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# Food Chemistry

journal homepage: [www.elsevier.com/locate/foodchem](http://www.elsevier.com/locate/foodchem)

## Effects of processing on anthocyanins, carotenoids and vitamin C in summer fruits and vegetables

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### ARTICLE INFO

#### Article history:

Received 20 June 2011

Received in revised form 25 November 2011

Accepted 8 February 2012

Available online xxx

#### Keywords:

New Zealand

Anthocyanins

Carotenoids

Vitamin C

Processing

Stability

### ABSTRACT

The purpose of this study was to evaluate the effects of processing, i.e. heating (98 °C, 10 min), freezing (−20 °C) and freeze-drying on anthocyanins, carotenoids, and vitamin C in summer fruits and vegetables, i.e. cherries, nectarines, apricots, peaches, plums, carrots and red bell peppers. The commodities were collected from growers located in the Otago region (namely Cromwell, Roxburgh, Mosgiel and Clinton), New Zealand. The results revealed that each commodity contained different contents of phytochemicals. The content and the process stability of phytochemicals in each commodity were influenced by the geographical location of the growers. In general, a high content of phytochemicals was found in summer fruits and vegetables grown in Otago compared to those grown in the Northern Hemisphere, e.g. anthocyanins in cherries, nectarines, peaches and plums; total carotenoids in red bell peppers and nectarines and vitamin C in cherries, peaches, red bell peppers and carrots. Heating and freezing enhanced the release of membrane bound anthocyanins, resulting in higher content after processing compared to fresh commodities. In the commodities studied, with the exception of red bell peppers, the stability of ascorbic acid was increased if ascorbic acid oxidase was inactivated for example by heating.

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### 1. Introduction

Regular consumption of phytochemical-rich diets from childhood has been reported to delay the initiation of cancer diseases (Boyer & Liu, 2004; Lampe, 1999; Liu, 2003; Song et al., 2010) and is necessary for a healthy lifestyle. Phytochemicals in fruits and vegetables, with antioxidant activity, are able to scavenge the free radicals and prevent the further abnormal growth of cells from entering into the tumour formation stage. Several researchers have demonstrated the health potentials of phytochemical compounds in horticultural produce in inhibiting the growth of cancer cells, such as berries (Seeram et al., 2006), cranberries (Cote, Caillet, Doyon, Sylvain, & Lacroix, 2010), apple (Bellion et al., 2010), strawberries (Hannum, 2004) and figs (Solomon et al., 2010). Since the human body is unable to synthesise these compounds, it is vital to supplement these compounds from dietary intake, and regular intake of fruits and vegetables is being strongly campaigned.

From a food system perspective, stability and functionality of phytochemical compounds in the human body varies, depending on the amount, the species, the linkage of the molecules, the location in food matrix, and the presence of other bioactive compounds in fruits and vegetables (Hannum, 2004). In fruits and vegetables, phytochemicals can be bound in the plant cell membranes or exist

as free compounds. Food processing, such as heating or freezing can disrupt the cell membrane leading to the release of membrane-bound phytochemicals, which implies higher bioaccessibility (Lemmens, Van Buggenhout, Oey, Van Loey, & Hendrickx, 2009). Moreover, the amount of phytochemicals retained in fruits and vegetables depends on their stability during food preparation and processing before consumption, which is mostly related to their sensitivity towards oxidation, and the environmental conditions.

Consumer choice and preference of fruits and vegetables are majorly influenced by factors, such as convenience, culture, price, appearance, taste, and not considerably by the nutrient value (Glanz, Basil, Maibach, Goldberg, & Snyder, 1998; Ragaert, Verbeke, Devlieghere, & Debevere, 2004). Nowadays consumers have access to various fruits and vegetables outside of their season coming from around the world due to international trade. Compared to imported fruits and vegetables, local seasonal fruits and vegetables are cheaper, fresher but available only for a short period. Therefore, to prolong the shelf life seasonal fruits and vegetables must be processed.

The purpose of this research was to investigate the effects of food processing, such as heating, freezing and freeze-drying on the stability of phytochemicals namely carotenoids, anthocyanins, and vitamin C in seasonal fruits and vegetables that are commonly consumed during summer, such as apricots, cherries, nectarines, plums, peaches, red bell peppers and carrots. In this research, summer fruits and vegetables were collected from the local

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growers located in the Otago Region (South Island, New Zealand). The content and the process stability of phytochemicals in fruits and vegetables obtained from different local growers was also compared.

## 2. Materials and methods

### 2.1. Reagents and chemicals

Sodium acetate, potassium sodium (+)-tartrate (Rochelle salt), sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ), ethylenediamine tetra-acetic acid (EDTA) and sodium hydroxide (NaOH) were purchased from BDH (Poole, England). Calcium chloride,  $\text{D}$ -glucose, ethanol (95%) and acetone from Biolab (Scoresby, Victoria, Australia); butylated hydroxytoluene (BHT), 3,5-dinitrosalicylic acid (DNS) and tris[2-carboxyethyl]phosphine hydrochloride (TCEP) from Sigma–Aldrich (St. Louis, MO); hydrochloric acid (37%) from Merck (Darmstadt, Germany); formic acid from Riedel–de Haen (Seelze, Germany); and  $\text{L}$ -ascorbic acid from Unilab (Auckland, New Zealand).  $N$ -hexane and methanol of HPLC grade were purchased from J.T. Baker (NJ, USA). Unless otherwise stated, all reagents and chemicals were of analytical grade and bi-distilled water was used in the entire study.

### 2.2. Fruits and vegetables samples

Cherries, nectarines, apricots, peaches, plums, carrots and red bell peppers (same variety, one batch per grower consisting of 5–6 individual packages, 0.7–1.5 kg per package, in total 4–6 kg of commodities per batch) were purchased between early January and mid February 2011 from local growers in the area of Otago region (South Island, New Zealand) located in Cromwell ( $45^\circ 02' \text{S}$ ,  $169^\circ 12' \text{E}$ , elevation 195 m), Roxburgh ( $45^\circ 32' \text{S}$ ,  $169^\circ 18' \text{E}$ , elevation 160 m), Mosgiel ( $45^\circ 52' \text{S}$ ,  $170^\circ 20' \text{E}$ , elevation 16 m) and Clinton ( $46^\circ 12' \text{S}$ ,  $169^\circ 22' \text{E}$ , elevation 144 m) and a local supermarket supplying locally grown commodities in Dunedin (New Zealand). The Otago climate between April 2006 and January 2011 is illustrated in Fig. 1. The growers controlled the maturity of fruits and vegetables based on their own standards. Therefore, upon arrival the fruits and vegetables were screened based on similarity in colour (indicator for ripening), shape (indicator for variety) and size (indicator for quality). Afterwards, the commodities were carefully washed, halved and stoned. The retaining edible portions (flesh and skin) were thinly sliced (5 mm thickness) and used as sample in this research.

To study the effects of processing on phytochemical compounds, samples were processed in three different ways: heat-

ing, freeze-drying and freezing. Heating was carried out by submerging the samples in thermostated water (5:1 water:sample by weight) at  $98^\circ \text{C}$  for 10 min (the average come up time of the samples from room temperature to  $98^\circ \text{C}$  was around 4 min, thermocouple type T). Afterwards, the water was drained off and the treated samples were immediately cooled in an ice bath before analysis. Freeze-drying was conducted by freezing the samples wrapped with perforated aluminium foil in liquid nitrogen prior to freeze-drying (Virtis Freezemobile 12SL freeze dryer, Gardiner, NY) for at least 48 h. Freezing was carried out similarly to the freeze-drying treatment in which the fresh samples were initially wrapped with aluminium foil, dipped in liquid nitrogen and stored frozen at  $-20^\circ \text{C}$ . Before analysis, the frozen samples were thawed at  $4^\circ \text{C}$  for 2 h. Raw and fresh samples were used as control/reference. The entire sample preparation step was carried out under subdued light to eliminate degradation of phytochemical compounds.

### 2.3. Determination of quality parameters

The dry matter and water content were determined gravimetrically. Five grams of raw sample was dried in a convection oven (Qualtex Solidstat Universal series 2000, Watson Victoria Limited, NZ; with the dimension of  $800 \times 600 \times 1200$  mm) at  $75^\circ \text{C}$  for at least 48 h or until a constant weight was achieved. All the calculations were made according to the dry matter basis since fruits and vegetables contained various water content. The pH values of fruits and vegetables were measured using a pH meter (CyberScan pH 2100, Eutech Instruments, Vernon Hills, IL, USA). The amount of total reducing sugars was quantified using a spectrophotometer following the method described by Lindsay (1973). Half a gram of sample (or 50 mg freeze-dried sample) was homogenised with 5 ml water for 3 s using Polytron PT2100 (Kinematic AG, Switzerland) at 26 rpm. The homogenates were centrifuged at 1000g and  $25^\circ \text{C}$  for 10 min (Beckman Coulter GPR centrifuge, CA, USA). The supernatant (0.25 ml) was transferred to a test tube containing 2 ml DNS reagent and 0.75 ml water; afterwards the reaction mixture was placed in boiling water bath for 10 min. The test tubes were cooled down to room temperature and the mixture was further diluted with 2 ml of milli-Q water and mixed using vortex for 60 s. The absorbance of the sample was read at 570 nm against the blank (DNS reagent:water, 2:3) using a UV/Visible spectrophotometer (Ultraspec 3300 pro, Amersham Biosciences, Sweden). The reducing sugars were quantified as milligrams of reducing sugars per gram of dry weight. The external standard glucose solution in a range of concentration from 0.4 to 2.0 mg/ml was used to

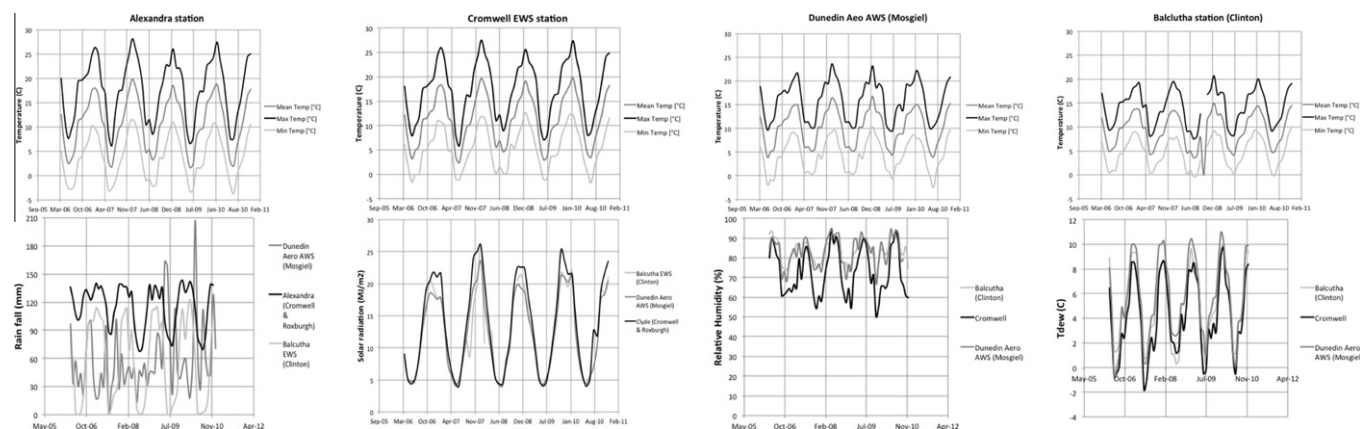


Fig. 1. Climate in the area of Cromwell, Roxburgh, Clinton and Mosgiel (April 2006–January 2011) based on New Zealand's National Climate database (free access under NIWA's Terms and Conditions via <http://cliflo.niwa.co.nz/>). Clyde and Alexandra stations are used for Cromwell and Roxburgh. Dunedin Aero AWS and Balclutha stations are used for Mosgiel and Clinton, respectively.

**Table 1**  
Molecular weights, extinction coefficients and wavelength of maximum absorption for determination of phytochemical compounds.

Bioactive compounds	Molecular weight (g mol <sup>-1</sup> )	Extinction coefficient (L mol <sup>-1</sup> cm <sup>-1</sup> )	Wavelength (nm)
Cyanidin-3-glucoside*	449.2	26,900	510
Cyanidin-3-rutinoside*	595.2	28,800	541
β-Carotene**	537	2560	450
β-Cryptoxanthin**	553	2460	451
α-Carotene**	537	2800	444
Lycopene**	537	3450	472
Lutein**	569	2550	445

\* Wrolstad (1976).

\*\* Hart and Scott (1995).

estimate the content of reducing sugars in the samples. The DNS reagent was prepared by dissolving 1 g of DNS in 20 ml of NaOH (2 M) and 50 ml water, with the addition of 30 g Rochelle salt. The mixture was then brought up to 100 ml with water.

#### 2.4. Determination of anthocyanin content

The total anthocyanin content was determined using pH differential method. The extract was prepared by mixing sample (25 g for nectarine and peach, 5 g for cherry and plum, 1.25 g for all freeze-dried samples) with 20 ml ethanol and homogenised using a waring blender (Watson Victor Limited, NZ). The extract was filtered through a glass wool and all the remaining pigments were washed with another 20 ml of ethanol. The filtrate was collected and brought to 50 ml in the volumetric flask with ethanol. The total anthocyanin content was determined spectrophotometrically against the blank (ethanol:water, 1:1) at pH 1.0 (a mixture of hydrochloric acid (2 M) and sodium acetate (0.1 M)) and at pH 4.5 (a mixture of hydrochloric acid (2 M) and sodium acetate (1 M)). The absorbance of the sample was calculated based on Eq. (1):

$$A = [(A_x - A_{700})_{\text{pH } 1.0} - (A_x - A_{700})_{\text{pH } 4.5}] \quad (1)$$

where  $A$  is the sample absorbance,  $A_x$  is the maximum sample absorbance reading at specific wavelength for pH 1.0 and pH 4.5 while  $A_{700}$  is the absorbance reading at 700 nm for pH 1.0 and pH 4.5. The concentrations were expressed as milligrams per gram dry weight of sample and calculated using appropriate extinction coefficients of the major anthocyanin compounds of interest, summarised in Table 1 as adapted from the work of Wrolstad (1976).

#### 2.5. Determination of carotenoid content

Samples were extracted according to the procedure of Lemmens et al. (2010) under dark condition to protect carotenoids from light degradation. Samples (5 g sample or 0.5 g freeze dried sample) were homogenised with 50 ml extraction solvent (50% hexane, 25% acetone, 25% ethanol, containing 0.1% BHT v/v). Meanwhile, 5 g calcium chloride were added gradually in order to have distinct separation between water and organic layers. The mixture was stirred for 20 min at 4 °C and further diluted by adding 15 ml of water, followed by another stirring step for 10 min at 4 °C. The mixture was transferred to a separation funnel to allow the separation of organic layer containing carotenoids. The organic layer was collected in volumetric flask and brought to 50 ml with extraction solvent. The carotenoids content was determined at specific maximum absorption wavelength and extinction coefficient of the carotenoids of interest, as listed in Table 1, against the blank (extraction solvent) (Hart & Scott, 1995). The results were expressed as micrograms per gram dry weight of sample.

#### 2.6. Determination of L-ascorbic acid (L-AA)

L-ascorbic acid (L-AA) content was determined using reverse phase high performance liquid chromatography (RP-HPLC) method using RP-Prevail C<sub>18</sub> column (5 μm, 250 × 4.6 mm, Grace Davidson Discovery Science, USA) and Agilent 1200 system (MA, USA). The sample (10 g fruit sample, 5 g vegetable sample, 1 g freeze dried fruit sample or 0.5 g freeze dried vegetable sample) was homogenised with 25 ml cold extraction buffer (NaH<sub>2</sub>PO<sub>4</sub> buffer solution (20 mM, pH 2.1) containing 1 mM EDTA) using a waring blender for 30 s. The extract was centrifuged at 34700g and 4 °C for 30 min (Beckman Coulter J2-2M/E centrifuge, CA, USA). The supernatant was stored at -80 °C (less than 48 h) before HPLC analysis. Upon sample injection, the frozen supernatant was thawed for 10 min at 25 °C. The pH of the supernatant was adjusted to pH 4.5 using NaOH (1 M) and afterwards filtered through 0.45 μm cellulose acetate filter (Raylab, NZ). L-AA content was estimated without pre-column reduction, while the total L-AA content was estimated using pre-column reduction based on the method of Lykkesfeldt (2000) modified for vegetable matrices (Munyaka, Oey, Van Loey, & Hendrickx, 2010). TCEP was used as a reducing agent. One part of sample supernatant was mixed with two parts of TCEP solution (2.5 mM TCEP dissolved in phosphate buffer (20 mM; pH 5.3 containing 1 mM EDTA)). The pre-column reduction was conducted at 4 °C and pH 4.5 for 10 h. The injection volume was 50 μl (for all fruit samples and carrots) and 20 μl for red bell peppers. The elution was conducted isocratically using a mixture of 90% formic acid (0.1%) and 10% methanol at a flow rate of 0.8 ml/min. L-AA was identified based on peak purity using diode array detector and retention time between 4.9 and 5 min. The quantification was performed at 245 nm. The L-AA content was estimated using external standard solution of L-AA (357 μg/ml) based on the peak area. The content of DHAA was calculated by subtracting the L-AA content with and without the TCEP reduction. The results were expressed as micrograms of L-AA equivalents per gram dry weight.

### 3. Results and discussion

Consumers evaluate the quality and ripeness of fruits and vegetables based on appearance, flavour and taste while nutritional value, the hidden quality parameter of fruits and vegetables, is not the main determinant factor at the point of purchase. The general sensory attributes, such as acidity (related to sourness) and water content (related to juiciness) were examined in this study. Fruit samples appeared to be more acidic than vegetable samples. The pH of stone fruits, namely cherries, nectarines, peaches and plums ranged from pH 3.27 to 4.38, carrots pH 6.48 and red bell peppers pH 5.15. Fruits and vegetables contained more than 85% of water in their matrix. Apricots, nectarines, peaches carrots and red bell peppers contained 90–91% water, while cherries and

**Table 2**  
The content of major anthocyanin compounds (mg/g DW) in cherries, nectarines, peaches and plums under different processing conditions.

Fruits grower	Fresh		Heating (98 °C, 10 min)		Freezing (–20 °C)		Freeze-drying	
	Cyd-3-glu <sup>a</sup>	Cyd-3-rut <sup>b</sup>	Cyd-3-glu	Cyd-3-rut	Cyd-3-glu	Cyd-3-rut	Cyd-3-glu	Cyd-3-rut
<i>Cherries</i>								
Cromwell	207.00 <sup>c</sup> ± 8.91 <sup>d</sup>	276.24 ± 10.48	419.34 ± 15.63	475.01 ± 16.69	570.08 ± 15.25	737.75 ± 22.14	158.95 ± 19.68	211.91 ± 19.28
Roxburgh	546.61 ± 5.56	698.32 ± 6.06	470.42 ± 6.77	615.65 ± 5.32	548.81 ± 20.00	706.16 ± 34.07	522.05 ± 16.00	628.24 ± 18.63
Dunedin	46.11 ± 3.41	49.70 ± 2.85	126.76 ± 9.47	172.33 ± 13.03	62.99 ± 1.32	89.37 ± 2.81	22.36 ± 4.28	28.09 ± 6.11
Average	266.89 <sup>e</sup> ± 255.39 <sup>f</sup>	341.42 ± 329.18	338.84 ± 185.43	421.00 ± 226.54	393.96 ± 286.83	511.09 ± 365.56	234.45 ± 258.26	289.41 ± 307.49
<i>Nectarines</i>								
Cromwell	24.26 ± 1.35	25.06 ± 0.26	27.531 ± 0.46	18.89 ± 1.35	33.25 ± 2.84	29.68 ± 9.13	58.23 ± 2.60	7.34 ± 0.03
Roxburgh	16.05 ± 2.30	16.65 ± 2.35	12.99 ± 3.56	12.17 ± 2.96	19.33 ± 1.82	18.87 ± 2.11	71.21 ± 12.34	9.70 ± 1.56
Dunedin	10.87 ± 0.39	15.95 ± 3.68	5.17 ± 0.14	4.21 ± 0.68	9.44 ± 1.14	7.12 ± 0.29	69.83 ± 2.56	7.46 ± 0.85
Average	17.06 ± 6.75	19.22 ± 5.07	15.23 ± 11.44	11.76 ± 7.35	20.67 ± 11.96	18.56 ± 3.84	66.42 ± 7.13	8.17 ± 1.33
<i>Peaches</i>								
Cromwell	7.69 ± 0.16	7.92 ± 0.70	12.94 ± 0.50	10.78 ± 2.50	17.17 ± 0.77	18.28 ± 4.95	10.06 ± 0.05	12.99 ± 0.78
Roxburgh	16.17 ± 2.67	17.00 ± 2.70	32.27 ± 4.62	27.56 ± 0.33	33.18 ± 4.65	29.10 ± 0.88	6.97 ± 1.35	8.13 ± 1.34
Dunedin	14.55 ± 0.29	15.98 ± 6.30	10.70 ± 0.01	9.98 ± 0.33	14.54 ± 0.10	8.30 ± 0.84	11.61 ± 1.80	15.07 ± 1.68
Average	12.80 ± 4.50	13.63 ± 4.97	18.64 ± 11.86	16.11 ± 9.93	21.63 ± 10.09	12.46 ± 10.40	9.54 ± 2.36	12.06 ± 3.56
<i>Plums</i>								
Cromwell	51.08 ± 0.34	52.11 ± 1.73	38.22 ± 0.56	40.77 ± 0.99	58.39 ± 0.82	63.40 ± 1.06	14.21 ± 0.03	18.16 ± 0.04
Roxburgh	12.32 ± 1.28	13.36 ± 2.32	37.07 ± 3.77	46.37 ± 4.60	46.26 ± 2.96	59.03 ± 4.17	7.68 ± 0.18	8.05 ± 0.19
Dunedin	18.46 ± 0.33	23.35 ± 0.83	48.61 ± 1.03	60.70 ± 1.29	66.08 ± 0.73	85.07 ± 1.24	19.51 ± 0.03	24.93 ± 0.89
Average	27.29 ± 20.84	29.60 ± 20.12	37.65 ± 0.82	49.28 ± 10.28	56.91 ± 10.00	69.17 ± 13.95	13.80 ± 5.93	17.05 ± 8.49

<sup>a</sup> Cyanidin-3-glucoside expressed in milligram per gram dry weight of fruits.<sup>b</sup> Cyanidin-3-rutinoside expressed in milligram per gram dry weight of fruits.<sup>c</sup> Average of replicate samples from the same grower for minimum 3 sample collections.<sup>d</sup> Standard deviation of replicate samples from the same grower for minimum 3 sample collections.<sup>e</sup> Mean of samples randomly collected from three different growers.<sup>f</sup> Standard deviation of samples randomly collected from three different growers.

plums contained lower water content (85%). Among the growers, the examined commodities had the same range of magnitude in terms of pH value and water content in contrast to the phytochemical content. The horticultural commodities studied had a great degree of variability, not only in the content but also in the type of phytochemicals.

### 3.1. Evaluation of anthocyanin content in seasonal fruits and vegetables

In this research, anthocyanins were found in cherries (highest), plums, nectarines and peaches (lowest) in the forms of cyanidin-3-glucoside and cyanidin-3-rutinoside (Table 2) and not detected in apricots, carrots and red bell peppers. This finding did not coincide with the result reported by Bureau, Renard, Reich, Ginies, and Audergon (2009), because in their study, cyanidin-3-glucoside was found as the main anthocyanins in French apricots, and the content was also highly dependent on the stage of ripeness. The average anthocyanins content was 0.22 mg cyanidin-3-glucoside equivalent (CGE)/g DW in French apricots. In the present study, the development of red colour in red bell peppers is not related to anthocyanins, rather it is a carotenoids. In other literature, it has been reported that anthocyanins were detected in trace amount (1 mg CGE/g DW) in red peppers from Israel (Gorinstein et al., 2009).

The various geographical locations from which the commodities were grown affected the composition and content of anthocyanins even though the plants were grown in the same region. The highest content of anthocyanins in cherries and peaches was found in the Roxburgh area while that in nectarines and plums was from the Cromwell area (Table 2). On average, the reducing sugar for apricots and nectarines from Cromwell was the highest while Roxburgh peaches, Mosgiel carrots and Clinton peppers had the highest content of reducing sugars (Table 3).

Anthocyanins are the phytochemical compounds that confer the visual quality of fruits and vegetables, contributing to the red, blue and purple pigments in plant tissues. They are mostly

distributed in the skin of fruits, therefore the external colour difference among each fruit is largely determined by the nature and the concentration of anthocyanins contained. Anthocyanins are glycosylated anthocyanidins in which sugars are normally linked to the 3-hydroxyl position of anthocyanidins (Castañeda-Ovando, Pacheco-Hernández, Páez-Hernández, Rodríguez, & Galán-Vidal, 2009). The major anthocyanins found in fruits are cyanidin, peonidin, delphinidin, petunidin, malvidin and pelargonidin (Wrolstad, 1976). In literature on this subject, the content of total anthocyanins in fruits varies considerably, but there is also variability of the specific anthocyanin compounds present in fruits.

Compared to other countries located in the Northern Hemisphere, the anthocyanin content of seasonal fruit and vegetables grown in the Otago region was much higher. For example, the content of anthocyanins (compared as CGE) in cherries grown in the United States (Wu et al., 2006), Northern Greece (Pantelidis, Vasilakakis, Manganaris, & Diamantidis, 2007), Croatia (Piljac-Zegarac & Samec, 2011), Portugal (Goncalves et al., 2004) and Finland (Koponen, Happonen, Mattila, & Torronen, 2007) ranges from 12.93 mg/100 g FW (approximately 1.3 mg/g DW) up to 223 mg/100 g FW (approximately 22 mg/g DW). Nectarines grown in United States (Tomas-Barberan et al., 2001; Wu et al., 2006) and Finland (Koponen et al., 2007) contains anthocyanins ranging from 2.4 mg/100 g FW (approximately 0.24 mg/g DW) to 260.9 mg/100 FW (approximately 26 mg/g DW). The anthocyanin content of peaches grown in Zaragoza, Spain (Cantin, Moreno, & Gogorcena, 2009), the United States (Tomas-Barberan et al., 2001; Wu et al., 2006) and Finland (Koponen et al., 2007) ranges between 3.1 mg/100 g FW (approximately 0.31 mg/g DW) and 273.6 mg/kg FW (2.7 mg/g DW). The anthocyanin content in plums grown in the United States (Chun, Kim, Moon, Kang, & Lee, 2003; Franke, Custer, Arakaki, & Murphy, 2004; Tomas-Barberan et al., 2001; Wu et al., 2006), Spain (Lozano et al., 2009) and Finland (Koponen et al., 2007) is found to be very low, between 19 mg/100 g FW (approximately 1.9 mg/g DW) and 69 mg/100 FW (approximately 6.9 mg/g DW). A high content of anthocyanin in plums is also found in other area in the Southern Hemisphere, such as New South Wales and



**Table 3**  
Effect of processing on the content of reducing sugar in fruits and vegetables.

Fruits or vegetables/grower	Reducing sugar (mg/g DW)			
	Fresh	Heating (98 °C, 10 min)	Freezing (–20 °C)	Freeze-drying
<i>Apricots</i>				
Cromwell	11.20 <sup>a</sup> ± 1.31 <sup>b</sup>	6.72 ± 0.75	3.20 <sup>a</sup> ± 0.49 <sup>b</sup>	8.17 <sup>a</sup> ± 0.25 <sup>b</sup>
Roxburgh	9.98 ± 0.13	6.04 ± 0.14	10.75 ± 0.31	10.80 ± 0.13
Dunedin	3.92 ± 0.29	2.05 ± 1.29	9.99 ± 0.42	8.40 ± 1.05
Average	8.37 <sup>c</sup> ± 3.90 <sup>d</sup>	4.94 ± 2.52	7.98 <sup>c</sup> ± 4.16 <sup>d</sup>	9.12 <sup>c</sup> ± 1.46 <sup>d</sup>
<i>Cherries</i>				
Cromwell	53.83 ± 3.69	33.69 ± 2.12	73.44 ± 3.43	58.89 ± 4.10
Roxburgh	69.16 ± 0.45	50.84 ± 0.71	84.72 ± 1.96	56.19 ± 7.95
Dunedin	72.71 ± 0.98	58.28 ± 1.97	53.65 ± 0.01	58.53 ± 1.51
Average	65.23 ± 10.03	47.60 ± 12.61	70.60 ± 15.73	57.77 ± 1.37
<i>Nectarines</i>				
Cromwell	14.91 ± 0.76	5.76 ± 1.29	10.98 ± 1.54	9.89 ± 0.37
Roxburgh	14.15 ± 0.05	6.64 ± 0.40	17.16 ± 0.72	11.54 ± 2.32
Dunedin	5.33 ± 0.46	4.48 ± 0.23	12.04 ± 0.61	11.38 ± 0.77
Average	11.46 ± 5.33	5.63 ± 1.09	13.39 ± 3.30	10.94 ± 0.91
<i>Peaches</i>				
Cromwell	7.44 ± 0.96	7.10 ± 1.77	13.99 ± 1.48	9.90 ± 0.35
Roxburgh	11.57 ± 1.40	13.38 ± 0.22	12.16 ± 1.12	7.93 ± 0.51
Dunedin	6.77 ± 0.73	2.29 ± 0.14	9.44 ± 0.76	14.09 ± 0.25
Average	8.59 ± 2.60	7.59 ± 5.56	11.86 ± 2.29	10.64 ± 3.15
<i>Plums</i>				
Cromwell	9.70 ± 0.98	12.14 ± 0.89	14.38 ± 1.20	4.38 ± 0.56
Roxburgh	11.76 ± 0.08	11.44 ± 0.10	20.67 ± 0.54	9.23 ± 0.29
Dunedin	16.54 ± 0.04	12.87 ± 1.21	28.30 ± 1.76	24.26 ± 1.45
Average	12.67 ± 3.51	12.15 ± 0.72	21.12 ± 6.97	12.62 ± 10.37
<i>Carrots</i>				
Dunedin	15.91 ± 2.89	6.54 ± 0.18	9.04 ± 0.75	15.00 ± 0.43
Roxburgh	35.27 ± 2.23	8.35 ± 0.57	25.73 ± 0.44	35.28 ± 3.33
Clinton	31.70 ± 1.18	3.97 ± 0.18	27.24 ± 3.84	31.37 ± 2.50
Average	27.63 ± 10.30	6.29 ± 2.20	20.67 ± 10.10	27.22 ± 10.76
<i>Peppers</i>				
Dunedin	55.12 ± 1.40	18.76 ± 0.22	43.86 ± 2.51	51.10 ± 5.06
Mosgiel	61.15 ± 1.08	22.94 ± 2.44	49.03 ± 1.02	57.84 ± 0.97
Clinton	74.80 ± 2.84	27.91 ± 1.65	39.04 ± 2.08	70.74 ± 1.19
Average	63.69 ± 10.08	23.20 ± 4.58	43.98 ± 5.00	59.89 ± 9.98

<sup>a</sup> Average of replicate samples from the same grower for minimum 3 sample collections.

<sup>b</sup> Standard deviation of replicate samples from the same grower for minimum 3 sample collections.

<sup>c</sup> Mean of samples randomly collected from three different growers.

<sup>d</sup> Standard deviation of samples randomly collected from three different growers.

Queensland in Australia (Konczak, Zabaraz, Dunstan, & Aguas, 2010; Netzel, Netzel, Tian, Schwartz, & Konczak, 2006; Tan, Konczak, Ramzan, & Sze, 2011). Netzel and others (2006) reported an anthocyanin content in Australia ranging from 1.27 µmol/g FW (approximately 5.7 mg/g DW) up to 19.39 µmol/g FW (approximately equal to 86 mg/g DW), in which the anthocyanin content of Otago plums was also found in this range.

The method used to quantify total anthocyanin was based on the ability of anthocyanin to remain stable under acidic condition, i.e. pH differential method. Although this method is fast and easy to perform, Wu and Prior (2005) questioned whether it is critical enough to identify the pattern of individual glycoside substitution of anthocyanins with sugar compounds. Moreover, it was undeniably difficult to achieve satisfactory results if the samples were not freed from their interfered substances during extraction. An ideal extraction method should depend upon the maximisation of anthocyanin recovery with a minimum degradation of their natural state. Owing to this, the anthocyanins were relatively difficult to extract independently from other flavonoids or interference substances. The substances that might interfere were pectin, proteins, lipids and polyphenol compounds, to name but a few (Hendry & Houghton, 1992). In addition to the extraction efficiency, the fruit ripening process was counted towards the changes in the total anthocyanin content. Anthocyanin content in fruits is at its highest during the

ripening stage, in which the biosynthesis rate is accelerated due to the action of the ripening hormone (ethylene), triggering the activation of many enzymes involved in anthocyanin biosynthesis, and eventually declining at the end of maturation stage (Gross, 1987). Since the anthocyanins are synthesised at an increasing rate during maturation, the total anthocyanin content quantified here may serve as the index of maturity, as an important quality parameter.

In the present study, the quantification of reducing sugars was of significance not only due to the analytical issue as described above, but also because sugars were reported as the stimulant for anthocyanin synthesis (Gross, 1987). A simultaneous measurement of reducing sugars as well as the anthocyanins is a good way to determine differences in content which could explain the pattern of reducing sugar and anthocyanin content in each fresh commodity (Table 3). However, sugars were also detected in apricots, carrots and peppers, though the content of the anthocyanin compounds were below the detection limit. This may be explained by the fact that sugars were not entirely linked to anthocyanins alone. Instead, their presence signifies the quality markers for ripened fruits (Lo Bianco, Farina, Indelicato, Filizzola, & Agozzino, 2010) and also helps to identify different fruits' cultivars (Gurrieri, Audergon, Albagnac, & Reich, 2001). The activity of sugar-synthesising enzymes in fruits and vegetables, such as  $\alpha$ - and  $\beta$ -amylase, converts the stored starch into sugar compounds, which is linked to

the mature state of the commodities (Ueda, Sasaki, Utsunomiya, Inaba, & Shimabayashi, 2000). Sugars are also associated with delivering the aroma of fruits. Particularly, sugar tends to accumulate during ripening and provides a great substrate for respiratory reactions. Hence, this will indirectly trigger the build-up of fatty acids, which is the precursor of volatile aromatic compounds and the aroma profile is independent for different types of commodities (Lo Bianco et al., 2010).

### 3.2. Evaluation of carotenoid content in seasonal fruits and vegetables

In all commodities studied,  $\beta$ -carotene,  $\beta$ -cryptoxanthin,  $\alpha$ -carotene, lycopene and lutein were most commonly detected. Red peppers had the highest carotenoid content, followed by carrots, apricots, nectarines, plums, peaches and the lowest in cherries (Table 4). Although anthocyanins were not detected in apricots, carrots and peppers, these three commodities are well recognised for their high carotenoid level. In this study, the major carotenoids in apricots were  $\beta$ -carotene,  $\beta$ -cryptoxanthin and  $\alpha$ -carotene while the study of Sass-Kiss and others (2005) showed that  $\beta$ -carotene comprised 60–70% of the total carotenoids in apricots, and the other minor carotenoids were  $\beta$ -cryptoxanthin,  $\alpha$ -carotene, lycopene and lutein. A high level of  $\beta$ -carotene was indicated by the intense orange colour in apricots. This phenomenon was not always the same for each commodity as colour was visualised differently when the pigments absorbed at different wavelengths, rather than being affected by the total carotenoid content. Generally, the total carotenoid content increases during ripening, in which the carotenogenesis will take over while the chlorophylls undergo degradation, hence synthesising greater amount of individual carotenoids compounds at chromoplasts rather than at chloroplasts (Gross, 1991).

Similar to anthocyanins, carotenoids also exist as plant pigments, responsible for red, yellow and orange colour, and also have health-promoting effects.  $\beta$ -Carotene,  $\beta$ -cryptoxanthin,  $\alpha$ -carotene, lycopene, and lutein are the main compounds that contribute to the total carotenoids present in fruits and vegetables (Hart & Scott, 1995). Of all the compounds,  $\beta$ -carotene,  $\beta$ -cryptoxanthin and  $\alpha$ -carotene are the main precursors of vitamin A, which cannot be synthesised within the body and must be supplemented through daily intake, hence are considered to help in reducing the incidence of cancer and other diseases (Block, Patterson, & Subar, 1992; Hennekens et al., 1996; Kris-Etherton et al., 2002; Omenn et al., 1996). It is important to bear in mind that carotenoids are highly unstable in nature; they are both photo- and thermolabile and tend to oxidise if they are not protected from light and atmosphere. As a result, the isolation of carotenoids for quantification might lead to the underestimation of the total carotenoids content due to the tendency of these compounds to degradation, structural rearrangement, formation of stereoisomers, and other physicochemical reactions.

Among the commodities, the highest total carotenoid content was found in cherries and nectarines from Cromwell, in carrots from Clinton and in red bell peppers grown in Mosgiel (Table 4). Compared to other countries located in the Northern Hemisphere, Otago red bell peppers had higher carotenoids content compared to these grown in Israel (Ben-Amotz & Fishler, 1998), United Kingdom (Hart & Scott, 1995) and Japan (Chuah et al., 2008). Additionally, nectarines grown in Otago had higher carotenoid content than those grown in the United States (Gil, Tomas-Barberan, Hess-Pierce, & Kader, 2002), Israel (Ben-Amotz & Fishler, 1998), China (Isabelle et al., 2010) and Italy (Di Vaio, Graziani, Marra, Cascone, & Ritieni, 2008). Otago-grown cherries and apricots had a similar carotenoid content to cherries grown in Israel (Ben-Amotz & Fishler, 1998) and Spain (de Pascual-Teresa, Santos-Buelga, & Rivas-Gonzalo, 2000) and apricots grown in France (Ruiz, Egea, Tomas-Barberan, & Gil, 2005), Turkey (Akin, Karabulut, & Topcu, 2008) and Hungary (Sass-Kiss, Kiss, Milotay, Kerek, & Toth-Markus,

2005). The carotenoid content in peaches grown in Otago was similar to California peaches (Gil et al., 2002) and higher than those grown in Israel (Ben-Amotz & Fishler, 1998) and Italy (Di Vaio et al., 2008), but lower than those grown in Spain (Cantin et al., 2009; de Pascual-Teresa et al., 2000).

### 3.3. Evaluation of vitamin C content in seasonal fruits and vegetables

In this study, a substantially high level of total L-AA content was found predominantly in peppers and carrots rather than in fruits such as apricots, cherries, plums, nectarines and peaches (Table 5), suggesting that summer fruits were not generally as rich in vitamin C. In fresh commodities, a low LAA/DHAA ratio was found in apricots, cherries, nectarines, peaches, plums and carrots, indicating that L-AA oxidation took place during vitamin C extraction. In the presence of oxygen and enzyme ascorbic acid oxidase during sample preparation and extraction, L-AA can be rapidly oxidised to dehydroascorbic acid (DHAA), which afterwards can be easily hydrolysed to diketogulonic acid (DKG). Consequently, the oxygen scavenger ability of ascorbic acid leads to the opening of lactone ring structure, destroying the vitamin C activity and the antioxidant ability. Therefore, low LAA/DHAA ratio and total vitamin C content was obtained in all the fruits and vegetables studied, except in red bell peppers. This could be due to the existence of chelating agents or ascorbic acid oxidase inhibitors in red bell peppers which can protect vitamin C against oxidation during extraction.

The Otago commodities contain higher vitamin C content than those grown in other countries, for example, when compared to peaches grown in Spain (Cantin et al., 2009) and California (Gil et al., 2002); cherries grown in Greece (Pantelidis et al., 2007); red bell pepper grown in Brazil (Hassimotto, Genovese, & Lajolo, 2005), New Mexico (Chassy, Bui, Renaud, Van Horn, & Mitchell, 2006) and Japan (Chuah et al., 2008) and carrots grown in the United States (Lee & Kader, 2000). However, some fruits contain lower vitamin C content when compared to apricots grown in Turkey (Akin et al., 2008) and nectarines grown in Spain (Cantin et al., 2009) and California (Gil et al., 2002). Compared with nectarines grown in China (Isabelle et al., 2010), Otago nectarines have a higher vitamin C content.

### 3.4. Processing stability of the phytochemicals and its implication to nutrient intake

The effects of processing on the content of reducing sugar, anthocyanins, carotenoids and vitamin C are depicted in Fig. 2. Even though the sampling location of this study was restricted to one small region, namely Otago, the stability of phytochemicals in the same horticultural commodity during heating, freezing and freeze-drying was also influenced by the location of the growers, such as in the case of anthocyanins (Table 2), carotenoids (Table 4) and vitamin C (Table 5). In this study, reducing sugars were used as an index for leaching and sweetness. A clear trend was observed, which is that heating results in a low content of reducing sugar. It indicated that leaching occurred during heating and the degree of sweetness was lower which could influence the sensory characteristics of the heated fruits and vegetables.

In most cases, heating increased the anthocyanin content in cherries, peaches and plums but not in nectarines. This study found that the heated fruits contained more anthocyanins than the fresh fruits (Table 2). Heating results in enzyme inactivation, texture changes of fruits and vegetables and unavoidable leaching of water-soluble compounds which could alter the entire phytochemical profile and content of fruit and vegetables. Phytochemicals do not exist as an individual compound; they are mostly bound to other compounds or to cell structures. Due to heat, the disruption of cell membranes occurred. Once the cell is damaged due to heat, this creates an opportunity for the bound

**Table 4**

The content of major carotenoid compounds (mg/g DW) in fruits and vegetables under different processing conditions.

Processing	Fruits or vegetables	$\beta$ -Carotene	$\beta$ -Cryptoxanthin	$\alpha$ -Carotene	Lycopene	Lutein
Fresh	Apricots	0.25 <sup>a</sup> ± 0.12 <sup>b</sup>	0.25 ± 0.13	0.20 ± 0.10	0.15 ± 0.07	0.12 ± 0.14
		0.48 <sup>c</sup>	0.52	0.50	0.47	1.17
	Cherries	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01
		0.50	0.50	0.50	1.00	0.50
	Nectarines	0.09 ± 0.05	0.09 ± 0.05	0.09 ± 0.05	0.06 ± 0.03	0.10 ± 0.05
		0.56	0.56	0.56	0.50	0.50
	Peaches	0.03 ± 0.02	0.03 ± 0.02	0.03 ± 0.02	0.02 ± 0.01	0.03 ± 0.02
		0.67	0.67	0.67	0.50	0.67
	Plums	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.04 ± 0.01
		0.25	0.25	0.33	0.50	0.25
	Carrots	0.44 ± 0.02	0.45 ± 0.02	0.38 ± 0.01	0.28 ± 0.00	0.42 ± 0.01
		0.05	0.04	0.03	0.01	0.02
	Peppers	0.84 ± 0.18	0.85 ± 0.25	0.70 ± 0.19	0.60 ± 0.15	0.76 ± 0.22
		0.21	0.29	0.27	0.25	0.29
Heating (98 °C, 10 min)	Apricots	0.17 ± 0.14	0.20 ± 0.18	0.17 ± 0.16	0.13 ± 0.12	0.19 ± 0.17
		0.82	0.90	0.94	0.92	0.89
	Cherries	0.02 ± 0.00 <sup>d</sup>	0.02 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.02 ± 0.00
		0.20	0.20	0.20	0.40	0.20
	Nectarines	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.04 ± 0.01
		0.33	0.25	0.33	0.50	0.25
	Peaches	0.04 ± 0.04	0.04 ± 0.04	0.04 ± 0.03	0.02 ± 0.02	0.04 ± 0.04
		0.93	1.00	0.75	1.00	1.00
	Plums	0.03 ± 0.03	0.03 ± 0.03	0.03 ± 0.02	0.02 ± 0.01	0.03 ± 0.03
		1.00	1.00	0.67	0.50	1.00
	Carrots	0.37 ± 0.05	0.38 ± 0.06	0.31 ± 0.04	0.22 ± 0.03	0.36 ± 0.06
		0.14	0.16	0.13	0.14	0.17
	Peppers	1.06 ± 0.15	1.02 ± 0.17	0.91 ± 0.12	0.75 ± 0.10	1.01 ± 0.14
		0.14	0.17	0.13	0.13	0.14
Freezing (−20 °C)	Apricots	0.28 ± 0.14	0.26 ± 0.11	0.24 ± 0.12	0.20 ± 0.13	0.25 ± 0.12
		0.50	0.42	0.50	0.65	0.48
	Cherries	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.02 ± 0.00
		0.05	0.07	0.05	0.10	0.010
	Nectarines	0.06 ± 0.05	0.06 ± 0.05	0.06 ± 0.05	0.05 ± 0.03	0.07 ± 0.06
		0.83	0.80	0.88	0.60	0.86
	Peaches	0.03 ± 0.03	0.03 ± 0.02	0.03 ± 0.02	0.02 ± 0.02	0.03 ± 0.02
		0.99	0.67	0.67	1.00	0.67
	Plums	0.03 ± 0.01	0.03 ± 0.02	0.03 ± 0.02	0.02 ± 0.01	0.03 ± 0.02
		0.33	0.67	0.67	0.51	0.66
	Carrots	0.44 ± 0.09	0.47 ± 0.07	0.36 ± 0.04	0.30 ± 0.02	0.90 ± 0.13
		0.20	0.15	0.11	0.07	0.14
	Peppers	1.30 ± 0.28	1.33 ± 0.27	1.02 ± 0.13	0.43 ± 0.11	1.31 ± 0.24
		0.22	0.20	0.13	0.26	0.18
Freeze drying	Apricots	0.12 ± 0.04	0.12 ± 0.04	0.10 ± 0.04	0.07 ± 0.03	0.11 ± 0.04
		0.33	0.33	0.40	0.43	0.36
	Cherries	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01
		0.50	0.50	0.50	1.00	0.50
	Nectarines	0.08 ± 0.04	0.09 ± 0.06	0.09 ± 0.06	0.06 ± 0.04	0.09 ± 0.06
		0.50	0.67	0.67	0.67	0.67
	Peaches	0.04 ± 0.03	0.04 ± 0.03	0.04 ± 0.03	0.03 ± 0.02	0.04 ± 0.03
		0.75	0.75	0.75	0.67	0.75
	Plums	0.03 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01
		0.33	0.33	0.50	1.00	0.50
	Carrots	0.39 ± 0.05	0.41 ± 0.04	0.34 ± 0.07	0.25 ± 0.05	0.37 ± 0.05
		0.13	0.10	0.21	0.20	0.14
	Peppers	0.72 ± 0.12	0.74 ± 0.11	0.66 ± 0.10	0.52 ± 0.17	0.68 ± 0.11
		0.17	0.15	0.15	0.33	0.16

<sup>a</sup> Mean of samples randomly collected from three different growers.<sup>b</sup> Standard deviation of samples randomly collected from three different growers.<sup>c</sup> Coefficient of variance (CV).<sup>d</sup> Standard deviation of 0.00 indicates value lower than 5 µg/g DW.

phytochemical compounds to be released into the medium, hence they are readily extracted. In fact, heating has been reported to increase the chemical extractability of phytochemical compounds, because of the release of phytochemicals from chromoplasts leading to an increment of concentration (Howard, Wong, Perry, & Klein, 1999). Heating also encourages the diffusion of cellular fluids, containing phytochemicals, from the plant cell to the water medium. As shown in Fig. 2, low sugar content is found after

heating, indicating the occurrence of leaching. Therefore, the content of phytochemicals after heating is a net result of a combined increase in phytochemical extractability, degradation and leaching. In this study, heating decreased the content of carotenoids in apricots, nectarines and carrots while maintaining the carotenoid content in cherries, peaches, plums and red bell peppers.

In the literature it is mostly stated that L-AA is heat sensitive, water soluble and prone to degradation under different influences

**Table 5**  
Effect of processing on the total vitamin C, L-AA and DHAA content (mg/g DW) in fruits and vegetables.

Processing	Fruits or vegetables	Total vitamin C	L-AA	DHAA	% LAA/DHAA	% retention total vitamin C
Fresh	Apricots	0.04 <sup>a</sup> ± 0.00 <sup>b</sup>	0.01 ± 0.00 <sup>d</sup>	0.03 ± 0.00	35.37 ± 7.45	100
		0.03 <sup>c</sup>	0.10	0.03		
	Cherries	0.09 ± 0.03	0.05 ± 0.04	0.05 ± 0.01	132.59 ± 122.30	100
		0.33	0.80	0.20		
	Nectarines	0.10 ± 0.01	0.01 ± 0.01	0.09 ± 0.01	13.69 ± 8.67	100
		0.10	0.80	0.11		
	Peaches	0.03 ± 0.04	0.07 ± 0.05	0.07 ± 0.05	56.57 ± 76.66	100
		1.33	0.71			
Plums	0.06 ± 0.04	0.01 ± 0.00	0.05 ± 0.04	12.41 ± 3.24	100	
	0.67	0.11	0.80			
Carrots	0.08 ± 0.03	0.03 ± 0.03	0.05 ± 0.04	126.64 ± 174.22	100	
	0.38	1.00	0.80			
Peppers	10.80 ± 2.67	9.40 ± 2.70	1.40 ± 0.19	680.90 ± 230.98	100	
	0.25	0.29	0.14			
Heating (98 °C, 10 min)	Apricots	0.06 ± 0.03	0.00 <sup>e</sup> ± 0.00	0.06 ± 0.03	6.19 ± 4.61	168.24 ± 93.77
		0.50	0.23	0.50		
	Cherries	0.12 ± 0.08	0.01 ± 0.01	0.12 ± 0.08	33.65 ± 53.33	143.87 ± 31.73
		0.67	1.00	0.67		
	Nectarines	0.17 ± 0.04	0.02 ± 0.01	0.15 ± 0.05	11.77 ± 7.35	170.93 ± 32.24
		0.24	0.50	0.33		
	Peaches	0.18 ± 0.12	0.01 ± 0.01	0.17 ± 0.11	11.63 ± 8.67	176.91 ± 53.50
		0.67	1.00	0.65		
Plums	0.06 ± 0.04	0.03 ± 0.04	0.04 ± 0.01	65.68 ± 73.19	116.42 ± 15.39	
	0.67	1.33	0.25			
Carrots	0.20 ± 0.13	0.01 ± 0.00	0.19 ± 0.13	4.56 ± 3.60	253.34 ± 128.98	
	0.65	0.88	0.68			
Peppers	13.60 ± 3.82	5.48 ± 0.51	8.11 ± 3.32	75.98 ± 30.79	125.03 ± 5.01	
	0.28	0.09	0.41			
Freezing (−20 °C)	Apricots	0.09 ± 0.03	0.01 ± 0.01	0.08 ± 0.03	14.68 ± 13.56	251.30 ± 88.87
		0.33	1.00	0.38		
	Cherries	0.21 ± 0.02	0.01 ± 0.00	0.21 ± 0.02	2.44 ± 1.16	254.44 ± 93.98
		0.10	0.22	1.00		
	Nectarines	0.19 ± 0.03	0.05 ± 0.06	0.14 ± 0.09	126.40 ± 208.55	198.50 ± 61.25
		0.16	1.20	0.64		
	Peaches	0.22 ± 0.08	0.01 ± 0.01	0.21 ± 0.07	5.37 ± 3.12	238.45 ± 152.40
		0.36	1.00	0.33		
Plums	0.09 ± 0.04	0.01 ± 0.00	0.08 ± 0.03	7.78 ± 3.39	174.10 ± 44.97	
	0.44	0.40	0.38			
Carrots	0.12 ± 0.05	0.04 ± 0.05	0.08 ± 0.07	170.66	158.15 ± 35.35	
	0.42	1.25	0.88			
Peppers	10.12 ± 1.63	9.13 ± 1.03	0.98 ± 0.61	1253.01 ± 830.25	98.84 ± 33.09	
	0.16	0.11	0.62			
Freeze drying	Apricots	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.01	269.73 ± 382.29	60.11 ± 20.24
		0.50	0.22	1.00		
	Cherries	0.06 ± 0.02	0.00 ± 0.00	0.06 ± 0.02	6.46 ± 1.15	71.91 ± 6.07
		0.33	0.01	0.33		
	Nectarines	0.10 ± 0.05	0.01 ± 0.00	0.09 ± 0.05	18.29 ± 15.37	99.02 ± 42.78
		0.50	0.40	0.56		
	Peaches	0.12 ± 0.06	0.01 ± 0.01	0.11 ± 0.05	8.53 ± 1.53	120.93 ± 18.58
		0.50	1.00	0.45		
Plums	0.06 ± 0.04	0.01 ± 0.00	0.05 ± 0.04	19.84 ± 15.44	108.02 ± 34.31	
	0.67	0.33	0.80			
Carrots	0.18 ± 0.06	0.02 ± 0.01	0.16 ± 0.05	13.43 ± 5.97	241.16 ± 43.17	
	0.33	0.50	0.31			
Peppers	9.47 ± 1.67	8.51 ± 1.58	0.95 ± 0.11	887.64 ± 94.08	89.59 ± 14.74	
	0.18	0.19	0.12			

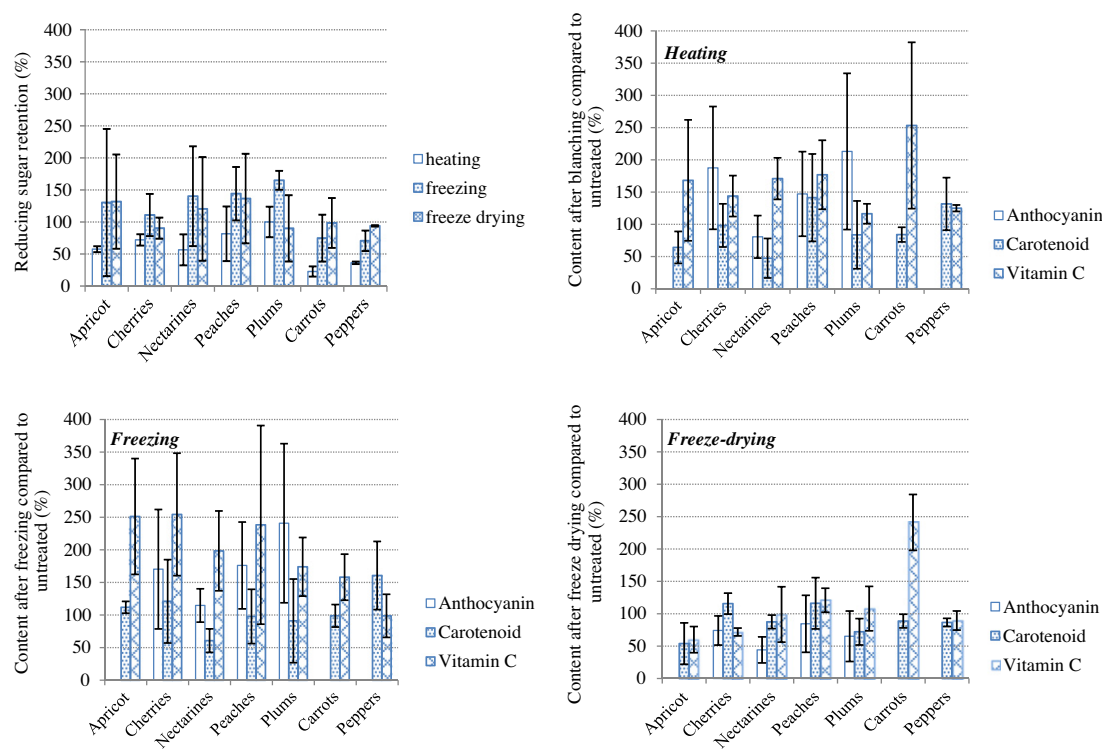
<sup>a</sup> Mean of samples randomly collected from three different growers.<sup>b</sup> Standard deviation of samples randomly collected from three different growers.<sup>c</sup> Coefficient of variance (CV).<sup>d</sup> Standard deviation of 0.00 indicates value lower than 5 µg/g DW.<sup>e</sup> Mean of 0.00 indicates the concentration is lower than 5 µg/g DW.

of pH, temperature, oxygen concentration, metal catalysts, enzymes and leaching, thus it leads to vitamin C degradation at elevated temperatures. In this study, an interesting discovery was that heating increased the content of the total vitamin C content, L-AA content and the LAA/DHAA ratio of all commodities studied except the red bell peppers (Table 5). This was due to ascorbic acid oxidase inactivation during heating leading to L-AA protection towards enzymatic oxidation as previously observed in broccoli

(Munyaka et al., 2010) and cowpea leaves (Wawire et al., 2011). In other words, heating could protect the L-AA from enzymatic oxidation (high percentage of retention for most commodities as seen in Fig. 2).

Compared to heating, freezing could maintain or slightly increase the content of phytochemicals and reducing sugar for most of the commodities (Tables 2 and 3). Freezing induces the formation of ice crystals that favours localised concentration of solutes





**Fig. 2.** Effects of processing on the content of reducing sugar, anthocyanins, total carotenoids and vitamin C in summer fruits and vegetables grown in the Otago region. Standard deviation bars represent the variation among the growers with normal distribution. Missing bars for anthocyanins in apricots, carrots and red bell peppers indicate a low level of anthocyanins in these commodities (under detection limit).

(including phytochemicals) and reallocation of water molecules in the cell structure. However, the common consequences of freezing due to cell damages by the growth of ice crystals from temperature fluctuation and turgor loss lead to softening texture (Szczesniak, 1998). It is noted that the rate of freezing influences the ice crystals formation that impact on the food structure by expanding the separation between cells. In other words, when the samples were rapidly frozen, large amounts of smaller ice crystals formed and caused a lesser degree of cell structure disruption than the samples being frozen slowly, which formed large intercellular ice crystals. In this study, cryogenic freezing involving the immersion of samples into liquid nitrogen promoted a rapid freezing rate. Direct contact of liquid nitrogen with samples absorbs latent heat, and the transition from solid phase to gas phase takes place. Liquid nitrogen was used in this research owing to its colourless, odourless and inert properties and freezing point at  $-196^{\circ}\text{C}$ . In general, the manner in which the frozen sample is thawed is a key factor that will attribute to the changes in phytochemical contents (Robards, 2003).

In contrast, freeze-dried samples mostly resulted in a lower amount of phytochemicals, as compared to fresh, heated and frozen commodities (Fig. 2 and Table 2). Basically, freeze-drying is the combination of dehydration and freezing, i.e. dehydrating the samples by freezing the immobilised water into ice and then removing the ice crystals via sublimation into vapour. While freeze-drying is incapable of inactivating all of the enzymes, it is effective in preserving the sensory and nutritional qualities. Usually, a minor loss of vitamin does occur but extensive reduction of water during freeze-drying will form the fragile porous structure in the end product. Sublimation of ice to vapour caused by drying in the sample slices gave an open and porous texture. The heat utilisation in freeze-drying may be harsher than the conventional freezing mechanism as the flavour and aroma compounds were

evaporated along with water as volatiles. In practice, thinly sliced samples were used to promote larger surface area available for dehydration had increased the water removal rate. Nevertheless, the phytochemicals in freeze-dried samples were more prone to degradation due to the large surface area exposed during processing. Hence, most of the labile phytochemicals were rapidly oxidised, because the water molecules attached on the sample surface that acted as a protecting film were evaporated as well (Gross, 1991).

#### 4. Conclusions

The content of the phytochemical compounds in fruits and vegetables and their stability during food processing vary depending on the geographical locations of the growers, the type and cultivar of fruits and vegetables (food matrix) and the growth condition. It is interestingly observed that most of the cultivars grown in the Otago region have a very high content of anthocyanins, and vitamin C (particularly carrots) compared to the respective commodities in some countries located in the Northern Hemisphere. Different growth conditions and environmental stress (such as high exposure to UV light, temperature) could be important factors influencing the levels of bioactive content as a result of the plant defence response. Therefore, to secure the micronutrient intake and to improve human health and the prevention of chronic diseases, different types of fruits and vegetables coming from different locations should be considered in one's daily diet.

Fruits and vegetables are highly perishable and hence have a short shelf life. To prolong the shelf life of seasonal fruits and vegetables whilst maintaining the health benefits and sensory characteristics (sweetness) of these commodities, freezing is the best method compared to heating and freeze-drying. Moreover the

release of membrane bound phytochemicals, such as anthocyanins is enhanced during heating and freezing. This indirectly gives implications to higher bioaccessibility of these bioactive compounds before absorption in human digestion. Heat treatment, such as blanching can also eliminate the enzymatic oxidation of vitamin C due to the inactivation of ascorbic acid oxidase. It should be taken into account that loss of phytochemicals during processing is also driven by leaching. For these reasons, heating in a closed system (sealed vacuum plastic bag) and recuperating fruit and vegetables medium leached out during thawing (after freezing) are required to achieve high retention of phytochemicals in heated and frozen horticultural produce.

## Acknowledgements

The authors would like to thank Otago Medical Research Foundation (OMRF) Summer Scholarship for funding of this research and Division of Sciences (University of Otago) for Performance Based Research Fund – 2012 Publication Outputs. The technical assistance of Ian Ross, Nerida Downes, Michelle Petrie, Brenda Holland and Sarah Henry, from Department of Food Science, University of Otago is greatly appreciated. We also thank Dr. Inga Smith from Department of Physics, University of Otago for her assistance to use the NIWA database related to this study.

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