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Extraction of natural dye from *Gardenia* and chromaticity analysis according to chi parameter

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ABSTRACT

Various methods of extracting natural dyes have been studied because of the increase of eco-friendly, non-toxic natural dyes. In this study, the natural dyes extraction process was optimized using *Gardenia jasminoides* Ellis containing crocin. Hansen solubility parameter values and chi parameter values (χ_{12}) of various organic solvents and crocin were calculated, and the extracted pigments were analyzed by experiments. Comparing to calculated values and analyzed values, the relevancy was found and the solvents yielding color close to the target color were selected. Four kinds of solvents (methanol, ethanol, 1-propanol, and 2-propanol) having color close to the target color were selected because their χ_{12} values were small and their Hansen solubility parameter values were similar to the Hansen solubility parameter value of crocin. These selected solvents were each mixed with distilled water at various volume ratios, and the extraction process was conducted. The results showed that L, a, b values closest to the target color were obtained when using 40–60 vol% of the solvents. Also, trends of χ_{12} values and the color difference (ΔE^*) values were well matched up with UV absorbance.

Introduction

For ages, natural dyes extracted from plants, animals, and minerals have been used to dye clothing, but their use gradually dwindled with the development of synthetic pigments [1–3]. However, most synthetic pigments have the toxic substances and carcinogenic ingredients, that can lead to various illnesses, such as atopic dermatitis. Due to the hazards of these synthetic pigments, the use of natural dyes, which are eco-friendly, offering a variety of colors, is gradually increasing [4–6]. Many researches about natural dyes from a variety of plants are being conducted even lichen that people commonly think useless [7–9]. Natural dyes maintain an ecological balance and do not pollute the environment during their production and use. Moreover, it can be used for food, cosmetics, clothing etc., because of their high biodegradability, low toxicity, and low allergy compared to synthesis pigments [10,11]. Natural dyes are organic compounds with a hydroxyl group attached to their nucleus, and most are water-soluble. *Gardenia jasminoides* Ellis is an evergreen shrub that is grown in temperate regions, belonging to *Rubiaceae*, and has been used as traditional medicine because of its homeostatic, anti-inflammatory, analgesic, and antipyretic properties [12–14]. Its oval fruit becomes well ripe red in late autumn. The extract from the fruit, which can show yellow, red, and blue colors, are widely used as natural pigment [15]. Crocin, which is the yellow pigment, is used in many fields as substitute for synthetic pigments, because it is non-toxic and chemically stable [16,17]. Especially, crocin's pharmacological effects, such as the prevention of cardiovascular diseases [18,19], inhibition of tumor cells proliferation [20], and protection of neural stem cells [21,22], and protection of interstitial cells [23], have been reported [24].

The solubility parameter represents the quantitative degree of affinity between a solute and a solvent, so it is used as an indicator of solubility. It includes the dispersion solubility parameter, polar solubility parameters, and hydrogen bonding solubility parameter. Solvents having similar solubility parameter values can be well mixed. The Flory-Huggins chi parameter (χ) has been used for several years to characterize the behavior of a polymer solution. However, in the present study, the chi parameter (χ_{12}) derived from the New Flory theory is used instead of χ. The widely-used Hansen solubility parameter and chi parameter (χ_{12}) are directly related to each other, so the chi parameter (χ_{12}) can be estimated if the Hansen solubility parameter value is known. In this study, the solubility parameter

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of crocin, which is the extracted yellow dye from the gardenia fruit, was calculated, and the chromaticity analysis of dyes extracted from solvents of various chi parameter values (χ_{12}) were conducted. In addition, the optimum solvent condition was determined to extract the target color dye.

Experimental

Materials

The organic solvents used in the experiments including distilled water are diethyl ether (99.0%), *n*-butyl acetate (99.5%), ethylbenzene (99.8%), *m*-xylene (99.0%), *o*-xylene (98.5%), toluene (99.5%), ethyl acetate (99.5%), methyl acetate (93.0%), acetone (99.7%), 1-butanol (99.5%), 2-propanol (99.0%), 1-propanol (99.5%), ethanol (99.9%), and methanol (99.8%). The gardenia fruits needed for the experiments were obtained by filtering bark and dirt using a sieve.

Extraction of crocin from Gardenia

The molar volume and the Hansen solubility parameter value of each solvent are listed in Table 1, and then total Hansen solubility parameter value and chi parameter value (χ_{12}) were calculated [25]. After a solvent of 200 ml and gardenia fruits of 1 g ground were stirred to extract pigment at room temperature (25 °C) for 1 h, the amount of extract was evaluated by using UV-Spectrophotometer (OPTIZEN 2120 UV, MECASYS), and after that the $CIEL \times a \times b$ chromaticity analysis of the pigment was conducted. Then, the four solvents that gave the lower chi parameter values (χ_{12}) were chosen, and each were mixed with distilled water by various volume ratios. Finally, after the Hansen solubility parameter values and molar volumes of these mixtures were calculated, then, extraction and chromaticity analysis were conducted.

Chromaticity analysis using CIEL × a × b color space

The $CIEL \times a \times b$ color space defined by the International Commission on Illumination in 1976 was used to quantify the results of this study. L represents the brightness, ranging in value from 0(black) to 100(white). $+a$ is the red direction, $-a$ is the green direction, $+b$ is the yellow direction, and $-b$ is the blue direction. Therefore, the center represents the achromatic color, and chroma increases when the point moves away from the center with increases of the $a$and$b$ values [26]. A color difference meter (CT-310, Konica Minolta) was used to obtain the $L, a,$ and$b$ values, and the L, a, b coordinate was represented.

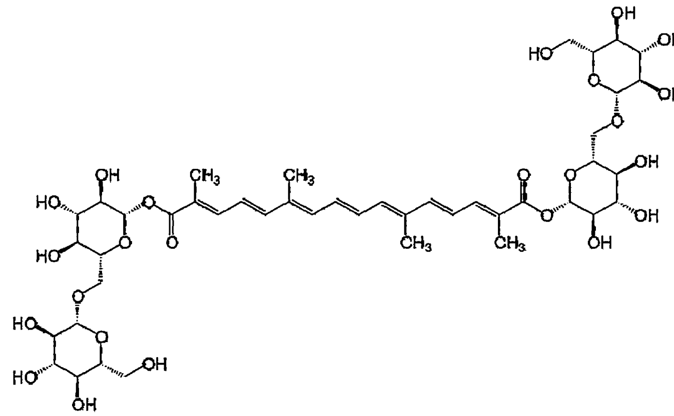

Fig. 1. Structure of crocin.

Results and discussion

Calculation of solubility parameter

The solubility parameter is important in the selection of a solvent. If a solvent which has a solubility parameter value similar to that of the solute is selected, the solvent would have the thermodynamic property to better dissolve the solute. According to the Hansen Solubility Parameter model suggested by van Krevelen, total solubility parameter (δ), which accounts for the dispersion effect, polar effect, and hydrogen bonding effect is represented as follows [27].

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

In this equation, δ_d^2, δ_p^2, and δ_h^2 are the solubility parameters representing the dispersion effect, polar effect, and hydrogen bonding effect, respectively. δ_d^2, δ_p^2, and δ_h^2 can be calculated quantitatively considering group contribution. The method of group contribution is a way to calculate the degrees of contribution of the various atomic groups in a molecular structure to the entire molecule. Dyes are basically classified by their structures. The structure of crocin is a kind of carotenoid [28]. Fig. 1 and Table 2 show the molecular structure of crocin and the solubility parameter value of its functional group, respectively [29]. The solubility parameter value of crocin is $29.96\,(\mathrm{J/cm^3})^{1/2}$, as calculated by equation (1) and Table 2. Comparing this value and the solubility parameters values of the solvents calculated on Table 1, it is expected that the solubility of crocin was large for methanol, ethanol, 1-propanol, and 2-propanol.

Table 1
Hansen Solubility Parameters of Various Solvents.

Solvent	V [cm^3/mol]	δ_d [MPa$^{1/2}$]	δ_p [MPa$^{1/2}$]	δ_h [MPa$^{1/2}$]	δ_t [MPa$^{1/2}$]
Diethyl ether	104.8	14.5	2.9	5.1	15.8
n-Butyl acetate	132.5	15.8	3.7	6.3	17.4
Ethylbenzene	123.1	17.8	0.6	1.4	17.8
m-Xylene	123.5	16.5	7.2	2.4	18.2
o-Xylene	121.2	17.8	1.0	3.1	18.0
Toluene	106.8	18.0	1.4	2.0	18.2
Ethyl acetate	98.5	15.8	5.3	7.2	18.1
Methyl acetate	79.7	15.5	7.2	7.6	18.7
Acetone	74.0	15.5	10.4	7.0	20.0
1-Butanol	91.5	16.0	5.7	15.8	23.1
2-Propanol	76.8	15.8	6.1	16.4	23.5
1-Propanol	75.2	16.0	6.8	17.4	24.5
Ethanol	58.5	15.8	8.8	19.4	26.5
Methanol	40.7	15.1	12.3	22.3	29.6
Water	18.0	15.6	16.0	42.3	47.8