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ScienceDirect
Food Chemistry 106 (2008) 277–284
Food Chemistry
www.elsevier.com/locate/foodchem

The flavonoid, carotenoid and pectin content in peels of citrus cultivated in Taiwan

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Received 30 November 2006; received in revised form 1 April 2007; accepted 30 May 2007

Abstract

The flavonoid, carotenoid and pectin composition in peels of eight varieties of citrus {Ponkan (*Citrus reticulata* Blanco), Tonkan (*C. tankan* Hayata), Murcott (*C. reticulate* × *C. sinensis*), Wendun (*C. grandis* Osbeck), Peiyou (*C. grandis* Osbeck CV), Kumquat (*C. microcarpa*), Liucheng [*C. sinensis* (L.) Osbeck], and Lemon [*C. limon* (L.) Bur]} cultivated in Taiwan was determined. The total flavonoid content exceeded the total carotenoid content. Ponkan (*C. reticulata* Blanco) peel had the highest total carotenoid content (2.04 ± 0.036 mg/g db) and Wendun (*C. grandis* Osbeck) and Peiyou (*C. grandis* Osbeck CV) peels, the lowest (0.036 ± 0.0006 and 0.021 ± 0.0004 mg/g db, respectively). Naringin was abundant in Peiyou (*C. grandis* Osbeck CV) and Wendun (*C. grandis* Osbeck) peels (29.8 ± 0.20 and 23.9 ± 0.32 mg/g db, respectively) and hesperidin was aboundant in Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata), and Liucheng [*C. sinensis* (L.) Osbeck] peels (29.5 ± 0.32, 23.4 ± 0.25, 20.7 ± 0.38 mg/g db, respectively). Kumquat (*C. microcarpa*) peel contained the most diosmin (1.12 ± 0.03 mg/g db) and quercetin (0.78 ± 0.003 mg/g db). Levels of caffeic acid (3.06 ± 0.03–80.8 ± 3.72 μg/g db) were much lower than that of chlorgenic acid, ferulic acid, sinapic acid and ρ-coumaric acid. Ponkan (*C. reticulata* Blanco), Kumquat (*C. microcarpa*) and Liucheng [*C. sinensis* (L.) Osbeck] peels contained the most total amounts of lutein, zeaxanthin, β-cryptoxanthin, and β-carotene (114, 113, and 108 mg/g db, respectively). The total pectin content ranged from 36.0 ± 1.46 to 86.4 ± 3.36 mg/g db.

Keywords: Citrus peel; Flavonoid; Carotenoid; Pectin

1. Introduction

Citrus fruit is a major product of Taiwanese agriculture and many varieties are cultivated, including (in order of importance) Liucheng [*Citrus sinensis* (L.) Osbeck], Ponkan (*Citrus reticulata* Blanco), Wendun (*C. grandis* Osbeck) and Tonkan (*C. tankan* Hayata). Of these of varieties, Murcott (*C. reticulata* × *C. sinensis*) is the earliest matured variety (January–March) in Taiwan, followed in order by Tonkan (*C. tankan* Hayata) (February–March), Lemon [*C. limon* (L.) Bur] (May–June), Wendun (*C. grandis* Osbeck) (September–October), Ponkan (*C. reticulata* Blanco) (October–December), Peiyou (*C. grandis* Osbeck CV) (October–November), Kumquat (*C. microcarpa*) (November–December) and Liucheng [*C. sinensis* (L.) Osbeck] (December–January). According to the Agricultural Statistics Year Book (Anonymous, 2005), about 33,000 hectares are dedicated to citrus cultivation in Taiwan and the production is about 534,000 tons annually.

During the processing of citrus fruit for juice, peels are the primary byproduct. If not processed, the peels become waste and a possible source of environmental pollution. In fact, phytochemicals that contribute to health (e.g., flavonoids, carotenoids and pectin) are abundant in citrus peels. The highest amount of flavonoids (a major group of citrus secondary metabolites) occurs in the peel. Neoeriocitrin, naringin and neohesperidin are the main flavanones in the peels of sour orange (*C. aurantium*), lemon (*C. limon*)

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doi:10.1016/j.foodchem.2007.05.086

and bergamote (*C. bergamia* Fantastico) (Bocco, Cuvelier, Richard, & Berset, 1998; Mandalari et al., 2006). Diosmetin derivatives are the major flavones in navel orange, bergamot and lemon peels (Lin & Harnly, 2007; Mandalari et al., 2006; Miyake, Yamamoto, Morimitsu, & Osawa, 1997). Hesperidin is the most abundant flavonoid in Valencia, Navel, Temple and Ambersweet orange peels (Manthey & Grohmann, 1996) and naringin is the most abundant flavonoid in grapefruit peel (Wu, Guan, & Ye, 2007). The levels of hydroxycinnamic acids (a group of phenolic acids) were much higher in the peel than in the juice (Manthey & Grohmann, 2001). The level of total carotenoids in citrus peel vary between varieties, being abundant in Cara Cara orange [*C. sinensis* (L.) Osbeck] and Star Ruby grapefruit (*C. paradisi* Macf.) (Xu, Fraser, Wang, & Bramley, 2006). Xanthophylls (a group of carotenoids) are abundant in Taiwanese orange peel (Yen & Chen, 1995). Pectin is a class of complex polysaccharides that function as a hydrating agent and cementing material for the cellulosic network. Commercial pectin is mostly derived from citrus (lime, grapefruit, and orange) and apple (Thakur, Singh, & Handa, 1997; Liu et al., 2001).

Flavonoids have a wide range of biological effects, such as inhibition of key enzymes in mitochondrial respiration, protection against coronary heart disease and anti-inflammatory, antitumour, and antimicrobial activities (Harborne & Williams, 2000). A high carotenoid intake might decrease the risk of cancer, age-related macular degeneration, cataracts, sunburn-induced skin damage and cardiovascular diseases (Aust, Sies, Stahl, & Polidori, 2001). Hydroxycinnamic acid compounds inhibit the oxidation of low-density lipoprotein (Meyer, Donovan, Pearson, Waterhouse, & Frankel, 1998) and have anticancer (Kual & Khanduja, 1998) and antimicrobial activities (Kernan et al., 1998). Citrus pectin has multiple biological activities, including glycemic and cholesterol level control (Baker, 1994).

In our previous study (Wang, Chuang, & Ku, 2007), we identified the bioactive compounds in Taiwanese citrus fruits. In this current study, we determined the flavonoid, carotenoid and pectin composition of peels from the same varieties of citrus and established a database of beneficial compounds in Taiwanese citrus fruits and peels.

2. Materials and methods

2.1. Plant materials and sample preparation

Eight varieties of citrus fruits, Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata), Murcott (*C. reticulate* × *C. sinensis*), Wendun (*C. grandis* Osbeck), Peiyou (*C. grandis* Osbeck CV), Kumquat (*C. microcarpa*), Liucheng [*C. sinensis* (L.) Osbeck], and Lemon [*C. limon* (L.) Bur] were harvested from trees at the local farms between October 2002 and January 2003. Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata), Murcott (*C. reticulate* × *C. sinensis*) and Lemon [*C. limon* (L.) Bur] were collected from Dongshih town, other varieties were collected from various locations, such as Wendun (*C. grandis* Osbeck) from Ruisuei town, Peiyou (*C. grandis* Osbeck CV) from Madou town, Kumquat (*C. microcarpa*) from Yuanshan town, and Liucheng [*C. sinensis* (L.) Osbeck] from Gukeng town. The citrus fruits were separated into edible and inedible portions (peel), and the peel was dried under a warm stream (below 50 °C), and finally stored at −30 °C before use.

2.2. Determination of total flavonoid and carotenoid contents

For total flavonoid examination, the method of Jia, Tang, and Wu (1999) was used. In brief, 2.5 g of a sample was placed in a Soxhlet extractor and refluxed with methanol for more than 12 h at 85 °C. The extract was evaporated to dryness in a rotary vacuum evaporator at less than 40 °C and then dissolved with methanol. Exactly 0.3 ml of 5% $NaNO_2$ was added to a 1 ml extract in a 10 ml volumetric flask and the mixture was kept for 6 min at room temperature. Addition of 0.3 ml of 10% $Al(NO_3)_3$ to the mixture, which was incubated for 6 min again, was followed by addition of 4 ml of 1 N NaOH and of methanol, up to volume. After incubating for 15 min at room temperature for colour development, absorbance at 510 nm was measured. Total flavonoid content was expressed as rutin equivalents, rutin was purchased from Acros (NJ, USA).

The method of Lee (2001) was used for total carotenoid quantitation. In brief, 5 g of a sample and 50 ml of *n*-hexane–acetone–ethanol (v/v; 50:25:25) were placed in a flask, extracted on a shaker at 200 rpm for 10 min at room temperature, centrifuged at 6500 rpm for 5 min at 4 °C and the supernatants were collected and made up to 50 ml with the extraction solvent. Absorbance was measured at 450 nm. The total carotenoid content was expressed as β-carotene equivalents, for which β-carotene was purchased from Acros (NJ, USA).

2.3. HPLC apparatus

Reversed-phase HPLC was used to assay compositions of the flavonoids and carotenoids. A Hitachi HPLC system (Tokyo, Japan) consisting of a Model L-7100 pump equipped with a multi-solvent delivery system and a L-7400 ultraviolet (UV) detector was used. The column was a LiChrospher®100 RP18e, 5 μm, 4.0 mm internal diameter (i.d.) × 250 mm, which was purchased from Merck (Darmstadt, Germany). The other individual chromatographic conditions for the compound detection were as described below.

2.4. Analysis of flavonoid composition by HPLC

The method of Schieber, Keller, and Carle (2001) for the analysis of flavonoid composition in citrus peel was used. The flavonoid standards included: (1) phenolic acids: caffeic

acid, ρ-coumaric acid, ferulic acid, sinapic acid and chlorogenic acid; (2) flavanones: naringin, hesperidin and neohesperidin; (3) flavonols: quercetin, kaempferol and rutin; and (4) flavones: sinensetin, luteolin and diosmin. All the standards were purchased from Sigma–Aldrich (St. Louis, MO, USA), prepared in methanol–dimethyl sulfoxide (DMSO) (v/v; 50:50) and stored at −18 °C before use.

A mixture of 0.1 g of sample and 1 ml of methanol–DMSO (v/v; 50:50) was placed in a centrifuge tube, stirred for 10 min at room temperature, and centrifuged at 9000 rpm for 15 min at 4 °C. The residues were extracted twice with 2 × 1 ml of the same extraction solvent. All the supernatants were combined and made up to 5 ml with methanol. The sample solution was filtered through a 0.45-μm membrane filter before use.

The mobile phase was composed of (A) 2% acetic acid (aqueous) and (B) 0.5% acetic acid (aqueous)-acetonitrile (v/v; 50:50) and gradient elution was performed as follows: 0 min, 95:5; 10 min, 90:10; 40 min, 60:40, 55 min, 45:55; 60 min, 20:80 and 65 min, 0:100. The mobile phase was filtered under vacuum through a 0.45-μm membrane filter before use. The flow rate was 1 ml/min. The UV absorbance for phenolic acids, flavanones and flavonols was measured at 280 nm and for flavones at 340 nm. The operating temperature was maintained at room temperature.

2.5. Analysis of carotenoid composition by HPLC

The carotenoid composition in citrus peels was determined. The carotenoid standards included lutein, zeaxanthin, β-cryptoxanthin and β-carotene. All, except β-carotene, which was purchased from Acros (NJ, USA), were purchased from Extrasynthese (Genay, France). Butylated hydroxytoluene (BHT) in chloroform (0.1%) was added to all the standards, and they were diluted with acetonitrile before use.

The sample preparation was according to Pupin, Dennis, and Toledo (1999). In brief, 10 parts 0.004% BHT in ethyl acetate mixed with 1 part of sample powder were stirred for 5 min at room temperature and centrifuged at 9000 rpm for 15 min at 4 °C. The residues were extracted twice with the same extraction solvent. All supernatants were combined and concentrated to dryness in a rotary vacuum evaporator below 40 °C. The concentrate was dissolved with acetonitrile–methanol–dichloromethane (v/v; 60:35:5) and filtered through a 0.45-μm membrane filter before use.

The mobile phase was composed of acetonitrile, methanol and dichloromethane, and gradient elution was performed as follows: 0 min, 100:0:0 (v/v/v), with 0.6 ml/min of flow rate; 25 min, 100:0:0, with 1.0 ml/min of flow rate; 30 min, 60:35:5, with 1.0 ml/min of flow rate and 80 min, 60:35:5, with 1.0 ml/min of flow rate. All mobile phases contained 0.1% BHT, 0.1% triethylamine and 0.005 M ammonium acetate (in methanol), and were filtered under vacuum through a 0.45-μm membrane filter before use. Absorbance was measured at 450 nm.

2.6. Determination of pectin content

The method of Yu and Love (1996) was used. A mixture of 5 g of sample powder and 30 ml of hot absolute ethanol was heated in a centrifuge tube for 10 min in a boiling water bath and centrifuged at 10,000 rpm for 10 min at 4 °C. The residues were dried for 24 h at 35 °C, and alcohol insoluble solids (AIS) were obtained.

One ml of water was added, dropwise with stirring, for 35 min to a mixture of 5 mg of AIS and 2 ml of concentrated sulfuric acid, in a test tube until the AIS were dissolved. The mixture was transferred into a 25-ml volumetric flask and made up to volume with distilled water for total pectin examination.

A mixture of 80 mg of AIS and 20 ml of distilled water was stirred in a centrifuge tube for 5 min at room temperature and centrifuged at 10,000 rpm for 10 min at 4 °C. The residues were extracted twice with 2 × 20 ml of distilled water. All the supernatants were transferred into a 100-ml volumetric flask and made up to volume with distilled water for water soluble pectin examination.

In an ice bath, 1 ml of the above sample solution was added to 6 ml of 0.0125 M sodium tetraborate (in concentrated sulfuric acid) and then heated for 5 min in a boiling water bath. Colour development followed addition of 0.1 ml of 0.15% *m*-hydroxydiphenyl and incubation for 20 min at room temperature. NaOH (0.1 ml) was added instead of 0.15% *m*-hydroxydiphenyl to the control. Both total pectin and water soluble contents were expressed as galacturonic acid equivalents, for which galacturonic acid was purchased from Fluka, Riedel-de-Haen (Sigma–Aldrich) (St. Louis, MO, USA).

2.7. Statistical analysis

Data regarding total flavonoid and carotenoid contents and flavonoid, carotenoid, and pectin composition were subjected to analysis of variance (ANOVA) and a *t*-test was used to identify differences among the means at $p < 0.05$.

3. Results and discussion

3.1. Total flavonoid and carotenoid contents

The amounts of total flavonoid and carotenoid in the peels of eight citrus fruits are shown in Table 1. Total flavonoid content ranged from 32.7 ± 1.06 to 49.2 ± 1.33 mg/g db (rutin equivalents), the highest levels being present in Ponkan (*C. reticulata* Blanco) and Peiyou (*C. grandis* Osbeck CV) peels [49.2 ± 1.33 and 48.7 ± 1.53 mg/g db (rutin equivalents), respectively], followed by Wenden (*C. grandis* Osbeck CV) peel (46.7 ± 1.51 mg/g db) ($p < 0.05$). The content in the other five citrus peels ranged from 32.7 ± 1.06 to 41.0 ± 1.37 mg/g db. The peels contained much less total carotenoids than total flavonoids, ranging from 0.021 ± 0.0004 to 2.04 ± 0.036 mg/g db (β-carotene

Table 1
Total flavonoid and carotenoid contents[A] (mg/g, db[B]) in citrus peel

Scientific name	Local name	Total flavonoid	Total carotenoid
Citrus reticulata Blanco	Ponkan	49.2 ± 1.33^{a}	2.04 ± 0.036^{a}
C. tankan Hayata	Tonkan	39.6 ± 0.92^{c}	1.42 ± 0.074^{c}
C. reticulate × *C. sinensis*	Murcott	39.8 ± 1.02^{c}	1.59 ± 0.011^{b}
C. grandis Osbeck	Wendun	46.7 ± 1.51^{b}	0.036 ± 0.0006^{g}
C. grandis Osbeck CV	Peiyou	48.7 ± 1.53^{a}	0.021 ± 0.0004^{g}
C. microcarpa	Kumquat	41.0 ± 1.37^{c}	0.737 ± 0.029^{d}
C. sinensis (L.) Osbeck	Liucheng	35.5 ± 1.04^{d}	0.445 ± 0.008^{e}
C. limon (L.) Bur	Lemon	32.7 ± 1.06^{e}	0.110 ± 0.001^{f}

[A] Data presented are in mean ± standard deviation ($n = 3$) which with different letters are significantly different at $p < 0.05$.
[B] Dried base.

equivalents). Of the eight citrus peels, Ponkan (*C. reticulata* Blanco), Murcott (*C. reticulate* × *C. sinensis*) and Tonkan (*C. tankan* Hayata) had the highest amount of total carotenoid [2.04 ± 0.036, 1.59 ± 0.011, and 1.42 ± 0.074 mg/g db (β-carotene equivalents), respectively] ($p < 0.05$).

The published total carotenoid content in the peels of oranges, pummelos and grapefruits were in the range of 0.151–0.218, 0.017–0.054 and 0.003–0.218 mg/g db, respectively (Xu et al., 2006). By comparison, total carotenoid content in the peels of our four oranges {Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata), Murcott (*C. reticulate* × *C. sinensis*) and Liucheng [*C. sinensis* (L.) Osbeck]} were much higher (0.445 ± 0.008–2.04 ± 0.036 mg/g db). On the other hand, total carotenoid content in pummelo, Wendun (*C. grandis* Osbeck) and Peiyou (*C. grandis* Osbeck CV) peels (0.036 ± 0.0006 and 0.021 ± 0.0004 mg/g db, respectively) were similar to the results of Xu et al. (2006). Comparing our previous results in the eight fruits (Wang et al., 2007) with our present results in the peels of these fruits shows that both total flavonoid and total carotenoid contents are higher in the peels than in the fruits. No other reports have focused on total flavonoid content in citrus peel.

3.2. Flavonoid composition

3.2.1. Flavanone compounds

The flavanone composition of eight citrus peels is shown in Table 2. Naringin, hesperidin and neohesperidin levels were, respectively, 0.21 ± 0.01–29.8 ± 0.20, 0.10 ± 0.004–29.5 ± 0.32, and 0.02 ± 0.001–0.34 ± 0.002 mg/g db. Moreover, naringin was abundant in pummelo peels [Peiyou (*C. grandis* Osbeck CV) and Wendun (*C. grandis* Osbeck), 29.8 ± 0.20 and 23.9 ± 0.32 mg/g db, respectively] and hesperidin was abundant in Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata) and Liucheng [*C. sinensis* (L.) Osbeck] peels (29.5 ± 0.32, 23.4 ± 0.25, and 20.7 ± 0.38 mg/g db, respectively) ($p < 0.05$). Lemon [*C. limon* (L.) Bur] peel contained a moderate level of hesperidin (9.42 ± 0.41 mg/g db) ($p < 0.05$).

The published levels of naringin in bergamot and Huyou (*C. Paradisi cv. Changshanhuyou*) peels were 2.33–11.0 mg/g db (Bocco et al., 1998; Calvarano et al., 1996; Mandalari et al., 2006) and 32.5 mg/g db (Lu, Zhang, Bucheli, & Wei, 2006), respectively. The levels of neohesperidin in bergamot (*C. bergamia* Risso) peel was 9.19 mg/g (Mandalari et al., 2006) and the level of hesperidin in the peels of bergamot (*C. bergamia* Fantastico), four oranges (Valencia, Navel, Temple, and Ambersweet), *C. Unshiu* and grapefruit were, respectively, 0.66 mg/g db (Bocco et al., 1998), 19.17–31.75 mg/g db (Manthey & Grohmann, 1996), up to 6.25 mg/g db (Lu et al., 2006) and 71.4 mg/100 g of fresh matter (Wu et al., 2007). The levels of naringin in our two pummelo peels were similar to those of Lu et al. (2006), levels of neohesperidin in all our citrus peels were much lower than those of authors and the levels of hesperidin in three of our four orange {Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata) and Liucheng [*C. sinensis* (L.) Osbeck]} peels were similar to those of Manthey and Grohmann (1996). The naringin, hesperidin and neohesperidin contents were much higher in the peels than in the fruits (Wang et al., 2007).

3.2.2. Flavone compounds

Table 3 shows the amounts of flavonone compounds (i.e. diosmin, luteolin and sinensetin) in the eight citrus peels. Of these, luteolin was present in the lowest amount and not even detectable in Wendun (*C. grandis* Osbeck), Peiyou (*C. grandis* Osbeck CV) and Kumquat (*C. microcarpa*) peels. Pummelo [Wendun (*C. grandis* Osbeck) and Peiyou (*C. grandis* Osbeck CV)] peels contained the lowest amount of flavone compounds. Kumquat (*C. microcarpa*) peel, notably, contained a large amount of diosmin (1.12 ± 0.03 mg/g db) ($p < 0.05$).

The published levels of sinensetin in the peels of four oranges including Valencia, Navel, Temple and Ambersweet ranged from ND (not detectable) to 0.475 mg/g db (Manthey & Grohmann, 1996) and were similar to those in the peels of our four oranges {Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata), Murcott (*C. reticulate* × *C. sinensis*) and Liucheng [*C. sinensis* (L.) Osbeck]; 0.29 ± 0.01 to 0.42 ± 0.01 mg/g db}. As with flavanones (above), the levels of the three flavone compounds were higher in the peels than in the fruits (Wang et al., 2007).

Table 2
Flavanone contents[A] (mg/g, db[B]) in citrus peel

Scientific name	Local name	Naringin	Hesperidin	Neohesperidin
Citrus reticulata Blanco	Ponkan	0.54 ± 0.02^{de}	29.5 ± 0.32^{a}	0.11 ± 0.003^{d}
C. tankan Hayata	Tonkan	0.58 ± 0.01^{d}	23.4 ± 0.25^{b}	0.06 ± 0.002^{f}
C. reticulate × *C. sinensis*	Murcott	0.54 ± 0.02^{de}	0.93 ± 0.04^{e}	0.13 ± 0.002^{c}
C. grandis Osbeck	Wendun	23.9 ± 0.32^{b}	0.32 ± 0.004^{f}	0.34 ± 0.002^{a}
C. grandis Osbeck CV	Peiyou	29.8 ± 0.20^{a}	0.34 ± 0.01^{f}	0.09 ± 0.002^{e}
C. microcarpa	Kumquat	0.21 ± 0.01^{f}	0.10 ± 0.004^{f}	0.02 ± 0.001^{g}
C. sinensis (L.) Osbeck	Liucheng	0.36 ± 0.004^{ef}	20.7 ± 0.38^{c}	0.09 ± 0.003^{e}
C. limon (L.) Bur	Lemon	1.51 ± 0.05^{c}	9.42 ± 0.41^{d}	0.16 ± 0.001^{b}

[A] Data presented are in mean ± standard deviation ($n = 3$) which with different letters are significantly different at $p < 0.05$.
[B] Dried base.

Table 3
Flavone contents[A] (mg/g, db[B]) in citrus peel

Scientific name	Local name	Diosmin	Luteolin	Sinensetin
Citrus reticulata Blanco	Ponkan	0.36 ± 0.01^{e}	0.21 ± 0.01^{a}	0.29 ± 0.01^{b}
C. tankan Hayata	Tonkan	0.33 ± 0.01^{d}	0.19 ± 0.01^{b}	0.41 ± 0.01^{a}
C. reticulate × *C. sinensis*	Murcott	0.40 ± 0.01^{b}	0.20 ± 0.01^{ab}	0.30 ± 0.01^{b}
C. grandis Osbeck	Wendun	0.16 ± 0.01^{e}	ND[C]	0.02 ± 0.0007^{d}
C. grandis Osbeck CV	Peiyou	0.12 ± 0.01^{f}	ND	0.06 ± 0.002^{c}
C. microcarpa	Kumquat	1.12 ± 0.03^{a}	ND	0.01 ± 0.0002^{d}
C. sinensis (L.) Osbeck	Liucheng	0.17 ± 0.004^{e}	0.11 ± 0.004^{c}	0.42 ± 0.01^{a}
C. limon (L.) Bur	Lemon	0.13 ± 0.004^{f}	0.08 ± 0.002^{d}	0.22 ± 0.008^{c}

[A] Data presented are in mean ± standard deviation ($n = 3$) which with different letters are significantly different at $p < 0.05$.
[B] Dried base.
[C] Not detectable.

3.2.3. Flavonol compounds

Levels of flavonols (i.e. rutin, quercetin and kaempferol) are listed in Table 4. The contents of these were similar (rutin, 0.09 ± 0.002–0.29 ± 0.002; quercetin, 0.14 ± 0.002–0.78 ± 0.003; and kaempferol, 0.13 ± 0.003–0.38 ± 0.002 mg/g db). The total content of flavonol (i.e. rutin, quercetin and kaempferol) was highest in Ponkan (*C. reticulata* Blanco) and Kumquat (*C. microcarpa*) (1.14 and 1.02 mg/g db, respectively). The quercetin content of Kumquat (*C. microcarpa*) peel, in particular, was remarkable (0.78 ± 0.003 mg/g db) ($p < 0.05$). Moreover, rutin and quercetin, but not kaempferol, were higher in the peels than in the fruits (Wang et al., 2007). No other literature on the flavonol composition of the citrus peel has been published.

3.2.4. Phenolic acid compounds

The content of phenolic acid compounds is shown in Table 5. In order of descending abundance, these compounds were chlorgenic acid (145 ± 3.93–339 ± 4.01 μg/g db), ρ-coumaric acid (41.7 ± 1.57–346 ± 2.45 μg/g db), ferulic acid (30.3 ± 1.21–150 ± 4.89 μg/g db), sinapinic acid (10.1 ± 0.37–178 ± 5.62 μg/g db), and caffeic acid (3.06 ± 0.03–80.0 ± 3.72 μg/g db). Of the eight citrus peels, those of Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata) and Murcott (*C. reticulate* × *C. sinensis*) had the highest total content of phenolic acids (i.e. caffeic, chlorgenic, ferulic, sinapic and ρ-coumaric acid content) (914, 946, and 852 μg/g db, respectively). Kumquat (*C. microcarpa*) peels, specifically, had the lowest ρ-coumaric acid content (41.7 ± 1.57 μg/g db) ($p < 0.05$).

Table 4
Flavonol contents[A] (mg/g, db[B]) in citrus peel

Scientific name	Local name	Rutin	Quercetin	Kaempferol
Citrus reticulata Blanco	Ponkan	0.29 ± 0.004^{a}	0.47 ± 0.004^{b}	0.38 ± 0.002^{a}
C. tankan Hayata	Tonkan	0.26 ± 0.01^{b}	0.26 ± 0.002^{c}	0.27 ± 0.003^{e}
C. reticulate × *C. sinensis*	Murcott	0.25 ± 0.002^{c}	0.15 ± 0.002^{g}	0.20 ± 0.003^{f}
C. grandis Osbeck	Wendun	0.18 ± 0.004^{e}	0.23 ± 0.001^{d}	0.33 ± 0.002^{b}
C. grandis Osbeck CV	Peiyou	0.17 ± 0.001^{f}	0.19 ± 0.001^{f}	0.13 ± 0.003^{h}
C. microcarpa	Kumquat	0.09 ± 0.002^{g}	0.78 ± 0.003^{a}	0.15 ± 0.004^{g}
C. sinensis (L.) Osbeck	Liucheng	0.23 ± 0.003^{d}	0.14 ± 0.002^{h}	0.32 ± 0.002^{c}
C. limon (L.) Bur	Lemon	0.29 ± 0.002^{a}	0.21 ± 0.003^{e}	0.31 ± 0.003^{d}

[A] Data presented are in mean ± standard deviation ($n = 3$) which with different letters are significantly different at $p < 0.05$.
[B] Dried base.

Table 5
Phenolic acid contents[A] (μg/g, db[B]) in citrus peel

Scientific name	Local name	Caffeic acid	Chlorgenic acid	Ferulic acid	Sinapic acid	ρ-Coumaric acid
Citrus reticulata Blanco	Ponkan	3.06 ± 0.03^{f}	321 ± 15.29^{b}	150 ± 4.89^{a}	94.2 ± 1.22^{c}	346 ± 2.45^{a}
C. tankan Hayata	Tonkan	7.30 ± 0.49^{e}	319 ± 15.09^{b}	139 ± 2.43^{c}	162 ± 0.49^{b}	319 ± 1.95^{b}
C. reticulate × *C. sinensis*	Murcott	7.23 ± 0.40^{e}	339 ± 4.01^{a}	145 ± 2.41^{b}	178 ± 5.62^{a}	183 ± 1.20^{f}
C. grandis Osbeck	Wendun	8.22 ± 0.75^{e}	230 ± 6.73^{d}	30.3 ± 1.21^{g}	10.1 ± 0.37^{h}	142 ± 1.21^{g}
C. grandis Osbeck CV	Peiyou	27.5 ± 1.74^{b}	173 ± 8.28^{e}	32.2 ± 1.31^{g}	29.2 ± 1.31^{g}	241 ± 0.87^{d}
C. microcarpa	Kumquat	17.3 ± 1.57^{c}	145 ± 3.93^{f}	52.7 ± 1.57^{e}	49.5 ± 0.79^{e}	41.7 ± 1.57^{h}
C. sinensis (L.) Osbeck	Liucheng	12.6 ± 1.21^{d}	300 ± 7.69^{c}	45.3 ± 0.40^{f}	44.9 ± 1.62^{f}	229 ± 1.21^{e}
C. limon (L.) Bur	Lemon	80.0 ± 3.72^{a}	179 ± 4.65^{e}	59.1 ± 0.93^{d}	59.6 ± 0.47^{d}	264 ± 4.19^{c}

[A] Data presented are in mean ± standard deviation ($n = 3$) which with different letters are significantly different at $p < 0.05$.
[B] Dried base.

Bocco et al. (1998) found that total content of phenolic acids (i.e., caffeic acid, ρ-coumaric acid, ferulic acid and sinapinic acid) in sour orange (*C. aurantium*) peel (2.956 mg/g db) was twenty times that found in bergamot (*C. bergamia* Fantastico) peel (0.143 mg/g db). The total phenolic acid contents in our study were intermediate between these two. Peleg, Naim, Rouseff, and Zehavi (1991) detected phenolic acids in the following order of abundance: ferulic acid > sinapinic acid > coumaric acid > caffeic acid, which contrasted with the order in our study. Similar to our findings for flavanoids, flavones and flavanols (above), all studied phenolic acid compounds, except caffeic acid, were present in higher amounts in the peels than in the fruits (Wang et al., 2007).

3.3. Carotenoid composition

The levels of carotenoids are shown in Table 6. The highest levels of carotenoid (i.e. lutein, zeaxanthin, β-cryptoxanthin and β-carotene) were found in Ponkan (*C. reticulata* Blanco) (114 μg/g db), Kumquat (*C. microcarpa*) (113 μg/g db) and Liucheng [*C. sinensis* (L.) Osbeck] (108 μg/g db) peels, intermediate levels in Murcott (*C. reticulate* × *C. sinensis*) (67.5 μg/g db) and Tonkan (*C. tankan* Hayata) (65.1 μg/g db) peels and lowest levels in Lemon [*C. limon* (L.) Bur] (14.9 μg/g db), Peiyou (*C. grandis* Osbeck CV) (3.12 μg/g db) and Wendun (*C. grandis* Osbeck) (2.67 μg/g db) peels. β-Cryptoxanthin (30.5 ± 1.26 μg/g db) and β-carotene (69.2 ± 2.67 μg/g db) were the main carotenoids in Ponkan (*C. reticulata* Blanco) peel. β-Carotene was also the major carotenoid in Tonkan (*C. tankan* Hayata) peel (36.9 ± 1.38 μg/g db). Kumquat (*C. microcarpa*) peel contained high amounts of lutein (36.4 ± 1.56 μg/g db), zeaxanthin (36.4 ± 1.57 μg/g db) and β-cryptoxanthin (37.0 ± 1.45 μg/g db) ($p < 0.05$). β-Carotene was the major carotenoid (50.2 ± 2.28 μg/g db) and β-cryptoxanthin a minor carotenoid (0.76 ± 0.04 μg/g db) in Liucheng [*C. sinensis* (L.) Osbeck] peel.

When comparing the citrus peel levels of lutein, zeaxanthin, β-cryptoxanthin and β-carotene found by Xu et al. (2006) to those found in this study, carotenoid levels in pummelos were similarly low (our study: 0.40 ± 0.02–1.03 ± 0.04 μg/g db *versus* Xu et al.: 0.06–7.45 μg/g db) but β-carotene contents in our orange peels {Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata) and Liucheng [*C. sinensis* (L.) Osbeck]} were much higher (our study: 50.2 ± 2.28–69.2 ± 2.67 μg/g db *versus* Xu et al.: not detectable) and β-cryptoxanthin levels were much higher (our study: 30.5 ± 1.26 μg/g db in Ponkan (*C. reticulata* Blanco) and 37.0 ± 1.45 μg/g db in Kumquat (*C. microcarpa*) *versus* Xu et al.: 4.40–7.80 μg/g db). In addition, the peel levels of lutein, zeaxanthin, β-cryptoxanthin, and β-carotene were much higher than the fruit levels (Wang et al., 2007).

3.4. Pectin content

The total pectin and water-soluble pectin contents are shown in Table 7. The total pectin was highest in Wendun (*C. grandis* Osbeck) peel (86.4 ± 3.36 mg/g db), followed

Table 6
Carotenoid contents[A] (μg/g, db[B]) in citrus peel

Scientific name	Local name	Lutein	Zeaxanthin	β-Cryptoxanthin	β-Carotene
Citrus reticulata Blanco	Ponkan	7.75 ± 0.33^{d}	6.46 ± 0.29^{e}	30.5 ± 1.26^{b}	69.2 ± 2.67^{a}
C. tankan Hayata	Tonkan	7.10 ± 0.25^{d}	11.6 ± 0.58^{d}	9.52 ± 0.43^{d}	36.9 ± 1.38^{c}
C. reticulate × *C. sinensis*	Murcott	13.3 ± 0.51^{c}	25.2 ± 0.99^{c}	16.9 ± 0.75^{c}	12.1 ± 0.51^{b}
C. grandis Osbeck	Wendun	0.80 ± 0.04^{f}	0.51 ± 0.02^{f}	0.40 ± 0.02^{e}	0.96 ± 0.05^{e}
C. grandis Osbeck CV	Peiyou	1.03 ± 0.04^{f}	0.73 ± 0.04^{f}	0.52 ± 0.03^{e}	0.84 ± 0.04^{e}
C. microcarpa	Kumquat	36.4 ± 1.56^{a}	36.4 ± 1.57^{a}	37.0 ± 1.45^{a}	2.79 ± 0.14^{e}
C. sinensis (L.) Osbeck	Liucheng	29.3 ± 1.17^{b}	27.7 ± 1.21^{b}	0.76 ± 0.04^{e}	50.2 ± 2.28^{b}
C. limon (L.) Bur	Lemon	2.95 ± 0.12^{e}	0.81 ± 0.04^{f}	0.81 ± 0.04^{e}	10.3 ± 0.47^{d}

[A] Data presented are in mean ± standard deviation ($n = 3$) which with different letters are significantly different at $p < 0.05$.
[B] Dried base.

Table 7
Pectin contents[A] (mg/g, db[B]) in citrus peel

Scientific name	Local name	Total pectin	Water soluble pectin
Citrus reticulata Blanco	Ponkan	37.3 ± 1.83^{f}	17.1 ± 0.79^{e}
C. tankan Hayata	Tonkan	36.0 ± 1.46^{f}	14.6 ± 0.63^{f}
C. reticulate × *C. sinensis*	Murcott	61.0 ± 2.41^{d}	26.5 ± 1.24^{c}
C. grandis Osbeck	Wendun	86.4 ± 3.36^{a}	33.3 ± 1.46^{a}
C. grandis Osbeck CV	Peiyou	81.9 ± 2.61^{b}	29.6 ± 1.09^{b}
C. microcarpa	Kumquat	62.1 ± 2.36^{cd}	27.5 ± 1.10^{c}
C. sinensis (L.) Osbeck	Liucheng	43.7 ± 1.62^{e}	24.7 ± 1.21^{d}
C. limon (L.) Bur	Lemon	65.2 ± 3.25^{c}	31.6 ± 1.44^{a}

[A] Data presented are in mean ± standard deviation ($n = 3$) which with different letters are significantly different at $p < 0.05$.
[B] Dried base.

by Peiyou (*C. grandis* Osbeck CV) peel (81.9 ± 2.61 mg/g db), moderately high in Lemon [*C. limon* (L.) Bur], Kumquat (*C. microcarpa*) and Murcott (*C. reticulate* × *C. sinensis*) peels (65.2 ± 3.25, 62.1 ± 2.36, and 61.0 ± 2.41 mg/g db, respectively), moderately low in Liucheng [*C. sinensis* (L.) Osbeck] peel (43.7 ± 1.62 mg/g db) and lowest in Ponkan (*C. reticulata* Blanco) and Tonkan (*C. tankan* Hayata) peels (37.3 ± 1.83, 36.0 ± 1.46 mg/g db, respectively) ($p < 0.05$). The total water soluble pectin content was highest in Wendun (*C. grandis* Osbeck) and Lemon [*C. limon* (L.) Bur] peels (33.3 ± 1.46 and 31.6 ± 1.44 mg/g db, respectively), followed in order by Peiyou (*C. grandis* Osbeck CV) (29.6 ± 1.09 mg/g db) peel, Kumquat (*C. microcarpa*) and Murcott (*C. reticulate* x *C. sinensis*) peels (27.5 ± 1.10 and 26.5 ± 1.24 mg/g db, respectively), Liucheng [*C. sinensis* (L.) Osbeck] peel (24.7 ± 1.21 mg/g db) and lowest in Ponkan (*C. reticulata* Blanco) and Tonkan (*C. tankan* Hayata) peels (17.1 ± 0.79 and 14.6 ± 0.63 mg/g db, respectively) ($p < 0.05$).

In the literature, the total pectin content in Navel peel was reported to be 60–90 mg/g db (Kratchanova, Pavlova, & Panchev, 2004) and 2.2 mg/g db (Liu, Shi, & Langrish, 2006). The total pectin content in peels is 1.91 ± 0.11 mg/100 g from fresh Meyer lemon, 2.99 ± 0.02 mg/100 g from fresh Marsh white grapefruit, 5.29 ± 0.04 mg/100 g from fresh Dancy tangerine and 3.68 ± 0.10 mg/100 g from fresh Marrs orange (Liu et al., 2001). Our results (Wang et al., 2007) for the total pectin content of Liucheng [*C. sinensis* (L.) Osbeck] (43.7 ± 1.62 mg/g) lies intermediate between the results of Kratchanova et al. (2004) and Liu et al. (2006). Moreover, the total pectin content in the peels and in the fruits are similar (Wang et al., 2007).

4. Conclusions

In this current study, the levels of flavonoids, carotenoids and pectin present in citrus peels in Taiwan have been well established. Overall, the amount of total flavonoids exceeded that of total carotenoids. The highest total carotenoid content was found in Ponkan (*C. reticulata* Blanco) peel and the lowest in Wendun (*C. grandis* Osbeck) and Peiyou (*C. grandis* Osbeck CV) peels. Naringin was abundant in Wendun (*C. grandis* Osbeck) and Peiyou (*C. grandis* Osbeck CV) peels and hesperidin was abundant in Ponkan (*C. reticulata* Blanco), Tonkan (*C. tankan* Hayata) and Liucheng [*C. sinensis* (L.) Osbeck] peels. Notably, Kumquat (*C. microcarpa*) peel had the most diosmin and quercetin.

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