Comparison of Chilean and New Zealand boysenberry fruit and concentrates
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Executive summary

We conducted a range of analyses on boysenberry fruits and concentrates. These analyses were conducted for Berryfruit Export Ltd in order to determine if New Zealand boysenberry products (frozen whole fruit and juice concentrate) had superior nutritional/health characteristics to their Chilean counterparts. In virtually all parameters measured the New Zealand samples were superior to the Chilean samples. This was true for both the fruit samples and the concentrates with differences between duplicate or triplicate analyses on the same sample type small in comparison to the differences between New Zealand and Chilean samples.

The key findings were:

- New Zealand boysenberry fruit had a slightly superior appearance, being larger and more uniform in shape and colour than the Chilean sample,
- colour measurements showed New Zealand boysenberry fruit to be more intensely red/purple than Chilean fruit,
- New Zealand boysenberry fruit had a significantly higher dietary fibre content than the Chilean fruit, although sugar content was similar,
- New Zealand boysenberry fruit was approximately 24% higher in total phenolics and the concentrate was approximately 20% higher in total phenolics than their Chilean counterparts,
- total anthocyanins were approximately 23% higher in New Zealand boysenberry fruit and the concentrate was approximately 31% higher in anthocyanins than the Chilean samples. The composition of the anthocyanins was similar with two main anthocyanin peaks and three or four minor peaks detected in all samples,
- HPLC analysis of the other phenolics showed a similar composition in the New Zealand and Chilean samples. However, most phenolics, such as ellagic acid, were higher in the New Zealand samples than in the Chilean ones,
- antioxidant activity, as measured by the ORAC assay, was 38% higher in the New Zealand boysenberry fruit and 29% higher in the concentrate than in the respective Chilean samples. Differences in antioxidant activity measured by the DPPH assay were smaller but New Zealand samples were still superior to their Chilean counterparts.
2 Introduction

The reason for comparing New Zealand and Chilean boysenberry fruit and concentrate was to identify characteristics and health attributes that show New Zealand products are superior to their Chilean counterparts. Tests initially suggested by Berryfruit Export Ltd were:

- general physical characteristics, e.g. fruit size, appearance, colour, seed content
- sensory characteristics
- anthocyanins, by type and by volume
- antioxidant capacity, e.g. ORAC/ABTS/FRAP
- phenolics, e.g. phenolic acids and flavonoids
- ellagic acid (free and total)
- folate
- dietary fibre (including types)
- vitamins, e.g. A and K

After discussion, the tests we recommended and that were finalised by Berryfruit Export Ltd were:

- general physical characteristics
  - size, appearance, colour, seed content for fruit
  - colour measurements (Hunterlab and spectrophotometric) for the concentrates
- general composition
  - moisture (dry matter)
  - total acidity (pH)
  - carbohydrates – dietary fibre and simple sugars
  - vitamins – folate only
- phenolic composition
  - total phenolics by Folin-Ciocalteu method
  - anthocyanins – quantification by HPLC to give breakdown of individual compounds and expressed as cyanidin 3-glucoside equivalents
  - other phenolics – analysis by HPLC (completed at same time as anthocyanins) and where possible identify compounds and quantify with authentic standards. This analysis will include ellagic acid
- antioxidant capacity – measurements by two assays
  - ORAC and DPPH.
Analysis was conducted on four samples provided by Berryfruit Export:

1. New Zealand boysenberry fruit – random sample of 1 kg IQF (Berryfruit Export) boysenberries,
2. New Zealand boysenberry concentrate – combined sample of Boysenberry Juice Concentrate Batch N7002, 7004 and 7006 (each 200 ml),
3. Chilean boysenberry fruit – random sample of 300 ml of Chilean Juice Concentrate,
4. Chilean boysenberry concentrate – random sample of 3 x 500 g packs of Chilean IQF Boysenberries.

Random subsamples were taken from these samples for the analyses outlined in this report.

3 Materials and methods

3.1 Physical characteristics

Boysenberry fruit was visually assessed by two staff members and comments recorded. Six replicates, each made up of a group of ten fruit, were weighed, and the average fruit weight was calculated. The berries were then pushed through a sieve and washed to separate the seeds, which were weighed (both wet and dry).

3.1.1 Colour measurements

The first method used for colour measurement involved spectrophotometric analysis. Fruit was first extracted in MeOH 2% HCL (~2 g in 40 ml then diluted 1:10) and concentrates were diluted by putting ~500 mg in 10 ml distilled water (dH₂O) then diluting this at a ratio of 1:10. Scanning spectra were recorded and absorption maxima noted. In addition, absorbance at fixed wavelengths (420, 430, 510 and 520 nm) was recorded.

A Hunterlab colorimeter was also used to assess fruit colour.

3.2 General composition

The following methodologies were used:

- dry matter: oven drying method
- fibre (dietary): AOAC 985.29
- pH: based on BS4401 Part 9 1975, AOAC 981.12
- sugars (sucrose, lactose, maltose, glucose and fructose): in-house GLC method
- folate: microbiological method
3.3 **Composition of anthocyanins and other phenolics**

3.3.1 **Total phenolics**

Total phenolics in fruit extracts or the liquid samples were measured using Folin-Ciocalteu reagent, adapted from the method of Spanos & Wrolstad (1990). This assay is based on the colour reaction of phenolics with a phosphomolybdic-phosphotungstic acid reagent (e.g. Folin-Ciocalteu reagent). Absorbance of the samples at 765 nm was compared to a control and a gallic acid standard curve, with results expressed as gallic acid equivalents (mg GAE/100 g). Fruit samples were extracted in 80% acetone and concentrate samples diluted with water as necessary.

3.3.2 **Quantification of anthocyanins by HPLC**

In order to perform HPLC, fruit samples were extracted with 15% acetic acid in methanol. Anthocyanin levels were quantified by HPLC using the method of Lister et al. (1994). Extracts were centrifuged at 20800 x g for 10 min before injecting directly on to a high-performance liquid chromatography (HPLC) column. The HPLC system comprised a solvent delivery system with an automatic sample injector and a variable wavelength UV detector (models W600, W717, and 996 PDA; Waters, Milford, MA). The RP-18 column (250 x 4.6 mm, Beckman Ultrasphere ODS, 5 µm C18; Beckman Instruments Inc., Fullerton, CA) was fitted with a guard column (7.5 x 4.6 mm, Ultrasphere, 5 µm C18; Alltech Associates Inc., Deerfield, IL). Chromatographic traces were recorded using the Waters Empower software program scanning a wavelength from 250 to 700 nm. Samples (5 µl) were injected on to the column, which was maintained at 25°C and eluted with a flow rate of 1.0 ml/min. Solvents were 10% (v/v) acetic acid in water (A) and acetonitrile (D). Initial solvent conditions were 100% A. A linear 48 min solvent gradient from 0 to 16% acetonitrile, then a linear 2 min solvent gradient from 16 to 20% acetonitrile, then a linear 0.1 min solvent gradient from 20 to 50% acetonitrile with a 1.9 min hold at the final concentration was used. The column was returned to initial solvent composition over 0.5 min and re-equilibrated for 15 min before the next analysis. Eluted components were monitored at 530 nm for anthocyanins. Samples were stored in the autosampler at 4°C during analysis. A standard curve was prepared using a cyanidin-3-glucoside standard (purchased from Extrasynthese) and total anthocyanins were calculated on this basis.

Other phenolics were also examined by monitoring absorbance over the range 250–700 nm. A range of standards was run, including gallic acid, ellagic acid, quercetin, rutin and catchin. Absorbance spectra and retention time of the standards were compared with unknowns in the HPLC traces. The spectra of unknown compounds were also compared with published data in order to identify the class of phenolics to which they belonged.
3.4 Antioxidant activity assays

3.4.1 ORAC assay
The Oxygen Radical Absorbance Capacity (ORAC) assay is one of the most popular tests being used today to rank the antioxidant potential of foods. The ORAC assay measures antioxidant inhibition of peroxyl radical-induced oxidation (Cao et al. 1993). The procedure used was based on a previous report by Ou et al. (2001). Trolox, a water-soluble analogue of vitamin E, was used as a control standard and samples were prepared in 50% acetone.

3.4.2 DPPH assay
This method was adapted from Brand-Williams et al. (1995) and Sanchez-Moreno et al. (1998). DPPH (2,2-diphenyl-1-picrylhydrazyl) is used to show the kinetic behaviour of polyphenols as free radical scavengers. The higher the antioxidant activity, the larger the decrease of DPPH\(^*\) concentration. A methanolic solution of the DPPH radical changes from purple to colourless when quenched by antioxidants. The decrease in DPPH\(^*\) is measured at 515 nm against Trolox and DPPH\(^*\) standard curves. Two different extractions/dilutions were performed – 100% methanol and 50% methanol.

4 Results

4.1 Physical characteristics
From initial visual inspection of the boysenberry fruit, the New Zealand and Chilean samples were fairly similar. More careful inspection revealed that the New Zealand berries were slightly larger and more uniform in shape (fewer poorly filled drupules) than the Chilean berries. The colour was very similar for both sets of fruit, but the New Zealand fruit appeared slightly more uniform in colour – fewer lighter purple patches on fruit (although these were minimal in both cases).

The general characteristics of the boysenberry fruit that were measured are shown in Table 1. These data backed up the visual assessment, confirming that the New Zealand fruit were on average larger than their Chilean counterparts. Differences between replicates for each sample were small compared to the differences between the New Zealand and Chilean samples. The seed content (weight) of the New Zealand fruit was higher, even when adjusted for relative fruit size (7.4% compared to 4.1% on a wet weight basis). The higher seed content in the New Zealand fruit was due to both a greater seed number as well as larger seeds. Dry matter of the New Zealand fruit, at 15.5% (84.5% water content), was slightly higher than that of Chilean fruit (14.7%) and this could in part be due to the higher seed content (seeds have a higher dry matter content than the fruit pulp). The dry matter content reported here is very much in line with that reported in the New Zealand Food Composition Database (Athar et al. 2003) with a water content of 85% for fresh boysenberry fruit (sourced from New Zealand, British and American data).
Table 1: General boysenberry fruit characteristics.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Average fruit weight (g)</th>
<th>Weight of seeds per berry (g)</th>
<th>Weight of seeds per berry (g)</th>
<th>Approx. number of seeds per berry</th>
<th>Dry matter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand fruit</td>
<td>7.39 ± 0.24&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.55</td>
<td>0.27</td>
<td>73</td>
<td>15.5</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>6.03 ± 0.34&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.31</td>
<td>0.18</td>
<td>53</td>
<td>14.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> SD based on weighing six groups of 10 berries.
<sup>b</sup> Weight of seeds is wet weight and figures in brackets are weight of seeds once dried.

4.1.1 Colour assessment

In addition to visual appearance, colour was assessed by two different methods. The first method involved extraction of the fruit or dilution of the concentrates and reading the resultant solutions on a spectrophotometer. The absorbance profiles of the two fruit samples were very similar (similar absorbance maxima), although the peak heights were higher for the New Zealand fruit (Table 2). These results would indicate that the phenolic composition was similar but the anthocyanin levels were higher in the New Zealand sample (for details of anthocyanin and phenolic composition see Section 4.3). For the concentrate samples, the absorbance maxima were at a lower wavelength than for the fruit samples. The New Zealand and Chilean concentrate samples were very similar although, as with the fruit samples, the New Zealand concentrate showed a higher peak absorbance than the Chilean sample.

Table 2: Spectrophotometric measurements of colour (average of duplicate samples ± standard deviation).

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Absorbance maxima</th>
<th>Absorbance at fixed wavelengths (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>420  430  510  520</td>
</tr>
<tr>
<td>NZ fruit</td>
<td>0.732 @ 527 nm</td>
<td>0.136  0.154  0.631  0.701</td>
</tr>
<tr>
<td></td>
<td>± 0.004</td>
<td>± 0.005  ± 0.010  ± 0.010</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>0.614 @ 529 nm</td>
<td>0.107  0.123  0.522  0.580</td>
</tr>
<tr>
<td></td>
<td>± 0.002</td>
<td>± 0.004  ± 0.013  ± 0.014</td>
</tr>
<tr>
<td>NZ concentrate</td>
<td>0.877 @ 517 nm</td>
<td>0.394  0.412  0.847  0.854</td>
</tr>
<tr>
<td></td>
<td>± 0.003</td>
<td>± 0.001  ± 0.006  ± 0.006</td>
</tr>
<tr>
<td>Chilean concentrate</td>
<td>0.535 @ 516 nm</td>
<td>0.284  0.289  0.503  0.507</td>
</tr>
<tr>
<td></td>
<td>± 0.001</td>
<td>± 0.002  ± 0.003  ± 0.002</td>
</tr>
</tbody>
</table>

The second method involved using a Hunterlab colorimeter. However, because of the nature of the boysenberry samples it was not possible to obtain meaningful measurements using this piece of equipment (results were inconsistent).
4.2 General composition

4.2.1 Acidity

The Chilean fruit were slightly more acidic than the New Zealand fruit, while the reverse was true for the concentrates (Table 3). However, absolute differences were fairly minor.

Table 3: Acidity of boysenberry fruit and concentrate samples.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ fruit</td>
<td>3.52</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>3.34</td>
</tr>
<tr>
<td>NZ juice concentrate</td>
<td>3.15</td>
</tr>
<tr>
<td>Chilean juice concentrate</td>
<td>3.20</td>
</tr>
</tbody>
</table>

4.2.2 Carbohydrates

The New Zealand boysenberry fruit had a significantly higher dietary fibre content than the Chilean fruit (Table 4). Dietary fibre contents reported here were higher than those given in the New Zealand Food Composition Database for boysenberry fruit at 3 g/100 g FW (Athar et al. 2003). Dietary fibre was not measured in the concentrates as it was not expected to be present in significant amounts.

Table 4: Carbohydrate content of boysenberry fruit and concentrates.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Dietary fibre (g/100 g FW)</th>
<th>Glucose (g/100 g FW)</th>
<th>Fructose (g/100 g FW)</th>
<th>Total sugars (g/100 g FW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ fruit</td>
<td>5.7</td>
<td>3.6</td>
<td>3.8</td>
<td>7.4</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>4.1</td>
<td>3.4</td>
<td>3.4</td>
<td>6.8</td>
</tr>
<tr>
<td>NZ juice concentrate</td>
<td>na(^a)</td>
<td>18.7</td>
<td>19.8</td>
<td>38.5</td>
</tr>
<tr>
<td>Chilean juice concentrate</td>
<td>na(^a)</td>
<td>21.9</td>
<td>22.8</td>
<td>44.7</td>
</tr>
</tbody>
</table>

\(^a\) na = not analysed.

The two main sugars present in both the fruit and concentrates were glucose and fructose, which were present in relatively similar amounts (Table 4). Other common sugars (e.g. sucrose, maltose and lactose) were not detected (or were present at less than 0.1 g/100 g). Sugar levels were slightly higher in the New Zealand fruit, but the Chilean concentrates had higher sugars, indicating samples may have been more concentrated. Total sugar content of the fruit samples was in line with that reported in the New Zealand Food Composition Database for boysenberry fruit at 7.1 g/100 g FW (Athar et al. 2003). Sugar contents of the concentrates were lower than may be expected based on Brix content of 651°. A refractometer was used to check Brix content – the New Zealand concentrate had a reading of 65° and the Chilean
concentrate 63°. These results indicate that other soluble solids probably contribute to the Brix values. It has been noted that organic acids can interfere with estimation of sugars using the refractive index method (Toldam-Anderson & Hansen 1997). The organic acid content of boysenberry fruit is typically at least 1% (Monro & Lee 1987) so it will be even higher in concentrates. This would cause considerable discrepancy in measured individual sugars and Brix measurements using a refractometer.

4.2.3 Folate

New Zealand boysenberry fruit had a slightly lower folate content than the Chilean fruit, while the concentrate samples had identical folate contents (Table 5). Both values were lower than that reported on the New Zealand Food Composition Database for boysenberry fruit at 63 µg/100 g FW (Athar et al. 2003). These differences may reflect differences in cultivars, variation due to growing conditions, or different analytical methods. Although folate studies have not been carried out with boysenberries, limited studies have been carried out with other fruit and vegetables. For example, it was shown that cultivar differences and growing conditions had a pronounced effect on the folate content of beetroots (Jastrebova et al. 2003).

Table 5: Folate content of boysenberry samples.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Folate (µg/100 g FW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ fruit</td>
<td>37.2</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>44.1</td>
</tr>
<tr>
<td>NZ juice concentrate</td>
<td>40</td>
</tr>
<tr>
<td>Chilean juice concentrate</td>
<td>40</td>
</tr>
</tbody>
</table>

Unlike many other components that were present in higher levels in the concentrates compared to the fruit, folate was present at relatively similar levels in the two types of samples (Table 5). This indicates that a significant proportion of folate is probably lost during processing. Other work has shown that folate can be significantly affected by processing and storage (Hawkes & Villota 1989). It is degraded during thermal processing, especially under acidic conditions. No studies have been carried out with boysenberries, but beetroot processing resulted in considerable loss of folates, whereas losses during storage appeared to be moderate (Jastrebova et al. 2003).

4.3 Composition of anthocyanins and other phenolics

4.3.1 Total phenolics

Total phenolic levels, as measured by the Folin-Ciocalteu method, were higher in the New Zealand boysenberry samples than in the Chilean samples (Table 6). This was true for both fruit samples and juice concentrates. New Zealand fruit was approximately 24% higher in phenolics and the concentrate was approximately 20% higher in phenolics than the Chilean fruit. The levels
of phenolics reported here are similar to those we have observed in other studies with New Zealand-grown boysenberries (typically between 450 and 650 mg GAE/100 g FW). It should be noted that this total phenolics assay is of a general nature and some other compounds can interfere with results. The phenolic levels in both fruit samples were lower than those reported by Wada & Ou (2002) for Oregon-grown boysenberries at 599 mg/100 g. However, this difference may relate to the experimental methodology as a different extraction method was used. Our previous studies with blackcurrants indicate that we may have higher levels of phenolics in New Zealand-grown fruit than in overseas fruit because of our higher UV light levels (Lister et al. 2002).

Table 6: Total phenolic levels in boysenberry samples, expressed as gallic acid equivalents (GAE) (average of triplicate samples ± standard deviation).

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Total phenolics (mg GAE/100 g FW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand fruit</td>
<td>541.8 ± 16.5</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>438.0 ± 4.2</td>
</tr>
<tr>
<td>New Zealand juice concentrate</td>
<td>2544.7 ± 34.5</td>
</tr>
<tr>
<td>Chilean juice concentrate</td>
<td>2126.7 ± 0.6</td>
</tr>
</tbody>
</table>

4.3.2 Quantification of anthocyanins by HPLC

As predicted from the colour measurements (Section 4.1.1), anthocyanin levels were higher in New Zealand boysenberry fruit than in the Chilean fruit (Table 7) with New Zealand fruit being approximately 23% higher in total anthocyanins. This difference between New Zealand and Chilean fruit was similar to that observed for total phenolics (24% higher). The anthocyanin levels in both fruit samples were higher than that reported by Wada & Ou (2002) for Oregon-grown boysenberries at 131 mg/100 g.

As with the fruit samples, the New Zealand concentrate sample had significantly higher levels of total anthocyanins (approximately 31% higher) than the Chilean sample. The difference in total anthocyanins between the New Zealand and Chilean samples was greater than that observed for the total phenolics (20% higher). This may indicate that the processing used in Chile was harsher (e.g. higher heat) than the New Zealand, because often anthocyanins are less stable than other phenolics.

In all samples there were two main anthocyanin peaks and three or four minor peaks. One of the major peaks was identified as cyanidin 3-glucoside based on comparison with an authentic standard. In the recent literature there has been some debate about the number and identification of the major peaks. Wada & Ou (2002) reported cyanidin 3-(6’-p-coumaryl)glucoside-5-glucoside and cyanidin 3-glucoside in relatively similar amounts. This matches our observation of peak numbers, relative concentrations and retention order. McGhie et al. (2006), on the other hand, reported three major
peaks and four minor peaks. The major peaks were cyanidin 3-[2-(glucosyl)glucoside], cyanidin-3-[2-(glucosyl0-6-(rhamnosyl)glucoside] and cyanidin 3-glucoside. The pattern of peaks that McGhie et al. (2006) reported, and even the relative ratios, did not match what we observed in the current experiment (even if we did have two compounds coeluting). However, McGhie et al. (2006) did use a different extraction solvent to that used here and by Wada & Ou (2002), which may explain the differences in the results. Torre & Barritt (1977), on the other hand, reported that boysenberries contained cyanidin 3-glucoside along with cyanidin-3-sophoroside and cyanidin-3-glucosylrutinoside. However, the methods they used are outdated and hence these identifications are questionable. No standards for the above compounds were available to confirm the identity of the second major peak we observed. However, it was conclusively categorised as a cyanidin glycoside based on absorption spectra. The sugars and their position of attachment could not be confirmed, which precluded a complete identification. The minor peaks were all cyanidin glycosides. To conclusively confirm anthocyanin composition LCMS should be carried out.

Table 7: Total anthocyanin levels in boysenberry samples, expressed as cyanidin 3-glucoside equivalents (average of duplicate samples ± standard deviation).

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Anthocyanins (mg/100 g FW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>New Zealand fruit</td>
<td>195.0 ± 2.7</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>159.1 ± 0.3</td>
</tr>
<tr>
<td>New Zealand juice concentrate</td>
<td>649.5 ± 10.0</td>
</tr>
<tr>
<td>Chilean juice concentrate</td>
<td>493.9 ± 12.6</td>
</tr>
</tbody>
</table>

* cyanidin glycoside not identified (see text).
* cyanidin 3-glucoside.
* sum of minor peaks (all cyanidin glycosides).

4.3.3 Analysis of other phenolics by HPLC

A range of other phenolics was present in all the boysenberry samples. These were not specifically identified but could be classed into groupings on the basis of their spectra. There were several flavonols in minor amounts, which from their spectra appeared to be quercetin glycosides. The identity of the particular glycosides could not be confirmed. All the samples contained a diversity of other phenolic compounds, including catechins and phenolic acids. Most compounds were present in fairly low levels although some phenolic acids were significant contributors to the total levels. Boysenberries contained around 14 compounds in detectable levels (in addition to the anthocyanins), and these appeared to be mainly phenolic acids. Gallic acid was tentatively identified, based on comparisons of retention time and absorption spectra with an authentic standard. Catechin was also likely to be present at very low levels based on comparison with a standard. In general,
individual phenolics were higher in the New Zealand samples than in the Chilean ones.

Ellagic acid was detected (by comparisons with an authentic standard) in all samples, but it was present in minor amounts in the fruit and the standard purity was questionable, so it was not possible to quantify levels accurately. The levels were relatively higher in the concentrate samples, and the New Zealand concentrate sample had 25% more ellagic acid than the Chilean sample (based on peak areas). This difference was similar to that observed for the total phenolics.

4.4 Antioxidant activity assays

4.4.1 ORAC

As would be expected from the differences in total phenolic and anthocyanin contents, the antioxidant activities, as measured by the ORAC assay, were significantly higher in the New Zealand samples than in the corresponding Chilean samples (Table 8). In the case of the fruit samples, the New Zealand sample was 38% higher, and for the concentrates the New Zealand sample was 29% higher. The ORAC values for the berries were significantly higher than that reported by Wada & Ou (2002) of 42.2 µmol Trolox/g FW (equivalent to 4220 µmol Trolox/100 g). Differences could relate to sample preparation, set up of the ORAC assay (large differences are observed between different laboratories), actual differences in fruit composition or other factors.

Table 8: Antioxidant activity of boysenberry samples as measured by the ORAC assay (average of triplicate samples ± standard deviation).

<table>
<thead>
<tr>
<th>Sample description</th>
<th>ORAC value (µmol Trolox/100 g FW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand fruit</td>
<td>19541 ± 546</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>14152 ± 167</td>
</tr>
<tr>
<td>New Zealand juice concentrate</td>
<td>40115 ± 37</td>
</tr>
<tr>
<td>Chilean juice concentrate</td>
<td>30993 ± 3</td>
</tr>
</tbody>
</table>

4.4.2 DPPH assay

This antioxidant activity assay was chosen as it can provide measures of both water and lipid soluble antioxidants. The two different extractions used will extract slightly different components of the fruit (more water-soluble components will be extracted with the 50% methanol solution). Like the ORAC assay, antioxidant activity as measured by the DPPH assay was higher in both New Zealand samples (Table 9). The percentage differences observed were slightly different to those observed for phenolics, anthocyanins or activity as measured by the ORAC assay. These results indicate possible differences in the ratio of individual phenolics and/or the presence of other compounds that affected antioxidant activity as measured...
by this assay. There are no data for comparison in the literature for boisenberries using this assay.

Table 9: Antioxidant activity of boysenberry samples as measured by the DPPH assay (average of triplicate samples ± standard deviation).

<table>
<thead>
<tr>
<th>Sample description</th>
<th>100% MeOH μmol TEAC/100 g FW</th>
<th>50% MeOH μmol TEAC/100 g FW</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Zealand fruit</td>
<td>1257 ± 58</td>
<td>2575 ± 30</td>
</tr>
<tr>
<td>Chilean fruit</td>
<td>992 ± 12</td>
<td>2215 ± 33</td>
</tr>
<tr>
<td>New Zealand juice concentrate</td>
<td>2888 ± 1</td>
<td>7084 ± 35</td>
</tr>
<tr>
<td>Chilean juice concentrate</td>
<td>2628 ± 0</td>
<td>6959 ± 8</td>
</tr>
</tbody>
</table>

5 Conclusion

New Zealand boysenberry fruit and juice concentrate were superior to their Chilean counterparts in virtually all aspects of composition. These are summarised in Table 10. Of particular note were:

- New Zealand boysenberry fruit had a slightly superior appearance, being larger and more uniform in shape and colour than the Chilean sample,
- colour measurements showed New Zealand boysenberry fruit to be more intensely red/purple,
- New Zealand boysenberry fruit had a significantly higher dietary fibre content than the Chilean fruit, although sugar content was relatively similar,
- New Zealand boysenberry fruit was approximately 24% higher in phenolics and the concentrate was approximately 20% higher in phenolics than the Chilean sample,
- total anthocyanins were approximately 23% higher in New Zealand boysenberry fruit and the concentrate was approximately 31% higher in anthocyanins than the Chilean samples. The composition of the anthocyanins was similar with two main anthocyanin peaks and three or four minor peaks detected in all samples,
- HPLC analysis of the other phenolics showed a similar composition in the New Zealand and Chilean samples. However, most phenolics, such as ellagic acid, were higher in the New Zealand samples than in the Chilean ones,
- antioxidant activity, as measured by the ORAC assay, was 38% higher in the New Zealand boysenberry fruit and 29% higher in New Zealand concentrates than in the corresponding Chilean samples. Differences for antioxidant activity, as measured by the DPPH assay, were smaller but New Zealand samples were still superior to their Chilean counterparts.
Table 10: Summary data comparing New Zealand and Chilean boysenberry samples.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>New Zealand fruit</th>
<th>Chilean fruit</th>
<th>New Zealand Concentrate</th>
<th>Chilean Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fruit size (g)</td>
<td>7.39</td>
<td>6.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Seed content per berry (g)</td>
<td>0.55</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dry matter (%)</td>
<td>15.5</td>
<td>14.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>3.52</td>
<td>3.34</td>
<td>3.15</td>
<td>3.20</td>
</tr>
<tr>
<td>Dietary fibre (g/100 g)</td>
<td>5.7</td>
<td>4.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total sugars (g/100 g)</td>
<td>7.4</td>
<td>6.8</td>
<td>38.5</td>
<td>44.7</td>
</tr>
<tr>
<td>Folate (μg/100 g)</td>
<td>37.2</td>
<td>44.1</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Total phenolics (mg GAE/100 g)</td>
<td>541.8</td>
<td>438.0</td>
<td>2544.7</td>
<td>2126.7</td>
</tr>
<tr>
<td>Total anthocyanins (mg/100 g)</td>
<td>195.0</td>
<td>159.1</td>
<td>649.5</td>
<td>493.9</td>
</tr>
<tr>
<td>ORAC assay (μmol Trolox/100 g)</td>
<td>19541</td>
<td>14152</td>
<td>40115</td>
<td>30993</td>
</tr>
<tr>
<td>DPPH – 100% MeOH (umol TEAC/100 g)</td>
<td>1257</td>
<td>992</td>
<td>2888</td>
<td>2628</td>
</tr>
<tr>
<td>DPPH – 50% MeOH (umol TEAC/100 g)</td>
<td>2575</td>
<td>2215</td>
<td>7084</td>
<td>6959</td>
</tr>
</tbody>
</table>

6 References


