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Note

Detection of Fake Jindo Hongju Using the pH-dependent Color Change of Gromwell (*Lithospermum erythrorhizon*) Pigment

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Gromwell (*Lithospermum erythrorhizon*) pigment solution and Jindo Hongju prepared in the laboratory showed characteristic pH-dependent color changes and a shift in absorption maxima. This phenomenon was not observed in the solution of the artificial food colorant Red No. 2 which was suspected to be used in the manufacture of fake Jindo Hongju. A few fake products could be detected by using the pH-dependent shift in absorption maxima among the Jindo Hongju on market.

Key words : *Jindo Hongju, pH-dependent color change,* Lithospermum erythrorhizon.

Jindo Hongju, also known as Jichoju, is a traditional liquor of Jindo island located in the south-western part of Korea and is famous for its unique color, flavor and taste.[1] The characteristic red color of Jindo Hongju is due to the naphthoquinone derivative pigments, shikonin and acetyl-shikonin, which are extracted from gromwell(*Lithopermum erythrorhizon*) root during distillation process.[2]

One of the major problems associated with Jindo Hongju is discoloration. Factors, such as visible light, temperature, and inorganic ions, have been known to affect the discoloration of the pigments.[3,4] Another problem is the fake products made with artificial colorants. However, no simple and scientific method for the detection of fake product has yet been developed. In this paper, we report a simple method for the detection of fake Jindo Hongju based on the pH-dependent color change of the gromwell root pigments.

Materials and Methods

Gromwell root samples were obtained from local producers. Jindo Hongju samples were collected from local producers, stores in Jindo, and department stores in Chonnam and Chonbuk provinces. Jindo Hongju was also prepared in the laboratory with barley Nuruk, rice, barley, and gromwell root according to the recipe provided by a local producer. The artificial food colorant Red No. 2 was purchased from a local department store. Ethanol was of analytical grade.

Dried gromwell roots were ground to powder with a mortar and a pestle. The pigments were then extracted with 45% ethanol(100 ml/g powder) for 24 hrs by rotary agitation in the dark condition. After filtration through a filter paper(Whatman No. 1), the absorbance of the solution at 520 nm was adjusted to 1.0 by the addition of 45% ethanol. The pH of the solution was adjusted to 4~11 with 0.1 N HCl or 0.1 N NaOH. The artificial food colorant Red No. 2 solution was prepared with 45% ethanol, and the absorbance and the pH of the solution were adjusted as above.

The absorption spectra in the visible region (400 to 700 nm) were obtained on a UV-visible spectrophotometer (Heλios β, Unicam, Cambridge, U.K.). CIE xy chromaticity coordinates and Hunter L(lightness), a(redness) and b(yellowness) values were calculated from CIE XYZ tristimulus values obtained from the absorption spectra.[5]

Results and Discussion

At normal pHs of Jindo Hongju, pH 4 and 5, an absorption maximum of the gromwell pigment solution appeared at 520 nm(Fig. 1a). At higher pHs the absorption maximum was shifted to a longer wavelength, 570 nm. The absorbance at 520 nm decreased as the pH went up, whereas the absorbances at 570 and 616 nm increased. The spectra of Jindo Hongju prepared in the laboratory at various pHs were the same as those of the gromwell pigment solution and showed the bathochromic shift(data not shown). The pH-dependent change in color from red to blue could also be viewed on the CIE chromaticity diagram(Fig. 2a). The visual color of the gromwell pigment solution and Jindo Hongju changed from red to violet and to blue as the pH went up. The Hunter values of the gromwell pigment solution at pH 4 (A_{520} = 1.0) were L = 37.75, a = 35.18 and b = 14.05. Those values at pH 11 were L = 13.09, a = 15.11 and b = -10.54. These pH-dependent changes in color, absorption spectrum and Hunter L, a, b values have been reported by Yoon et al.[3] and Kim and Park.[4]

It was suspected that the artificial food colorant Red No. 2

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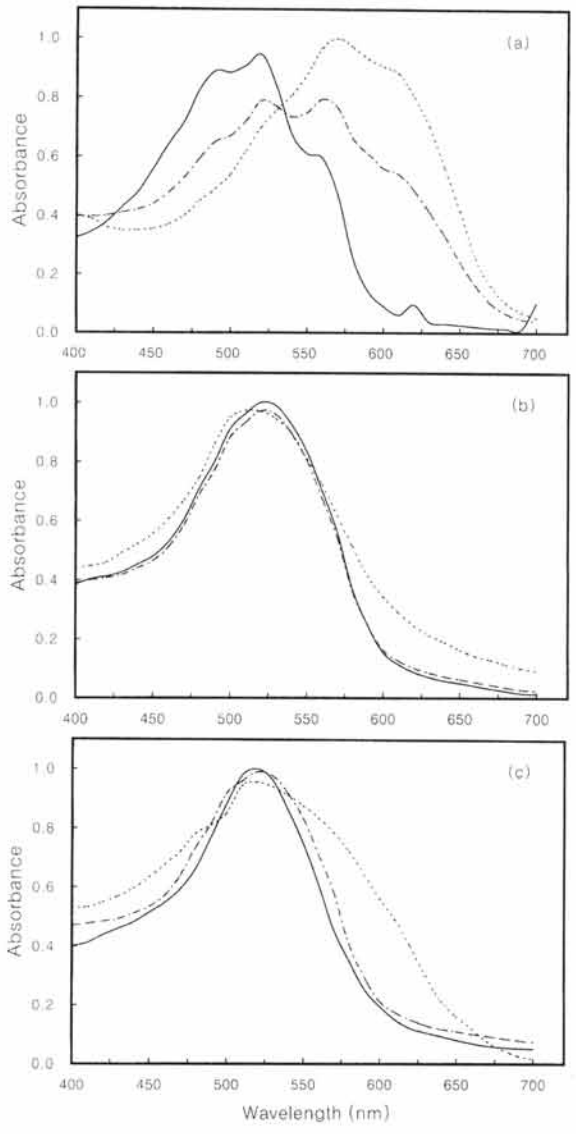

Fig. 1. Absorption spectra of (a) the gromwell pigment solution, (b) artificial food colorant Red No. 2 solution, and (c) suspected fake Jindo Hongju at various pHs. — , pH 4 ; — · —, pH 7; and ·····, pH 11.

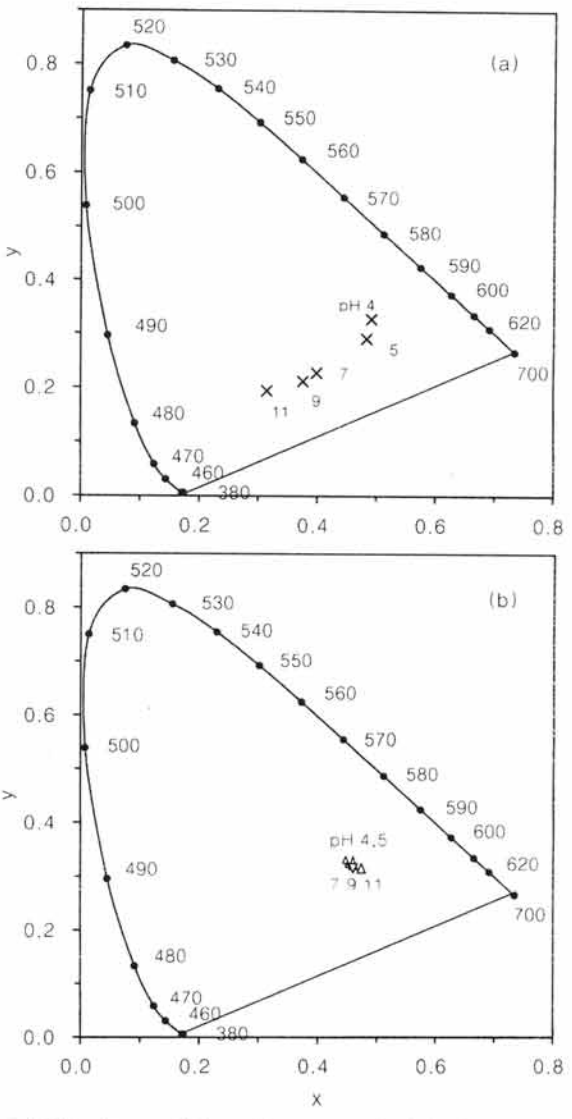

Fig. 2. CIE chromaticity diagrams of (a) the gromwell pigment solution and (b) artificial food colorant Red No. 2 solution at various pHs.

had been used alone or along with gromwell root by some small-scale producers. In an organoleptic test, the panels could not distinguish the color of the Red No. 2 solution prepared with 45% ethanol from those of Jindo Hongju and the gromwell pigment solution as long as the absorbances at 520 nm were the same. When the absorption spectra of the Red No. 2 solutions at various pHs were obtained, no shift of the absorption maxima or CIE xy chromaticity coordinates was observed(Fig. 1b and 2b). Though the absorbance at 520 nm decreased slightly as pH went up, the organoleptic panels could not detect any significant visual color changes. These results indicated that the fake Jindo Hongju products containing artificial food colorant could easily be detected by comparing the absorption spectra at normal product pH (4~5) and at a pH above 10. Even without a spectrophotometer, it could be done easily by adding sufficient alkali and then visually observing the color.

Absorption spectra of 20 Jindo Hongju samples collected from various sources were obtained to see whether the pH-dependent color change could actually be used for the detection of the fake products. Most of the samples showed the characteristic absorption spectra of the gromwell pigment solution and the pH-dependent shift of the absorption maxima. However, the spectra of a few products at various pHs were similar to, though not identical to, those of the artificial food colorant Red No. 2 solution(Fig. 1c). When NaOH was added to these products, neither visual change in the color nor the characteristic pH-dependent shift of the absorption maxima of the gromwell pigment solution was observed. This result might support the suspicion that some producers had used the artificial food colorant along with gromwell root.

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