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Effect of Cooking on the Soluble and Insoluble Oxalate Content of Some New Zealand Foods

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Oxalates occur as end products of metabolism in a number of plant tissues; some leafy plants and some root crops contain markedly high levels of soluble and insoluble oxalates. When consumed these oxalates can bind calcium and other minerals. Measurement of oxalate content in vegetables commonly consumed in New Zealand shows that cooking reduces the oxalate content of the food by leaching losses into the cooking water. Roots and brassicas grown in New Zealand appear to contain relatively low levels of oxalates. Leafy vegetables such as silverbeet and NZ spinach appear to approach and exceed levels found in rhubarb stalks, although New Zealand silverbeet stems contain lower levels.

Key Words: Oxalic acid; soluble oxalates; insoluble oxalates; vegetables; raw; boiled.

INTRODUCTION

Oxalic acid forms water-soluble salts with Na$^+$, K$^+$ and NH$_4^+$ ions, it also binds with Ca$^{2+}$, Fe$^{2+}$ and Mg$^{2+}$ rendering these minerals unavailable. Oxalates can be found in relatively small amounts in many plants. Oxalate-rich foods are usually minor components in human diets but are sometimes important in seasonal diets in certain areas of the world. Plants such as spinach and beetroot are well known for containing higher concentrations of oxalates than other plants but until recently no attempt has been made to summarize the world literature. The review published by Noonan and Savage (1999) highlighted the lack of data available on the oxalate content of common foods. It also showed that little data are available on the effect of cooking on oxalate content. Almost all high oxalate containing foods are cooked before consumption and much of the available data have been determined on raw foods. In addition, some of the data that are often quoted in the literature have been derived from older analytical techniques. The gas chromatographic technique (Ohkawa, 1985) and HPLC methods (Holloway et al., 1989) have made accurate and reliable determinations of oxalic acid in plant materials possible.

The oxalic acid content is variable within some species; some cultivars of spinach (Universal, Winter Giant) contain 400–600 mg/100 g fresh weight, FW while others range from 700 to 900 mg/100 g FW (Gontzea and Sutzescu, 1968). Oxalic acid...
accumulates in plants especially during dry conditions (Bressani, 1993). A study comparing two cultivars of spinach, Magic (cv. summer) and Lead (cv. autumn), revealed that the summer cultivar contained greater amounts of oxalate (740 mg/100 g FW) than the autumn cultivar (560 mg/100 g FW) (Watanabe et al., 1994).

The distribution of oxalate within plants is also uneven. In general, oxalate content is highest in the leaves, intermediate in the seeds and lowest in the stems (Osweiler et al., 1985; Lilbert and Franceschi, 1987). Reports show that the petiole (stalks) of plants, such as amaranth (Bressani, 1993) spinach and beet (Fassett, 1973; Concon, 1988) contain significantly lower levels of oxalates than the leaves. In the buckwheat family, which includes rhubarb, the content of oxalic acid in leaves has been reported in the past to be greater than in the petioles but the more recent study by Lilbert (1987) shows that the levels are lower in the petioles of rhubarb grown in Sweden. The high toxicity of the leaves of rhubarb are more likely due to toxic anthraquinone derivatives. It should be noted that the leaves of rhubarb are rarely eaten and therefore the oxalate content of the leaf is of no concern in human nutrition. Lilbert (1987) was able to show that the oxalate concentration of the petioles of rhubarb increased as it aged but if the plant was grown under forcing conditions less total oxalate but more water-soluble oxalate accumulates than in field-cultivated rhubarb.

High oxalate levels in tropical plants are of some concern. Taro (Colocasia esculenta) and sweet potato (Ipomoea batatas) were reported to contain 278–574 mg/10 g FW (Holloway et al., 1989) and 470 mg/100 g FW (Mosha et al., 1995), respectively. Total oxalate levels in tropical yam (Dioscorea alata) tubers were reported in the range 486–781 mg/100 g DW, but may be of little nutritional concern since 50–75% of the oxalates were present in the water-soluble form and therefore may leach out during cooking (Wanasundera and Ravindran, 1994). It is important to note, however, that some foods are traditionally baked and this form of cooking gives no opportunity for leaching losses to occur.

In this study, it was proposed to determine the total and soluble oxalate content of some New Zealand grown foods and to investigate the effect of cooking these foods on the final content of the two fractions of oxalate.

MATERIALS AND METHODS

Sample Preparation

Representative samples of fresh vegetables were purchased from three local supermarkets in Christchurch. The vegetables were chopped and peeled and any non-edible portions discarded. The fresh samples were frozen at −180°C and freeze-dried. The normally consumed portions of each food were also cooked by boiling in a small quantity of tap water (100 g wet wt. of food to 100 mL cold tap water) until edible, the cooking water was discarded. The cooking times taken from when the water began to boil were, NZ spinach and spinach 2 min; silverbeet leaves, 6 min; silverbeet stems, rhubarb stalks, broccoli, carrot and parsnip 10 min. The beetroot was pressure cooked for 45 min at 15 psi. The cooked foods were then freeze-dried, ground through a 100 mm mesh and stored in a desiccator.

Dry Matter Determination

Representative samples of fresh raw and cooked foods were dried to constant weight in an oven set at 105°C for 24 h to allow the calculation of oxalic acid content per 100 g of fresh weight.
Soluble Oxalic Acid

One gram samples of finely ground freeze-dried food were weighed into 250 mL beakers and 50 mL distilled water was added. The beakers were placed in a waterbath at 80°C for 15 min. The extract was allowed to cool and then transferred quantitatively to a 100 mL volumetric flask and made up to volume with distilled water (Barnstead Nanopure II). Three extractions were carried out for each food sample.

Total Oxalic Acid

One gram samples of finely ground freeze-dried food were weighed into a 250 mL beaker and 50 mL 2 M HCL was added. The beakers were placed in a waterbath at 80°C for 15 min. The extract was allowed to cool and then transferred quantitatively to a 100 mL volumetric flask and made up to volume with 2 M HCl. Three extractions were carried out for each food sample.

Sample Analysis

The extracts were then centrifuged at 3000 rpm and 10 mL of the supernatant was filtered through a 0.45 mm cellulose acetate membrane (Satorius, Goettingen, Germany). A 5 µL sample was analysed using a Waters Chromatography System, consisting of a Waters 717 plus autosampler, Waters 600-MS Isocratic/Gradient Pump and a Waters UV/VIS detector set at 210 nm. Data capture and processing were carried out using the Millennium (ver 2.15) chromatographic software. The chromatographic separation was carried out using an Aminex Ion exclusion HPX-87H 300 × 7.8 mm analytical column attached to an Aminex Cation-H guard column, using an isocratic elution at 0.5 mL/min with 0.0125 M sulphuric acid (Analar, BDH, UK) as a mobile phase. The analytical column was held at room temperature and the columns were equilibrated at a flow rate of 0.1 mL/min prior to use and in between sample sets. Before use the mobile phase was filtered through a 0.45 µm membrane and degassed using vacuum. The oxalic acid peak was identified by comparison of the retention time to a range of common plant organic acid standards.

Standard Calibration

Two standard curves were prepared in the range 1–20 mg/100 mL; one set of standard solutions were prepared by adding oxalic acid (Analar, BDH, UK) to 100 mL volumetric flasks and making up to volume with distilled water. This set was used to analyse the soluble oxalic acid content of the water extracts. A further set of standard solutions were prepared by diluting the standard oxalic acid to 100 mL with 2.0 M HCl. This set of standards was used to quantify the total oxalic acid content of the samples. All blank and standard solutions were filtered through a 0.45 mm cellulose acetate membrane syringe filter prior to analysis.

Recovery Study

The recovery of oxalic acid from the silverbeet leaf extracts was studied by adding 10 mg of oxalic acid to 1 g samples of dried silverbeet leaves. These samples were extracted using the method for total and soluble oxalic acid and determined using the methods outlined above.
Statistical Analysis

The data are presented as the mean of three determinations ± S.E.

RESULTS AND DISCUSSION

There were differences in the analytical response of the HPLC between the water and the acid extracts. The standard curve prepared using 2.0 M HCl (pH 0.09) always produced a higher response at high values than the curve prepared using distilled water (pH 6.90) so the respective curves were used to calculate the acid and water extracted samples. The $r^2$ of the water prepared curve was 0.986 while the $r^2$ of the acid prepared curve was 0.999.

Recovery of added oxalic acid was studied by adding standard additions of oxalic acid to samples of freeze-dried silverbeet leaves. These samples were extracted using the methods for soluble and total oxalic acid and determined using the methods outlined above. Mean ($\pm$ S.E.) recovery using water extraction was 93.9% ± 1.6, acid extraction of the freeze-dried silverbeet leaves gave a recovery of 98.6% ± 2.3 (Table 1).

A consistent feature of the chromatograms resulting from the acid extraction of the vegetable samples was the appearance of an additional peak at the beginning of the trace. This peak (retention time 8.45 min) was thought to arise from an impurity in the concentrated HCl used to extract the samples and to prepare the acid-extract standard curve. As this peak occurred well before the oxalic acid peak (retention time 9.45 min) and it did not raise the baseline prior to the oxalic acid peak, further investigation did not take place. Holloway et al. (1989) also observed this unknown peak prior to oxalic acid in their chromatograms but they were unable to separate it from the oxalic acid peak using the ion-exclusion column available to them at that time.

Mean values for the total, soluble and insoluble oxalic acid content of the raw and boiled vegetables expressed on a wet wt. basis are shown in Table 2. In almost all foods there was a significant loss of soluble oxalates into the cooking water. For many of the foods there also appeared to be either moderate or small losses of insoluble oxalate during cooking. The oxalate contents of raw spinach and rhubarb were within previously published ranges (Noonan and Savage, 1999) while a lower oxalate content was found in beetroot. Recent reliable data on the oxalate content of other New Zealand grown vegetables studied does not appear to be available in the literature. Between 80 and 90% of the oxalate in New Zealand spinach, rhubarb stalks and

<table>
<thead>
<tr>
<th>Replicate</th>
<th>Water extraction</th>
<th>Acid extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89.6</td>
<td>101.1</td>
</tr>
<tr>
<td>2</td>
<td>95.5</td>
<td>91.8</td>
</tr>
<tr>
<td>3</td>
<td>93.3</td>
<td>99.8</td>
</tr>
<tr>
<td>4</td>
<td>97.1</td>
<td>101.6</td>
</tr>
<tr>
<td>Mean recovery %</td>
<td>93.9</td>
<td>98.6</td>
</tr>
<tr>
<td>S.D.</td>
<td>3.2</td>
<td>4.6</td>
</tr>
<tr>
<td>S.E.</td>
<td>1.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

TABLE 1
Recovery of oxalic acid added to raw silverbeet leaves
silverbeet stems is insoluble oxalate, though the levels in silverbeet stems are much lower. Although New Zealand spinach and rhubarb stalks contain high levels of oxalate it is largely insoluble and may not pose any nutritional problems.

The presence of oxalates in foods has been implicated in reducing the bioavailability of essential minerals such as calcium (Kelsay, 1985). Noonan and Savage (1999) have highlighted the fact that while oxalic acid forms water-soluble salts with Na⁺, K⁺ and NH₄⁺ ions, oxalate also binds with Ca²⁺, Fe²⁺ and Mg²⁺ to form insoluble salts. Although silverbeet, NZ spinach, spinach and rhubarb contain significant amounts of oxalates (Table 2) it is not possible to be sure that it is either already bound to calcium in the food (the insoluble oxalate fraction) or potentially able to bind to calcium in the food (soluble oxalate) because although it is often stated that hypocalcaemia occurs after ingestion of high levels of soluble oxalates (Connor, 1977) there is no clear evidence that oxalates in foods bind to Ca²⁺ preferentially. It is possible that some of the insoluble oxalate fraction may also be bound to the fibre in the food and that some of the soluble oxalate fraction may bound to plant fibres during passage through the digestive tract.

It is interesting to note that silverbeet stems like rhubarb contain significantly lower levels of soluble and insoluble oxalates when compared to the levels in the leaves. This confirms the earlier reports by Fasset (1973) and Concon (1988). The lower oxalate levels in silverbeet stems has led to suggestions that the leaves should be discarded and the stems should be regarded as a delicacy. These results suggest that silverbeet leaves, NZ spinach and spinach will not be good sources of available calcium and iron.

The mean daily intake of oxalate in English diets has been calculated to be 70–150 mg; tea appears to contribute the greatest proportion in these diets; rhubarb, spinach and beet are other common high oxalate-containing foods (Zarembski and Hodgkinson, 1962). Vegetarians who consume greater amounts of vegetables will have a higher

### TABLE 2

Mean oxalate content of some common raw and cooked New Zealand foods (mg/100 g WM) (± s.e.)

<table>
<thead>
<tr>
<th>Foodstuffs</th>
<th>Total oxalate</th>
<th>Soluble oxalate</th>
<th>Insoluble oxalate¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>Cooked</td>
<td>Raw</td>
</tr>
<tr>
<td>Silverbeet² leaves</td>
<td>525.5 (13.0)</td>
<td>291.1 (37.7)</td>
<td>252.3 (1.8)</td>
</tr>
<tr>
<td></td>
<td>Silverbeet stems (Beta vulgaris v. cicla)</td>
<td>(7.4) (22.6)</td>
<td>(1.9) (1.1)</td>
</tr>
<tr>
<td>NZ spinach (Tetragonia expansa)</td>
<td>1764.7 (95.7)</td>
<td>1322.6 (75.3)</td>
<td>364.6 (15.3)</td>
</tr>
<tr>
<td>Spinach (Spinacia oleracea)</td>
<td>329.6 (0.8)</td>
<td>154.8 (1.5)</td>
<td>266.2 (5.1)</td>
</tr>
<tr>
<td>Rhubarb stalks (Rheum rhaponticum)</td>
<td>986.7 (50.0)</td>
<td>756.3 (38.1)</td>
<td>287.3 (6.4)</td>
</tr>
<tr>
<td>Beetroot (Beta vulgaris)</td>
<td>45.6 (0.2)</td>
<td>76.0³ (0.5)</td>
<td>38.6 (0.6)</td>
</tr>
<tr>
<td>Broccoli (Brassica oleracea italica)</td>
<td>16.1 (2.8)</td>
<td>10.1 (1.4)</td>
<td>11.6 (1.2)</td>
</tr>
<tr>
<td>Carrot (Daucus carota)</td>
<td>35.6 (6.6)</td>
<td>32.3 (2.7)</td>
<td>22.6 (0.8)</td>
</tr>
<tr>
<td>Parsnip (Peucedanum sativum)</td>
<td>12.0 (0.8)</td>
<td>10.5 (0.8)</td>
<td>9.2 (0.5)</td>
</tr>
</tbody>
</table>

¹ Insoluble oxalate = total oxalate – soluble oxalate (Holloway et al., 1989).
² Also known as Swiss chard.
³ Pressure cooked for 45 min at 15 psi.
intake of oxalates, which may reduce calcium availability. This may be more important for women, who require greater amounts of calcium in the diet. In humans, diets low in calcium and high in oxalates are not recommended but the occasional consumption of high oxalate foods as part of a balanced diet does not appear to pose any particular problem.

REFERENCES


