A Study on Pink Discoloration of Canned Sand Pears (*Pyrus pyrifolia* Nakai)

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The pink discoloration occurring in canned sand pears is considered a sign of poor quality in this product. Factors contributing to pink discoloration were investigated. The major precursor of pink discoloration in canned sand pears existed in the insoluble solids of the sand pear. This precursor belonged to the flavonoids which became a pink color after being heated in acidic conditions. The pink compound was a cyanidin which was the only aglycone component in the canned sand pear. The addition of citric acid at 0.15% was sufficient to lower the pH below 4.6. The use of syrup at the same degree Brix and the same sugar profile of the fruit flesh resulted in less pink discoloration than those with heavy syrup.

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Occasionally, canned pears show a pink discoloration, which is considered undesirable^(3),4),8),9). LUH *et al.*⁽⁸⁾ showed that growing area and soil types were found to be related to pink discoloration. Pears from certain growing areas had low pH, high acidity, high tannin and leucoanthocyanin content. The pink color was found in these pears after canning, especially when excessive heating and delayed cooling processes were used.

WU⁽¹³⁾ studied the pink discoloration of canned lychees and found that the sterilization temperature and pH greatly affect the development of pink color. He also postulated that the pink discoloration in canned lychees might result from the hydrolysis of condensed tannin to catechin and leucoanthocyanin. This postulation has been reconfirmed by WU and FANG⁽¹⁴⁾. Cyanidin compounds isolated from lychee flesh were identified with the pigment from synthesized leucocyanidin produced by heating in acidic solution. The pigment in the pink discoloration of lychee flesh was a cyanidin containing compound. CHAKRABORTY *et al.*⁽²⁾ showed that pink discoloration

in canned lychees could be prevented with a 20 °Brix syrup containing 0.1~0.15% citric acid when boiled in water for less than 10 minutes. WU and FANG⁽¹⁴⁾ showed the pink discoloration of canned lychees could be reduced if the °Brix in syrup was adjusted to that of the fruit flesh.

The canned pear is a popular canned fruit in the market, and it occasionally shows a pink discoloration during storage. The objective of this study was to survey the pink discoloration in canned sand pears according to the above studies, and to investigate the role of leucoanthocyanidin and the effect of sugar and citric acid content on the pink discoloration in canned sand pears.

MATERIALS AND METHODS

Sample

Sand pears were picked at pear orchards from Central Taiwan. The fruits used for tests were cv. Ko-j-lee and Sin-sin.

Extraction and identification of flavonoids

The flavonoids which cause the pink discoloration of pear flesh were extracted according to the method of Forkmann⁽⁵⁾. LEE and WICKER⁽⁷⁾ with a

slight modification. Four times of methanol containing 1% HCl was added to the pear flesh, then blended with a Warling blender for 3 minutes. The blended pear mash was put for reaction at 4°C for 48 hours with periodic stirring then filtered with a Whatman No.1 filter. The filtrate containing the flavonoids was heated at 100°C with a Soxhlet apparatus for 2 hrs resulting in the filtrate changing to a pink color. The methanol in the pink solution was evaporated using a vacuum evaporator and the residue was extracted with pentanol. The pentanol extracted solution was scanned with a spectrophotometer. The flavonoid solution and the pink flavonoid solution from the pear flesh were filtered through 0.45µm cellulose acetate film. The filtrate was analyzed using HPLC with a Waters µ-Bondapak C 10 (30×0.49cm) column. The mobile phase was a mixture of pure water, methanol and acetic acid at a ratio of 70:20:10 (V/V).

The aglycone from the extract of pear flesh was prepared according to the methods of PRASAD and JHA¹⁰⁾. The methanol in the pink solution was removed by evaporation using a vacuum evaporator. Four normality of HCl was added to the solution and then it was heated with boiling water for 30 min. in a vacuum state. After cooling, the solution was extracted with pentanol. The pentanol was then evaporated using a vacuum evaporator and the residue was dissolved in methanol with 0.1% HCl. This solution was filtered through 0.45µm cellulose acetate film. The filtrate was analyzed using HPLC under the previous conditions.

Total soluble solids

The fruit flesh was mashed with a blender and the juice obtained was filtered and analyzed. The total soluble solids were measured by refractometer (Bausch and Lomb Abbe-3L) at 25°C and the results were expressed using °Brix¹⁾.

Sugar analysis by HPLC

Sugar profile was analyzed by HPLC according to the method of WILSON *et al.*¹²⁾ with a slight modification. The solvents and reagents used were of analytical grade and the water was prepared

using reverse osmosis. Acetonitrile: H₂O=80:20 (V/V) was used as the mobile phase¹²⁾

Titrateable acidity

The samples were titrated with 0.1 N NaOH to pH 8.1¹⁾. The results were expressed as per cent citric acid.

Preparation of canned sand pears

The fruits were washed, drained and peeled by a peeling machine. The peeled fruits were washed and cut into slices with the knife and then dipped in 0.1% citric acid solution. Six syrups were prepared with three different levels of sugar content (i.e., 10.5, 18.0 and 25.5° Brix) and three different levels of citric acid (i.e., 0.15, 0.25 and 0.35%), respectively. The slices weighed 230g with the same weight of syrup and 0.1% CaCl₂ were packed into a No.303 plain can. After being exhausted at 85°C for 10 minutes, those cans were sealed, sterilized in boiling water for 12 minutes, and cooled to 38°C¹⁴⁾. All of the canned sand pears from the different treatments were stored at 26±1°C for one year.

Color measurement

A colorimeter (JUKI JP 7100 F, Tokyo, Japan) calibrated to a standard plate (L:98.29, a=+0.03, b=-0.36) was used for color measurement. The values recorded for each type of pear flesh were the average of 5 readings on different sites of the flesh. The "a" value was measured to represent the degree of the pink discoloration⁶⁾.

Statistical analysis

Data were analyzed using a Statistical Analysis¹¹⁾ program package. After an analysis of variance (ANOVA), a significant difference among means was determined by the Duncan Teat. Significance of differences was defined at p<0.05.

RESULTS AND DISCUSSION

The characteristics of pink substance in canned pears.

The precursor of the pink substance extracted by methanol from that was colorless which became pink through heating. LUH *et al.*⁸⁾ extracted the flavonoids of pear flesh using 10g of

pear flesh with 1.5g of NaCl, 2ml of 6N HCl and 50 ml of butanol. This process produced the precursor of the pink substance. The aglycone type of cyanidin was produced as a result of heating. In order to understand the pathway for converting leuco compounds into the pink

substance, it was necessary to use methanol with 1% HCl as the extracting solution. This method could extract the leucocyanidin as the intermediate, and this intermediate could be regarded as the precursor of the pink substance. The effect of heating on changes of the pink substance is shown in Fig.1. The maximum absorption of the pink extract was at 533nm. CHANDLER and CLEGG³⁾ showed the reflectance spectrum of pink pear debris had a minimum at 530-540nm recorded on a Sepetrophotometer against a standard magnesium oxide block. The result from Fig.1. was similar to that of CHANDLER and CLEGG³⁾. The longer the heating time, the higher the optical density was. From Fig.1, it is shown that the heating time of 100 min. would reach the maximum peak at 533nm in this study, so the heating tests in this study were conducted in 100 min.

The extract of pear flesh had the highest peak at a retention time of 2.93 and 3.01 min in previous analytical condition at 280 nm absorption as shown in Fig. 2. After the heating of the extract from pear flesh, the highest peak shifted to 3.89 min. These result indicated that the heating caused some changes in the compounds of the extract. Some compounds became less polar due to decomposition or polymerization. The retention time of the heated compounds had a longer retention in the analysis than the unheated compounds. These results were similar to those of WU¹³⁾.

CHANDLER and CLEGG¹³⁾ reported that the precursor of pink color contained the leucocyanidin. In this study, aglycone was produced by hydrolysis of the extract of pink compound being heated in 4 normality of HCl. The synthetical leucocyanidin and the perilla leaf extracted by methanol with 1% HCl were treated with the same procedure to produce aglycone. These three samples were analyzed using HPLC. The result indicated that the cyanidin was only aglycone in the extract of sand pear flesh (Fig.3). This result was in agreement with the findings of LUH *et al.*⁸⁾ and CHANDLER and CLEGG¹³⁾.

Fig. 1 The spectra of sand pear flesh extracts heated for 40 min (left) or 80 min (right)

Fig. 2 High performance liquid chromatogram of sand pear flesh extract with 1% hydrochloric acid in methanol. Using μ -Bondapak (Water Assoc.).

Mobile phase: methanol:acetic acid= 7 : 2 : 1 (v/v)

Speed: 1 ml/min and detected at 280nm.

Left: unheated. Right: heated.

Fig. 3 High performance liquid chromatograms of cisleucocyanidin (upper) and sand pear flesh extract (left) and perilla leaf extract (right) that were extracted with 1% HCl in methanol and after being hydrolyzed. Using μ -Bondapak C_{18} column (Waters Assoc.) Mobile phase: Water: methanol: acetic acid = 7 : 2 : 1 (v/v/v), Speed : 1 ml/min. and detected at 533 nm.

Effect of citric acid content on the pink discoloration

Tables 1 and 2, show the "a" values for cultivars Ko-j-lee and Sin-sin. In each cultivar of sand pear, the "a" value varied with the amount of citric acid and the Brix of sugar in the syrup. The greater the amount of citric acid, the "a" value. The data in Tables 1 and 2 showed the addition of 0.15% citric acid added was sufficient to lower the pH below 4.6 and could prevent the pink discoloration in canned sand pears. Increasing the amounts of acids in syrup had been reported to enhance the conversion of leucoanthocyanin into anthocyanin in canned lychees, which would promote the development of a pink discoloration²⁾.

Effect of sugar content on the pink discoloration

From Table 1 and 2, the °Brix of cv. Ko-j-lee and Hsin-shui are 10.5 and 12.5, respectively, with the same °Brix of added sugar in the syrup, the tendency toward pink discoloration can be restrained. CHAKRABORTY *et al*²⁾ showed that there was less pink discoloration if 20 °Brix syrup was added to the canned lychee. The 20 °Brix of syrup is nearer the °Brix of lychee flesh than the 30 °Brix syrup, so the syrup containing 20 °Brix maintained better color in lychee flesh than 30

Table 1 Effect of citric acid and sugar on the "a" value of canned sand pears cv. Ko-j-lee storage at 26 ± 1 °C for one year

°Brix of fresh flesh	Citric acid % of pear flesh	Citric acid % added in syrup	Sugar added in syrup* °Brix	"a" value of canned sand
10.5	0.14	0.15	10.5	-1.49h
		0.25	10.5	-1.39g
		0.35	10.5	-1.07f
		0.15	18.0	-1.09f
		0.25	18.0	-0.87e
		0.35	18.0	-0.49d
		0.15	25.5	0.04c
		0.25	25.5	0.21b
		0.35	25.5	0.53a

*-h: Means with a column followed by the same subscript letter are not significantly different ($p > 0.05$) separated by the Duncan Method.

*The fraction of sugar is fructose : glucose : sucrose = 7 : 5 : 2.3 : 0.7

Table 2 Effect of citric acid and sugar on the "a" value of canned sand pears cv. Sin-sin storage at 26 ± 1 °C for one year

°Brix of fresh flesh	Citric acid % of pear flesh	Citric acid % added in syrup	Sugar added in syrup* °Brix	"a" value of canned sand pear
12.5	0.13	0.15	12.5	-1.75h
		0.25	12.5	-1.57g
		0.35	12.5	-1.29f
		0.15	18.0	-1.22f
		0.25	18.0	-1.07e
		0.35	18.0	-0.69d
		0.15	23.5	-0.23c
		0.25	23.5	0.06b
		0.35	23.5	0.16a

*-h: Means with a column followed by the same superscript letter are not significantly different ($p > 0.05$) separated by the Duncan Method.

*The fraction of sugar is fructose : glucose : sucrose = 8 : 8 : 2.9 : 0.8

°Brix syrup. The results showed that the addition of 0.15% citric acid to the syrup with the °Brix of sugars in the same as the sand pear flesh, the “a” value of the canned sand pear flesh was lower than those with higher Brix levels and could reduce the pink discoloration in canned sand pears (Tables 1 and 2). This could be explained in terms of the effect of osmotic pressure. If the osmotic pressure in the syrup were greater than the osmotic pressure in the flesh, more of the flesh texture would be degraded, and the pink discoloration would be increased as shown by the results of WU and FANG¹⁴⁾.

CONCLUSIONS

The major precursor of pink discoloration in canned pears existed in the soluble solids of the sand pear. This precursor belonged to the flavonoid which became a pink color after being heated in acidic conditions. The addition of 0.15% citric acid to the syrup was sufficient to lower the pH of the canned sand pear below 4.6. The more citric acid added, the greater the occurrence of pink discoloration was observed in the sand pear flesh. The results indicated that the use of syrup at the same °Brix level and the same sugar profile of the fruit flesh could reduce the pink discoloration in canned pear products.

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缶詰梨 (*Pyrus pyrifolia* Nakai) の桃色変化

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缶詰にした梨が品質劣化を起こし、桃色となった。本試験は桃色になった原因を探ったものである。缶詰にした梨が桃色となった主原因は梨の中の不溶性固体物質であることが判明した。この前駆物質はフラボノイドであり、酸化の環境の中で加熱すると桃色に変化した。桃色の物質の成分はシアニンであり、これは缶詰にした梨のアグリコンの中の成分である。クエン酸を0.15%に調整し、pHを4.6に低下させ、同じ Brix と sugar の濃度とした結果、梨の桃色への変化は高濃度のものより減少した。(平成11年7月12日受付、平成12年1月24日受理)