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Anthocyanin Compounds in Japanese Ginger (*Zingiber officinale* Roscoe) and Their Quantitative Characteristics

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Two types of anthocyanin, cyanidin 3-*O*-β-D-glucopyranoside (cyanidin 3-glucoside) and peonidin 3-*O*-(6-*O*-α-L-rhamnopyranosyl-β-D-glucopyranoside) (peonidin 3-rutinoside) were isolated from ginger rhizomes by various chromatographic methods. A comparison of the content of these compounds showed their presence in many kinds of Japanese ginger, but not in Chinese ginger. In particular, peonidin 3-rutinoside, which we identified for the first time in the ginger rhizome, was the main anthocyanin constituent at 0.67–2.38 mg/100 g of fresh ginger rhizome, and its concentration was 2.0–43.4 times higher than that of cyanidin 3-glucoside. These two anthocyanins were only present in the lower stem and rhizome in the ginger plant, and their proportions in the lower stem were different from those in the rhizome, cyanidin 3-glucoside being much more abundant than peonidin 3-rutinoside in the lower stem. These results suggest that the anthocyanin formation in ginger varies according to its variety, the part of the plant, and the place of cultivation.

Keywords: ginger (*Zingiber officinale* Roscoe), anthocyanin, cyanidin 3-glucoside, peonidin 3-rutinoside

Ginger (*Zingiber officinale* Roscoe) is one of the most familiar spices used throughout the world. Ginger pickle, "*gari*" in Japanese, which is the processed ginger soaked in a vinegar solution that contains salt and sugar, is the most popular ginger product in Japan and is eaten with fish and meat dishes. When ginger is soaked in vinegar, its color changes to soft pink and it is most effective in not only improving the taste and aroma, but also in providing a colorful decoration for cooked dishes. This change in color under acidic condition suggests that ginger contains anthocyanin compounds. In fact, Fu *et al*. (1993) first identified cyanidin 3-glucoside from young green Chinese ginger. However, little information about the chemical structure and amount of other anthocyanins in ginger is presently available.

Anthocyanins are the major water-soluble pigments in plant derived foods such as fruits, vegetables and cereals, and their potential health benefits have recently been the subject of increasing interest. Numerous articles have been published regarding their antioxidative activities (Tsuda *et al*., 1994; Satue-Grancia *et al*., 1997; Wang *et al*., 1997; Pool-Zobel *et al*., 1999; Ramirez-Tortosa *et al*., 2001; Wang *et al*., 1999; Seeram *et al*., 2001) and their potential pharmaceutical effects on coronary heart disease, inflammatory disease, and circulatory disorders have also been examined (Wang *et al*., 1999; Youdim *et al*., 2000; Bettini *et al*., 1985; Waterhouse, 1995). These effects have indicated the possibility that the anthocyanins in ginger may also have some value as food constituents. There are several cultivars of ginger with distinct colors and morphology suggesting that the anthocyanin contents differ according to the ginger variety of the plant.

It is also possible that the chemical composition in ginger differs in different parts of the plant, depending on place of cultivation, growth stage and storage method. Ginger is generally classified into three groups: small immature ginger (*ha-shoga*), fresh rhizome (*shin-shoga*) and stored old rhizome (*hine-shoga*). *Ha-shoga* is usually sold with the leaves still attached to the rhizome, although only the rhizome is eaten as a vegetable in Japan.

In this work, we determined the structures of the anthocyanins found in ginger and quantified their amounts. We also investigated and compared the contents of anthocyanins among different ginger varieties and from different parts of the plant to characterize their generation and accumulation.

Materials and Methods

Materials Seven kinds of fresh ginger samples (*Zingiber officinale* Roscoe) were purchased from Tokyo Central Market or from a harvesting company (Sakata-Nobuo Shoten, Kochi) in Japan. Among them, "*tosaichi*" and "*kogane-no-sato*" (Kochi, Japan), and "*oumi*" (Wakayama, Japan) are medium-size ginger rhizomes that can commonly be obtained. "*Me*", "*bouzu*", "*tsubame*" and "*yanaka*" (Saitama, Japan) are different in appearance from each other, but all can be categorized as small immature ginger. Among them, "*me*", "*tsubame*", "*yanaka*" and "*tosaichi*" were evaluated for their individual accumulation of anthocyanins in the leaf, upper stem, lower stem and rhizome. All stored old ginger was purchased at a local supermarket, except *"tosaichi"* and *"koganenosato"*.

Isolation of the anthocyanins "*Tosaichi*" ginger rhizomes were used for the isolation and determination of their anthocyanin structures. Ginger rhizomes (3 kg) were chopped and homogenized in 6 *l* of methanol solution containing 0.2% TFA for 70% methanol concentration. After soaking overnight, the acidic methanol extraction solution was filtered through filter paper (No. 2) under vacuum. This extraction procedure was repeated

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three times, and methanol was evaporated from the extracted solution. To extract the abundant volatiles and free phenolic compounds, the resulting aqueous solution was washed with diethyl ether (200 ml×5) and chloroform (100 ml×2), before being loaded into a column filled with Amberlite XAD-7. After washing with water, the resin-bound anthocyanins were eluted with methanol containing 0.2% TFA. This concentrated fraction was successively fractionated by flash column chromatography (ODS resin), and bound material was eluted with a stepwise change of 0.2% TFA methanol/water (30%, 40%, 50%, 70% and 100%). A strong red color was obtained from the 40% acidic methanol-eluted fraction, and this fraction was further applied to isolate each anthocyanin compound separately by preparative HPLC in an ODS column (Pegasil ODS, 20 mm×250 mm, 0.2%TFA acetonitrile/H_2O gradient elution) with UV detection at 520 nm or 220 nm. After continuous HPLC separation while checking the degree of purification by TLC (EtOAc : formic acid : H_2O=14 : 3 : 3), two anthocyanins **1** (7.4 mg) and **2** (13.2 mg) were obtained.

Spectral analysis FAB-MS data were obtained by a JEOL JMS-700 Mstation instrument with glycerol as a matrix. ^{1}H- and ^{13}C-NMR spectra and HMBC data were measured by a JEOL JNM-GX 270 and 400 spectrometers in 10%TFA-*d*/CD_3OD containing TMS as an internal standard.

Compound 1 FABMS: *m/z* 409.0 $[M]^+$; ^{1}H-NMR (ppm, *J* in Hz): 8.99 (1H, s, H-4), 6.66 (1H, br.s, H-6), 6.87 (1H, br.s, H-8), 8.02 (1H, d, *J*=2.0, H-2′), 7.00 (1H, d, *J*=8.5, H-5′), 8.21 (1H, dd, *J*=2.1, 8.5, H-6′), 5.31 (1H, d, *J*=8.1, glcH-1), 3.69–3.79 (1H, m, glcH-2), 3.69–3.79 (1H, m, glcH-3), 3.46–3.62 (1H, m, glcH-4), 3.46–3.62 (1H, m, glcH-5), 3.60 (1H, m, glcH-6′), 3.95 (1H, d, *J*=12.8, glcH-6″); ^{13}C-NMR (ppm): 163.8 (C-2), 145.4 (C-3), 136.6 (C-4), 160.2 (C-5), 103.4 (C-6), 170.4 (C-7), 95.1 (C-8), 157.4 (C-9), 113.3 (C-10), 121.1 (C-1′), 118.3 (C-2′), 147.2 (C-3′), 155.6 (C-4′), 117.3 (C-5′), 128.1 (C-6′), 103.6 (glcC-1), 74.7 (glcC-2), 78.1 (glcC-3), 71.0 (glcC-4), 78.7 (glcC-5), 62.3 (glcC-6).

Compound 2 FABMS: *m/z* 609.8 $[M]^+$; ^{1}H-NMR (ppm, *J* in Hz): 8.95 (1H, s, H-4), 6.69 (1H, br.s, H-6), 6.92 (1H, br.s, H-8), 8.19 (1H, d, *J*=2.2, H-2′), 7.06 (1H, d, *J*=8.8, H-5′), 8.25 (1H, dd, *J*=2.1, 8.6, H-6′), 4.02 (3H, s, -OMe), 5.32 (1H, d, *J*=7.6, glcH-1), 3.55–3.69 (1H, m, glcH-2), 3.55–3.69 (1H, m, glcH-3), 3.32–3.40 (1H, m, glcH-4), 3.83 (1H, m, glcH-5), 3.44 (1H, m, glcH-6′), 4.09 (1H, d, *J*=11.0, glcH-6″), 4.68 (1H, d, *J*=1.3, rhaH-1), 3.73–3.77 (1H, m, rhaH-2), 3.55–3.69 (1H, m, rhaH-3), 3.32–3.40 (1H, m, rhaH-4), 3.55–3.69 (1H, m, rhaH-5), 1.18 (1H, d, *J*=6.1, rhaH-6); ^{13}C-NMR (ppm): 163.6 (C-2), 145.4 (C-3), 136.4 (C-4), 159.7 (C-5), 103.5 (C-6), 170.7 (C-7), 95.3 (C-8), 156.5 (C-9), 113.4 (C-10), 120.9 (C-1′), 117.6 (C-2′), 149.4 (C-3′), 160.5 (C-4′), 115.0 (C-5′), 128.9 (C-6′), 56.9 (-OMe), 103.6 (glcC-1), 74.8 (glcC-2), 78.1 (glcC-3), 71.2 (glcC-4), 77.5 (glcC-5), 67.6 (glcC-6), 102.1 (rhaC-1), 71.8 (rhaC-2), 72.4 (rhaC-3), 73.9 (rhaC-4), 69.8 (rhaC-5), 17.9 (rhaC-6).

Quantification analysis of the anthocyanins in various types and different parts of ginger To characterize their anthocyanin content, various types and parts of ginger were examined. Thirty grams of each sample was homogenized in a 0.2% TFA/MeOH solution (100 ml) and then extracted for three hours. After vacuum filtration, the resulting residue was extracted again with the same solution (80 ml). The combined filtrate was evaporated and made up to 25 ml with 0.2%TFA/MeOH for an HPLC analysis, each sample extract being analyzed in triplicate.

A Waters 600 gradient HPLC system connected to a Waters 996 photodiode array detector was used for the analysis. Chromatographic separation was performed in a Develosil ODS-5 column (4.6 mm×250 mm, Nomura Chemicals, Aichi) with detection at 520 nm. The mobile phase was a linear gradient of 0.2% TFA/H_2O (solvent A) with 0.2% TFA/acetonitrile (solvent B) programmed from 10% B to 50% in 40 min at a flow rate of 1.2 ml/min. Each sample was injected into the HPLC instrument in duplicate. The anthocyanin contents were quantified by comparing the measured peak areas with the calibration curve for cynidin 3-rutinoside as a standard.

The recovery of anthocyanins by extraction was confirmed by adding standard cyanidin 3-rutinoside to the ginger samples. Cyanidin 3-rutinoside (2.0 mg/100 g ginger) was added to a ginger sample before homogenizing, and HPLC samples were prepared and analyzed as shown above. These procedures were performed in triplicate. The final recovery of cyanidin 3-rutinoside was 92.4%.

Results and Discussion

Structures of the anthocyanins in ginger The dark pink color and high absorbance at 530–534 nm of the acidic MeOH extract of ginger indicated that some anthocyanins were likely to be present. A HPLC chromatogram of the acidic MeOH extract from *tosaichi* cultivar is shown in Fig. 1. This chromatogram pattern of two clear peaks, **1** (11.3 min) and **2** (13.4 min), was shown in all ginger samples, although the *"kogane-no-sato"* variety alone showed one more small peak at 12.9 min. To elucidate the structures of compounds **1** and **2**, the acidic MeOH fraction was first subjected to various chromatographic operations to isolate these compounds. After several steps, **1** and **2,** showing a dark pink color, were finally isolated, and their structures were elucidated by NMR and FAB-MS analyses. The ^{1}H-NMR analysis of compound **1** detected six aromatic protons in the range 6.69–8.95 ppm that were assigned as protons of cyanidin. The

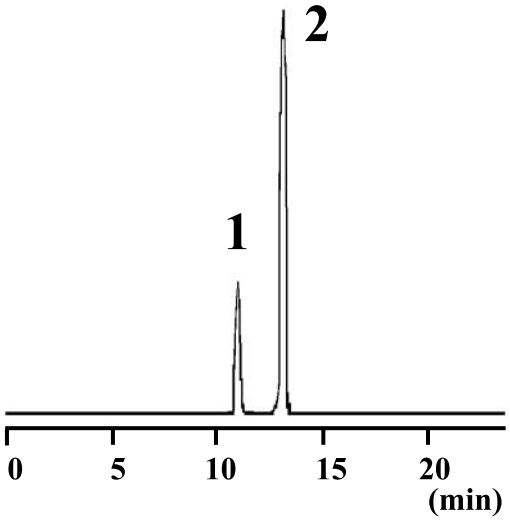

Fig. 1. HPLC profile of crude anthocyanin extract from ginger rhizome (*Tosaitchi* cultivar) at 520 nm. Each number is correlated to those in Fig. 2.

^{13}C-NMR analysis showed 13 aromatic carbon signals and supported the structure of cyanidin as the aglycon. The FAB-MS analysis detected a clear peak at *m/z* 449 $[M]^+$ as the molecular ion. The signal patterns from NMR and one anomeric proton at 5.31 ppm (J=8.1 Hz) in the ^{1}H-NMR spectrum were assigned as β-D-glucopyranoside. Furthermore, the NMR signals of compound **1** were in agreement with those of cyanidin 3-*O*-β-D-glucopyranoside reported in the literature (Johansen *et al*., 1991). Therefore, compound **1** was identified as cyanidin 3- *O*-β-D-glucopyranoside. Compound **2** showed *m/z* 609 $[M]^+$ as the molecular ion and gave similar NMR signals to those of compound **1**, although one strong methoxy proton signal at 4.02 ppm in the ^{1}H-NMR spectrum and disaccharide signals 67.6–78.1 ppm in the ^{13}C-NMR spectrum were characteristic. The HMBC analysis indicated that the methoxy group was bound to the 3′ carbon on the B-ring, and the aglycon of compound **2** was assigned as peonidin. One anomeric proton and carbon signals, and three carbon signals at 2, 3, 4 on glucose were almost the same as those in compound **1**, suggesting that β-D-glucopyranoside was directly bound to peonidin. Moreover, a strong doublet proton at 1.18 ppm (J=6.1 Hz) and another anomeric proton signal at 4.68 ppm (J=1.3 Hz) in the ^{1}H-NMR spectrum indicated that the next sugar was α-L-rhamnopyranoside. A comparison with the ^{1}H-NMR data for commercial cyanidin 3-rutinoside showed the signals for the sugar parts to be completely consistent. Moreover, a comparison of the signals for this compound with reference data (Yoshida *et al*., 1996) identified compound **2** as peonidin 3-*O*- (6-*O*-α-L-rhamnopyranosyl-β-D-glucopyranoside) (peonidin 3-rutinoside). Fu *et al*. (1993) have previously detected cyanidin 3-glucoside in Chinese green ginger. Although peonidin 3-rutinoside has been reported in beans (Yoshida *et al*., 1996), banana bracts (Pazmino-Duran *et al*., 2001), rose flower (Mikanagi *et al*., 2000) and blackcurrant fruit (Froytlog *et al*., 1998), this is the first time it has been identified in ginger. We have already found some glycosides of alcohols and gingerdiol in ginger (Sekiwa *et al*., 1999; Sekiwa *et al*., 2000; Sekiwa *et al*., 2001), but rutinoside as the sugar part is the first glycoside to be found in this plant.

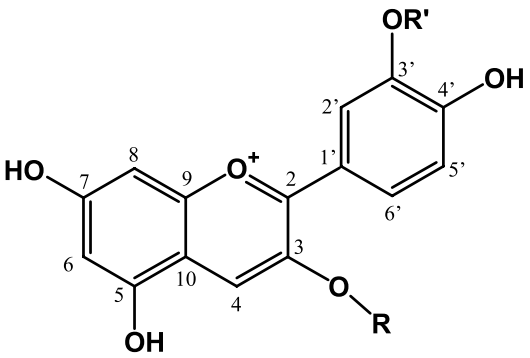

Fig. 2. Structure of the anthocyanins identified in ginger: Cyanidin glucoside (**1**), R=β-D-glucopyranose, R′=H; Peonidin 3-rutinoside (**2**) R=α-L-rhamnopyranosyl-β-D-glucopyranose, R′=CH_3

To confirm that these anthocyanin compounds cause the change in ginger color to pink during food preparation, the compounds were soaked in a model vinegar solution (4.5% acetic acid solution, pH 3.2). The pink color was quickly formed, and changed to a weak color in the solution under a neutral condition. We conclude that these anthocyanins are the main compounds responsible for the pink coloration of prepared ginger.

Quantification of the anthocyanins in various commercial samples of ginger To compare and characterize the anthocyanins among various commercial samples of ginger, the contents of compounds **1** and **2** were quantified. Four samples of small fresh ginger (*ha-shoga*), three of medium size fresh ginger (*shin-shoga*) and eight of stored old ginger of medium size (*hine-shoga*) were chosen. The anthocyanin content of each was calculated from the calibration curve for cyanidin 3-rutinoside as a standard, and is shown in Table 1. In all the ginger samples containing anthocyanins, the peonidin 3-rutinoside (**2**) content was 2.0–43.4 times higher than that of cyanidin 3-glucoside (**1**). These results indicate that peonidin 3-rutinoside is the main anthocyanin in ginger. Among the samples evaluated, small ginger contained the highest amount of anthocyanins, with about 0.5

Table 1. Anthocyanin contents in the rhizomes of various kinds of commercial ginger (mean±S.D.).

Ginger Sample	Cultivation District	Anthocyanin contents (mg/100 g fresh ginger)	
		Cy-3-glc[a] (**1**)	Pn-3-rut[b] (**2**)
Small ginger *(ha-shoga)*			
Tsubame-shoga	Japan (Saitama)	0.52±0.065	2.12±0.27
Me-shoga	Japan (Saitama)	0.77±0.40	1.70±0.12
Yanaka-shoga	Japan (Chiba)	0.43±0.23	2.38±0.14
Bouzu-shoga	Japan (Saitama)	0.56±0.19	1.90±0.48
Immature medium ginger *(sin-shoga)*			
Tosaichi	Japan (Kochi)	0.19±0.10	0.92±0.18
Koganenosato	Japan (Kochi)	0.50±0.04	1.02±0.01
Shin-shoga	Japan (Wakayama)	0.21±0.00	0.98±0.12
Stored medium ginger (*hine-shoga*)			
Oumi	Japan (Kumamoto)	0.07±0.00	0.67±0.01
Kochikou	Japan (Kochi)	0.15±0.00	1.65±0.12
Kochi	Japan (Kochi)	0.05±0.01	2.35±0.12
Tosaichi	Japan (Kochi)	0.15±0.01	1.37±0.00
Koganenosato	Japan (Kochi)	0.50±0.05	1.02±0.01
Oumi (chuugoku)	China	n.d.	n.d.
Kouteichuugoku	China	n.d.	n.d.
Chuugoku shoga	China	n.d.	n.d.

[a] cyanidin 3-glucoside, [b] peonidin 3-rutinoside

Table 2. Anthocyanin contents in lower stem parts[a)] of *ha-shoga* (mean± S.D.)

Ginger Sample	Anthocyanin contents (mg/100 g fresh ginger stem)	
	Cy-3-glc[b)] (**1**)	Pn-3-rut[c)] (**2**)
Tsubame-shoga	7.89±0.47	0.84±0.15
Me-shoga	12.66±0.25	0.51±0.12
Yanaka-shoga	4.47±0.08	0.81±0.10
Tosaichi	10.57±0.87	1.10±0.10
Kogane	10.21±0.70	0.40±0.06

[a)] Lower stem represents the stem part in 5 cm above rhizome.
[b)] cyanidin 3-glucoside, [c)] peonidin 3-rutinoside

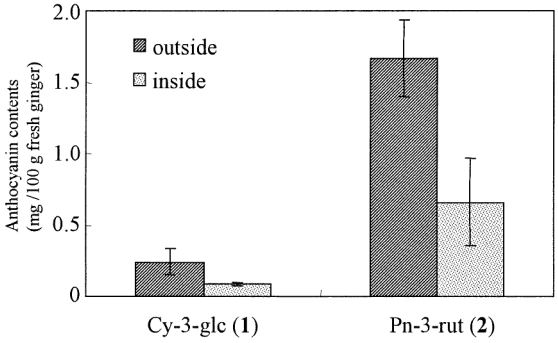

Fig. 3. The comparison of anthocyanin contents between outside (within 5 mm of the peel) and inside (more than 5 mm from the peel) of ginger rhizome.

mg of cyanidin 3-glucoside and 2.0 mg of peonidin 3-rutinoside per 100 g of fresh ginger. The contents of these two anthocyanins in fresh medium size ginger were 1/2–1/3 those in small fresh ginger, except for "*kogane-no-sato*". The samples of stored old ginger of medium-size differed in content and ratio between cyanidin 3-glucoside and peonidin 3-rutinoside according to the region of origin. Of note was that no anthocyanin was detected in the sample imported from China. Because the samples of "*Tosaichi* " and "*kogane-no-sato*" were obtained from the same growing field, it was possible to compare the amounts of anthocyanin between the fresh and stored ginger conditions. It is known that the composition of volatile and pungent components that determine ginger qualities varies during maturation, and that some related enzymatic activities also change with growth stage (Sakamura, 1987; Baranowski, 1986; Sekiwa-Iijima *et al*., 2001). However, we could not detect any significant change in the anthocyanin contents among the gingers of different age. These results indicate that the anthocyanins in ginger are stable and their contents mainly depend on their variety and region of origin.

Comparison of anthocyanins in different ginger parts To quantify the accumulation of anthocyanins in the ginger plant, their content in different parts of the plant was measured. Five whole plants of ginger were purchased as samples: "*tsubame,*" "*me,*" "*yanaka,*" "*tosaichi*" and "*kogane-no-sato*". Each sample was carefully separated into leaves, upper stems (more than 5 cm above the rhizome), lower stems (within 5 cm of rhizome) and rhizomes, before the anthocyanins were extracted with acidic MeOH for subsequent analysis by HPLC. No peak for anthocyanins was detected in the leaf or upper stem samples, while the lower stems of all samples contained cyanidin 3-glucoside and peonidin 3-rutinoside as exclusive compounds as found in the rhizome (Table 2). Interestingly, the ratio of these two anthocyanins in the lower stems was the inverse of those in the rhizomes. The cyanidin 3-glucoside content in the lower stems was particularly high, being almost 10 times more than that in the rhizome. This suggests that cyanidin 3-glucoside and peonidin 3-rutinoside are differently generated in different parts of the plant, and that differential transport and accumulation may also play a part.

The content of each anthocyanin between 5 mm thick peel (outside) and rest of the ginger rhizome (inside) was compared in "*tosaichi*" (Fig. 3). The cyanidin 3-glucoside content was 0.09 mg and 0.24 mg, and the peonidin 3-rutinoside content was 0.66 mg and 1.67 mg/100 g of fresh ginger at the inside and outside of ginger rhizome, respectively. Thus both of these contents were almost 2.5 times more on the outside.

In conclusion, anthocyanin content in the ginger plant varies among the parts of the plant, the varieties, and the region of origin. The content in ginger is not high in comparison with other anthocyanin-rich plant derived food such as grapes and berries (Nyman & Kumpulainen, 2001; Wang *et al*., 2000; Goiffon *et al*., 1991). However, the presence of anthocyanins in ginger seems to be significant for its food quality with a pungent and flavor compound.

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