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Visual Color Deterioration of the Extract of Lithospermi radix

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紫草추출물의 외관상 변색

윤희남 · 김 호 · 신용달 · 유무영

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Abstract

The effects of temperature on the visual color deterioration of Lithospermi radix were investigated under steady conditions of various pH and temperature. The changes of Hunter L, a, b, and ΔE values related to the color deterioration were sharply increased above 50°C and the deteriorations were expressed linear relationships with the temperature above 60°C. Linear regression coefficients of Hunter L, a, b values decreased with an increase of heat treatment time, whereas the color difference was increased. The linear regression coefficients of Hunter L, a, b, ΔE values in 66.7% ethanol extract solution of Lithospermi radix for 1 hr were -0.3696, -0.4124, -0.2279, and 0.5983, respectively. Inear regression coefficients in color difference (ΔE) could be calculated from the coefficients in Hunter L, a, b values. The low pH treatment of extract from pH 6.07 to pH 1.35 led to decrease of Hunter a value and a little increase of Hunter L, b values, but the high pH treatment above pH 6.07 decreased all Hunter values. Particularly, the visual color of the extract of Lithospermiradix was appeared to be faborable at pH 4.0-6.5, which was a bright red color.

Introduction

Lithospermi radix is the root of Lithospermum erythrorhizon (Borraginaceae) growing in the Far East. Closely related to Lithospermum officinale in Europe, it is famous Korean, Chinese, and Japanese traditional medicine and has been used as a coloring matter of cosmetics and wines in industry.

Active ingredients of Lithospermi radix are the naphthoquinone derivatives, which are shown in Table 1 and are known as shikonin or alkannin.[1] This ingredients are soluble in organic solvents and sparingly soluble in water. Buffered aqueous solutions of this ingredients are red at pH 6.1; purple at pH 8.8; blue at pH 10.0 and it has been applied as a pH indicator called Alkannin paper.

Several workers have investigated the extraction, application, and synthesis of active ingredients of Lithospermi radix.[1-3] Futagoishi and Abe [1] studied the extraction of shikonin using various menstrum and reported that isopropyl myristate was the most effective of the eight menstrum and for stability of shikonin. Kertesz and Sondheimer [4] studied time-temperature relationships with color degradation of strawberry preserves and determined 65°F (18°C) to be a critical temperature, above which accelerated loss of red color and subsequent formation

of brown color occurred. Case[5] reported similar observations. Studies conducted on Zinfandel grapes to degermine the effects of heating on grape juice color showed that heating in sealed tube in a boiling water bath for 1-2 hr caused the juice color to fade. However, after prolonged heating, the juice turned out.[6]

Hunter color parameters have previously proved valuable in describing visual color deterioration in anthocyanin-containing products.[7-10] Color Difference Meter L and a values have been found to be a useful guide in determining the amount of browning and red color development in grape juice.[11-13] Particularly, Wrolsted et al.[14] reported that Color Difference Meter L values gave a good correlation with visual scores on color of fresh and frozen strawberries.

The objective of this work was undertaken to determine effects temperature and time in heating the extract of Lithospermi radix which resulted in visual color deterioration, to compare the degree of deterioration-time relationships at various temperature, and to study the effect of pH treatment on the extract of Lighospermi radix.

Materials and Methods

Lithospermi radix was purchased in local drug markets and stored at 4.0°C until used.

Preparation of extracts

Lithospermi radix was immersed in water for 2 hr, washed using distilled water, grinded through use of pin mill, and classified with 60 mesh screen. The extraction was carried out by maceration: 40 of Lithospermi radix were immersed in 1,200 of 66.7% ethanol solution, kept at 24.5°C for 1 hr and agitated with the speed of 150 .. After then, the extract was filtrated through Whatman # 1 filter paper. The extrated solution had presented a red color and the pH of the solution was 6.07 (pope, mod' 1502 pH/Ion meter). The pH of the extract was adjusted by using 1N HCl and 1N NaOH.

Heat treatments

The ethanol extracted solution were sealed in 10.0 ml vials to minimize heat transfer limitations in come-up time and placed into a criculating, controlled temperature, oil bath at each temperature (40,50,60,70,80,90, and 100°C). After heat treatment at each temperature, samples were quickly placed into a ice bath to inhibit further color deterioration.

Color analyses

The color deterioration was measured at Hunter L, a, b values, which were calculated from Hunter XYZ trismulus values obtained from transmission spectra (Model C5120, Tokyo Denshoku, Co., Ltd). L = 10 Y, a = 17.5 (1.02 – Y)/ Y, b = 7.0(Y – 0.8472Z)/ Y.[15] Lightsource C was used for calculation. The Hunter values of the ethanol extracted solution were L=31.30, a=52.61, and b=13.88 at 24.5°C. all analyses were made in triplicates.

Deterioration temperature relationship.

Linear regression coefficients were obtained for visual color deterioration assuming a linear relationship. This relationship is defined as follows;

$$V = V_0 + kT$$

where V is the Hunter value at T(above 60°C); V_0 is the Hunter value extrapolated to T=0; k is the linear regression coefficient; T is the temperature (°C).

Results and Discussion

Visual color of the extracted solution of Lithospermi radix exhibited high values for Hunter color lightness(L), redness(a), and yellowness(b).

Fig. 1 shows the plot of the extent of Hunter L, a, b, and ΔE values resulted in the visual color deterioration as a function of temperature during heat treatment for the ethanol solution extracted from Lighospermi radix. Hunter a values were high while Hunter b values were correspondingly low. ΔE is shown a total color difference indicating the changes of chromaticity and lightness and defined as follows:

$$\Delta L=L_T - L_{24.5}, \quad \Delta a=a_T - a_{24.5},$$

$$\Delta b=b_T-b_{24.5}, \quad \Delta E=(\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}.$$

As can be seen, the data exhibit no difference of Hunter values under 50°C and linear relationship with a temperature above 60°C. It is also obvious from Fig. 1 that the critical temperature in visual color deterioration of Lithospermi radix is 50°C and visual color is significantly deteriorated above 60°C. In this investigation the pH of samples heated for 3 hr at 80°C was 6.06 and in original extract solution was 6.07. This fact indicates that heat treatment of extract solution was no effect to the change of pH value. Therefore, it is possible to says that the temperature would be an important factor related to the visual color deterioration during heating process.

Color deterioration was greatly influenced by the heat treatment time. As the heating time was increased from 1 hr to 3 hr, all Hunter values was shown to be more decreased at any temperature except below 50°C. Decreases in Hunter values also appeared linear relationship with no relation to the difference of heating time above 60°C.

Linear regression coefficients (Hunter C) for visual color deterioration listed in Table 2 were obtained from the slopes of linear plot of measured Hunter value versus temperature above 60°C for each condition of extract tested. As seen in Table 2, linear regression coefficients in decrease of Hunter L, a, b values are shown to decrease with an increase of heat treatment time and the one in crease of color difference is appeared to increase. It seems that the increase of heat treatment time resulted in more visual color deterioration in comparison of original samples. The possiblilty to obtain coefficients of color difference from the coefficients of Hunter L, a, b values is also presented in Table 2. It should be noted that the predicted coefficients of color difference are almost alike to the experimental coefficients and could be easily calculated from.

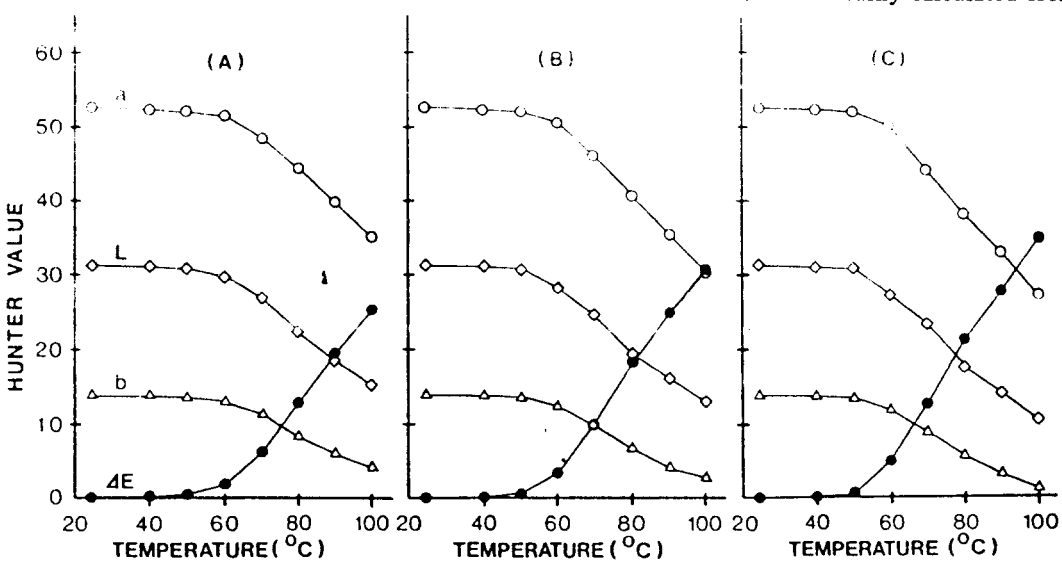
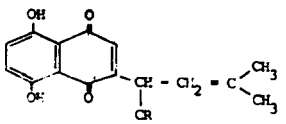


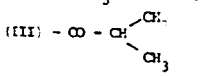
Fig. 1. Shift of Hunter values in ethanol extract of Lithospermi radix at various temperature: (A) 1hr; (B) 2hr; (C) 3hr

Table 1. Naphthoquinone derivatives

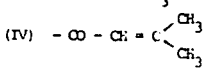


(I)* - H Shikonin

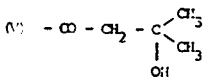
(II) - C OCH$_3$ Acetyl - shikonin



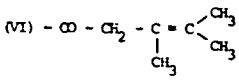
Isobutyl - shikonin



β·β - Dimethylacryl - shikonin



β - Hydroxy isovaleryl - shikonin



Teracryl - shikonin

* R groups of side chain in molecular structure

Table 2. Linear regression coefficients of visual color deterioration (Hunter value/°C) above 60°C

Hunter Value	Heating Time (hr)		
	1	2	3
L	−0.3696	−0.3869	−0.4220
a	−0.4124	−0.5185	−0.5653
b	−0.2279	−0.2510	−0.2649
$\Delta E_{experi.}$	0.5983	0.7000	0.6479
$\Delta E^*_{predic.}$	0.5986	0.6940	0.7535

* $k_{\Delta E} = (k_L^2 + k_a^2 + k_a^2)^{1/2}$

By the above results, color deterioration of extract of Lithospermi radix was related to the temperature and time during heat treatment. Therefore, it must be necessary to be kept below 50°C and to decrease the heating time as possible.

Fig. 2 shows the changes of Hunter values at various pH treatment. It is evident that the visual color of the extract is pH dependent. The low pH treatment of the extract from pH 6.07 to pH 1.35 led to decrease of Hunter a value (redness) and a little increase of Hunter L, b

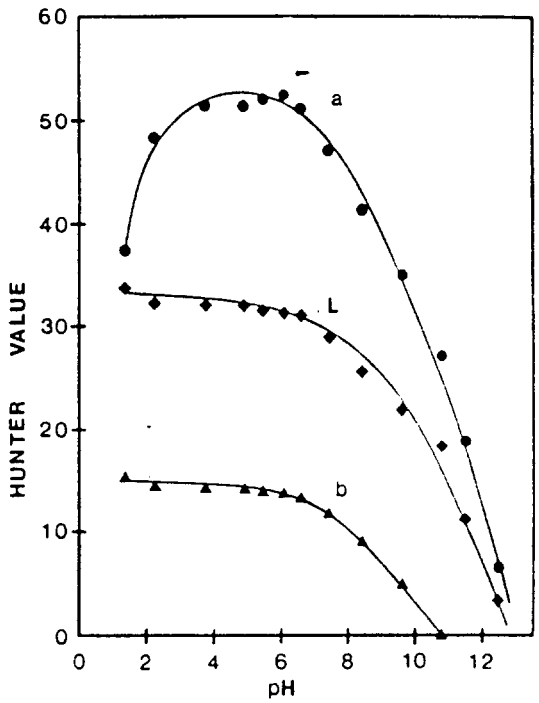


Fig. 2. Plot of Hunter values versus pH of ethanol extract of Lithospermi radix at 24.5°C

values. This indicated a visual color deterioration of the extract from bright red color to dark red color. On the other hand, the high pH treatment above 6.07 decreased the values of all Hunter parameters. Particularly, visual color is significiantly deteriorated above pH 6.50 and the values on the Hunter b parameter were shown a negative value above pH 10.8, indicating a blue color.

In conclusion, it was shown in Fig 2 that the visual color of the extract of Lithospermi radix was light and clear-red between pH 4.0 and pH 6.5, which color was most favorable.

This extract had been applied to cosmetics and wines in many countries, and especially to red-liquor (ong-Ju) which is known as a traditional and native liquor in Jin-Do district of South Korea. But at present the degree of application is actually negligible. In the future, much more care would be needed in order to apply the extract of Lithospermi radix to various industrial products as a colorant and to be stable original red color during heating or other process.

Acknowledgment

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요 약

紫草추출물의 외관상 변색에 영향을 주는 온도와 pH에 대해 조사하였다. 변색은 Hunter値의 차이로 표시할 수 있으며 자초추출물의 Hunter値는 50℃ 이상에서 변화하기 시작하고 60℃이상에서는 온도와 상관관계를 이루었다. 온도에 따른 Hunter L, a, b値의 변이상관계수는 열처리 시간이 증가함에 따라 감소하였으며, 전체변색의 상관계수는 증가하였다. 66.7% 에탄올로 추출한 추출물을 1시간 열처리 할때 Hunter値의 변이상관계수는 L値의 경우-0.3696, a値의 경우-0.4124, b値의 경우-0.2279, 전체 변색에 있어선 0.5983이었다. 이때 전체변색의 상관계수는 Hunter L, a, b 각각의 상관계수로 부터 직접 계산할 수 있었으며 0.5988로서 거의 비슷한 값을 보여주었다. 한편 pH를 낮추면 Hunter a値는 감도하고 L, b値는 약간 증가하였으나 pH를 증가시키면 pH6.5를 전후로 해서 Hunter L, a, b値 모두 다 급격히 감소하여 외관상 색깔이 좋지 않았다. 紫草추출물은 pH가 4.0-6.5일때 외관상 가장 좋은 '선명한 붉은색'을 나타내었다.

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