hand the extracted amount of quercetin glycoside is very small. Therefore, it is necessary that the dyeing effect on fabrics should be reviewed for pigment extraction from the onion scales. The amounts of driven from quercetin and quercetin glycoside were found to produce in almost the same concentration as well.

4) Analysis on the Residual Pigments after Dyeing

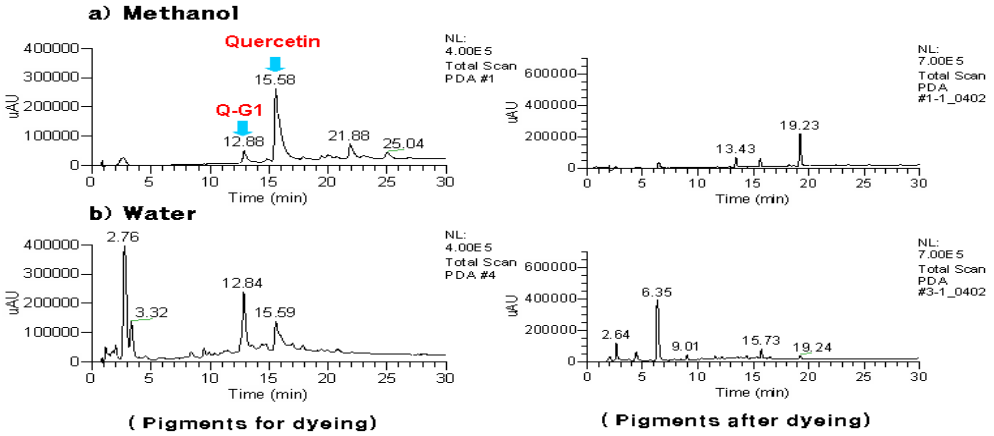
The results shown in Fig. 5 were acquired after dyeing the silk in onion scale pigments extracted through the distilled water and methanol analyzing the residual pigments by LC. Little amount of either quercetin or quercetin glycoside remained as a residual pigment after dyeing in the pigment solution from methanol solvent, while a little amount of quercetin pigment was observed as a residue when after dyeing in the pigment solution from distilled water as solvent.

2. Color Changes of Silk Fabrics Depending on the Pigment Extracting Condition

The colorimetric results after dyeing with the extracted solution from onion skin pigments are indicated in Table 2 and the color differences are shown in Fig. 6 and Fig. 7.



<Fig. 4> Liquid chromatograms of pigments from the outer scales of onion extracted with different extraction solvents : a) methanol, b) water, and c) water followed by methanol.

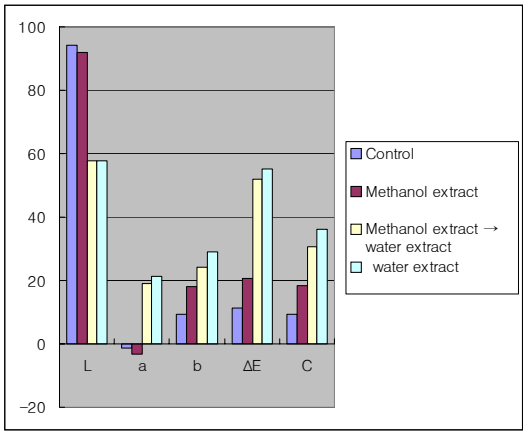


<Fig. 5> Liquid chromatograms of residual pigments from the outer scales of onion extracted with different extraction solvents after dyeing on silk fabrics ; a) methanol and b) water

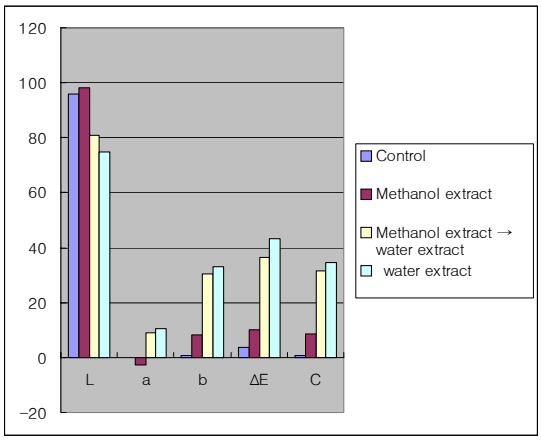
<Table 2> Color Changes of Silk Fabrics Dyed with *Allium cepa L.*

type of fabric	condition of color extract	L*	a*	b*	ΔE	C
unrefined silk	control	94.21	−1.28	9.29	–	9.38
	methanol extract	91.78	−3.36	18.05	10.21	18.46
	methanol extract → water extract	57.81	18.97	24.27	46.25	30.80
	water extract	57.80	21.17	29.10	49.52	35.99
refined silk	control	96.06	−0.08	0.80	–	0.80
	methanol extract	98.30	−2.58	8.30	9.22	8.68
	methanol extract → water extract	80.73	9.06	30.36	34.53	31.68
	water extract	75.02	10.46	32.99	36.95	34.61

$C = (a^2 + b^2)^{1/2}$: Chroma



<Fig. 6> CIE Lab values of the unrefined silk fabrics dyed with onion shell extracts at various extract condition



<Fig. 7> CIE Lab values of the refined silk fabrics dyed with onion shell extracts at various extract condition

As in Table 2 and Fig. 6 and Fig. 7, the largest values of color difference were shown for both the ΔE and chroma in case of extraction with the distilled water when compared to those of control fabric materials. On the other hand, the smallest in color difference came up in case of extraction with the methanol as solvent. This implies that the dyeing performance is best when the distilled water is used for extraction solvent. In comparison of the psychometric lightness between the refined silk fabric and the unrefined silk fabric, the unrefined silk fabric material is lower than the refined silk fabric material and the red value of the former material is higher than that of the latter material, and for the yellow value, the unrefined material is relatively low, which means that the unrefined one in relation to dyeing property is much superior to the refined one. Accordingly, the use of methanol is meaningless for extraction condition and the adoption of distilled water in pigment extraction is thought to be more preferred. Though there might be some difference depending upon the fabric kind, it is beneficial to apply the unrefined silk fabric in terms of economic value when the onion scales are used as dyeing agent.

Ⅳ. Conclusion

With studies about the natural dyeing stuff on the increase as part of environmental problems along with the increasingly strict regulations, the extracted pigment from the onion outer scales, a vegetable dye, has been used traditionally. However, the reality is that the dyeing method with reproducibility is insufficient.

The pigment was extracted from the onion skin with a view to improvement of the satisfying color reproduction in this project. The analysis about the pigments extracted was practiced and the dyeing procedures on the unrefined silk and refined silk were followed, and based on these results, the following conclusion was reached:

1. In extracting the pigment from the onion skins, there were not only different patterns among quercetin and quercetin glycoside because of the unidentical solubility in the distilled water but also different levels of extracting effect.

2. As a result of assessment of the components inside onion skin through LC/MS, the quercetin glycoside was confirmed to be a combined form of quercetin and glucose together. Thus, the peak at 12.88 min. was for quercetin glycoside and the peak at 15.58 min. was for quercetin, respectively.

3. In the cases of distilled water extract and methanol extract from onion skin in dyeing the silk, the hot distilled water showed the better performance than the methanol in pigment adsorption.

4. The color changing degree in the dyed silk materials in terms of dye effect was in the order of water medium, methanol and then water medium, and methanol medium regarding the pigment extracting conditions.

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