



Nutritional properties of commercially grown native Australian fruits: Lipophilic antioxidants and minerals

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ABSTRACT

A high level of antioxidant activity of lipophilic fractions obtained from commercially grown native Australian fruits, as evaluated in the oxygen radical absorbance capacity assay for lipophilic antioxidants (ORAC-L), was identified for the first time. The level of contribution of lipophilic fractions varied from 5.8% (quandong) to 30.7% (riberry) of the total oxygen radical scavenging capacity (ORAC-T). Vitamin E components – α -tocopherol, γ -tocopherol and δ -tocopherol and lutein – were identified as the main sources of this activity. Among the evaluated sources, Kakadu plum emerges as a fruit with unique nutritional qualities: it exhibited a superior ORAC-T value (430.0 μ M trolox eq/g fresh weight, TEq/g FW) with 26.7% contribution of the lipophilic fraction. The major compounds of Kakadu plum's lipophilic fraction were α -tocopherol (1.022 \pm 0.1 mg/100 g, FW), lutein (0.26 \pm 0.01 mg/100 g FW) and chlorophyll a and b (2.72 \pm 0.1 and 0.54 \pm 0.1 mg/100 g FW, respectively). With regards to mineral content, the levels of major minerals, such as potassium, phosphorus, calcium, magnesium, and trace elements such as iron, zinc, manganese, selenium and copper as well as cobalt, nickel, aluminium and lead in native Australian fruits are similar to the levels of these elements in a range of vegetables and fruits produced and consumed elsewhere.

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1. Introduction

The variable geological conditions and climate of Australia lead to the establishment of regions with contrasting characteristics: the arid and dry regions in the centre of the country, the high-rainfall tropical regions of the north and the sub-tropical temperate regions in the east and south. This variation resulted in a unique biodiversity, with approximately 25,000 endemic plant species (Michael, 2000). The rich Australian flora, although served as a food and medicine to the local Aboriginal population for thousands of years, remains largely unexplored. Over the last few decades a number of studies on Australian edible and medicinal plants have been published. For example, Cribb and Cribb (1981) described over 200 traditional plants with medicinal uses. Low (1991) complemented this study with detailed information on over 150 edible plant species from inland areas, the tropics and south eastern regions of Australia, based on 19th century texts on traditional plant uses and the author's own exploratory testing. Most of the edible plant species of Australia remain unknown to the wider community, both in Australia and overseas.

In recent year a search for new edible plant species with health-enhancing properties prompted interest in indigenous fruits (Puente,

Pinto-Munoz, Castro, & Cortes, 2010; Kong et al., 2010) and native Australian fruits should be considered as a valuable source. The number of native fruiting plants growing in tropical forests of Australia that have the potential to be developed into exotic fruits for consumers around the world exceeds 2000. The majority of these plants exist in tropical Queensland, with 500 species extending into New South Wales, 500 into Northern Territory and up to 300 to Western Australia (Cooper, 2004). Selected native fruits entered commercial production in the 1990s, when Davidson's plum, muntries, ribberries, quandong, Illawarra plum and Kakadu Plum were chosen for a massive production, with the first four species receiving the status of "most commercially acceptable" (Graham & Hart, 1997). Two additional species, lemon aspen and native citrus, joined the list of commercially used native Australian fruits shortly after (Robins, 2004). The number of commercially grown species continuously increases and research towards the development of new and improved cultivars through selection from the wild and through traditional breeding has been undertaken. Products containing native fruits, herbs and spices are available locally in chain supermarkets, in delicatessens and specialty shops. Originally sold as tourist souvenirs, they now enter and enrich the everyday diets of Australian consumers.

Research into understanding the nutritional values of native Australian fruits has been initiated by Brand and co-workers, who evaluated selected foods for the presence of protein, fat, carbohydrate, fiber, ash, energy, major minerals and vitamins (Brand et al., 1983; Brand-Miller, James, & Maggiore, 1993). The findings suggested similar

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composition to common western foods in the same categories. To date, information on the presence of phytochemicals associated with health benefits of Australian native fruits has been missing. Recently, major phenolic compounds, organic acids, vitamin C levels, and antioxidant capacity of hydrophilic extracts obtained from commercially grown native Australian fruits have been reported (Konczak, Zabarar, Dunstan, & Aguas, 2010). This study evaluates for the first time the oxygen radical absorbance capacity of lipophilic (ORAC-L) extracts of the same fruits, their contribution to the total oxygen radical absorbance capacity (ORAC-T) and possible sources of this capacity.

Beside phytochemicals, minerals are essential regulators of physiological processes in humans. More than one-third of all human proteins require metal ions to function, and lacking these ions may have a significant impact on human health (Bertini, Sigel, & Sigel, 2001). Fruits are important contributors of minerals in the diet and individual fruits may have a very different mineral content. The content varies according to the plant source, its maturity, soil conditions, weather and agricultural practices (Mirdehghan & Rahemi, 2007). To ensure the presence of minerals and trace elements in the diet at the required level, their amounts in plants need to be monitored. This is especially important in case of the redox-active elements (iron, copper, manganese). These elements, when present at higher levels than required, may exert toxic effects through generation of free radicals, which subsequently damage organic molecules (Kozłowski et al., 2009). Here we report for the first time on the levels of biologically essential minerals in commercially grown native Australian fruits: calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P) and sodium (Na), eight essential or potentially essential trace elements: cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) and three toxic elements: aluminium (Al), cadmium (Cd) and lead (Pb), comparing these data with the levels of micronutrients in fruits and/or vegetables consumed elsewhere.

It needs to be mentioned that the results presented in this study originate from a single lot of samples, produced during one vegetative season, provided by the native food industry and represent plant sources selected by the industry for a commercial production. Variations arising from the genetic diversity and the environmental factors were not evaluated.

2. Materials and methods

2.1. Plant material

Commercially produced samples of Australian native fruits were provided by the Australian Native Food Industry Ltd. (ANFIL). Australian desert lime (*Citrus glauca* (Lindl.) Burkill; *Rutaceae*) was obtained from the Australian Desert Limes company (Queensland, Australia). Kakadu plum (*Terminalia ferdinandiana* Excell, *Combretaceae*), finger lime (*Citrus australasica* F. Muell.; *Rutaceae*), green and pink, and lemon aspen (*Acronychia acidula* F. Muell., *Rutaceae*) were obtained from the Australian Produce Company Pty Ltd. (Queensland, Australia). Davidson's plum (*Davidsonia pruriens* F. Muell., *Cunoniaceae*) was provided by the Australian Rainforest Products (NSW, Australia). Dry sample of quandong (*Santalum acuminatum*, A.D.C., *Santalaceae*) was supplied by the Australian Native Food "Outback Pride" and frozen sample was purchased from the Tanamera Bush Foods, South Australia, Australia. Riberry (*Syzygium luehmannii* (F. Muell.) L.A.S. Johnson, *Myrtaceae*) was supplied by the Woolgoolga Rainforest Products, NSW. The frozen samples were freeze-dried on arrival. In case of plums, the fruits were defrosted to allow stone removal, immediately frozen using liquid nitrogen and freeze-dried. The freeze-dried samples were finely ground and placed in air-tight containers. Subsequently they were stored at -20°C until analyzed. In case of finger lime and Australian desert lime the peel was included in analysis.

2.2. Reagents and standards

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich (Sydney, Australia) and were of analytical or HPLC grade. Deionized water was used throughout.

2.3. Extraction of lipophilic compounds

Two hundred mg of the pulverized samples were placed in test tubes and extracted with 10 ml of cold acetone. The samples were shaken for 20 min, centrifuged (10 min, 2500 rpm; Jouan C3i Multifunction Centrifuge, rotor T40), and the supernatants were collected. The pellet was re-extracted two more times. Freshly prepared aliquots of the combined supernatants (30 ml) were filtered with 13 mm \times 0.45 μm polytetrafluoroethylene (PTFE) filter (Millipore, Australia) and immediately analyzed. The extraction was carried out in triplicate for each sample.

2.4. Oxygen radical absorbance capacity for lipophilic compounds (ORAC-L) and total oxygen radical absorbance capacity (ORAC-T)

All the reagents were prepared using 75 mM phosphate buffer (pH 7.4) as previously described (Konczak et al., 2010). According to Huang, Ou, Hampsch-Woodill, Flanagan, and Deemer (2002), samples and Trolox standards were prepared in 7% (w/v) randomly methylated β -cyclodextrin (RMCD) solvent to ensure solubility of the lipophilic antioxidant in the reaction mixture. The 7% RMCD solvent was prepared in a 50% acetone-water mixture (v/v) and was shaken for 1 h at room temperature on an orbital shaker at 200 rpm prior to use. The sample solution was ready for analysis after further dilution with 7% RMCD. The measurements were conducted as described previously for the ORAC-H method (Konczak et al., 2010). The results are expressed as μM Trolox equivalents per 100 g fresh weight (μM TEq/g FW). The total oxygen radical absorbance capacity (ORAC-T) was calculated as the sum of the average values for ORAC-H and ORAC-L and presented as μM TEq/g FW according to Wu et al. (2004).

2.5. Analysis of lipophilic compounds by HPLC-DAD and HPLC-FD

Quantification and identification of lipophilic compounds were carried out using a HPLC system that consisted of two LC-10 AD pumps, SPD-M10A diode array detector, RF-10AXL fluorescence detector, CTO-10AS column oven, DGU-12A degasser, SIL-10 AD auto-injector and SCL-10A system controller (Shimadzu Co., Kyoto, Japan). The mobile phase consisted of methanol, methyl tert-butyl ether and water in proportions: 81:15:4 (Solvent A) and 6:90:4 (Solvent B). The compounds were detected with a help of YMC Carotenoid (C30, 4.6 \times 520mm, 5 μm) column. Detection of tocopherols was carried out using a fluorescence detector RF-10AXL. The detection of all other compounds was carried out using a diode array SPD-M10A detector at 445 nm with flow rate of 1.5 ml/min. The elution profile was 0–100% B over 15 min, followed by 10 min of isocratic run of 100% B. Calibration curves were prepared for eight standards: α -tocopherol, δ -tocopherol, γ -tocopherol, β -carotene, chlorophyll a and chlorophyll b, lycopene and lutein. The solutions of tocopherols and β -carotene standards were prepared in acetone; lutein, chlorophyll a and b were dissolved in solvent A (81% MeOH, 15% MTBE, 4% H_2O), and lycopene was dissolved in chloroform. Lipophilic compounds in native fruits were identified by comparing the retention time and characteristic UV-VIS spectra with these of standards and confirmed by co-chromatography with a standard. The results, based on three independent measurements, were quantified using calibration curves and calculated as milligrams per 100 g fresh weight (mg/100 g FW). The limits of detection were 15.0 $\mu\text{g}/\text{ml}$ for α -tocopherol, δ -tocopherol and lycopene, and 3.9 $\mu\text{g}/\text{ml}$ for β -carotene, lutein, chlorophyll a, chlorophyll b and γ -tocopherol.

2.6. Analysis of minerals

The analysis has been conducted by the National Association of Testing Authorities accredited laboratory, as follows: dried samples (0.5 g) were accurately weighed into 50 mL centrifuge tubes in duplicate. Nitric acid (4 ml) (Merck, AnalR, sub-boiling quartz still redistilled) was added to each sample. The tubes were placed in a water bath (90 °C) with the lids placed on top. The samples were allowed to react for 12 h. Once digested, the lids were removed and the samples evaporated to near dryness. A further volume of nitric acid (2 ml) was added and the resulting solution was allowed to evaporate to approximately 1 ml. The temperature was reduced (50 °C) and the samples were treated with hydrogen peroxide (1 ml) (Univar 30%). Once the reaction had subsided, the samples were cooled to room temperature and were made up to 20 g with milliQ water, and the lids were replaced. Certified reference materials (CRMs), peach leaves and apple leaves (National Institute of Standards and Technology) were also included as samples during the digest. The CRMs were weighed (0.5 g) in triplicate and underwent the same dissolution procedure as the samples. Three reagent blanks were also included in the procedure. The elemental concentrations of the solutions were then determined against Multi Element standards using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thermo Scientific iCAP 6500) and inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500CS). A multi-element standard was run every 12 samples to monitor instrumental drift. The quality of the data was assessed using the certified reference materials.

3. Results and discussion

3.1. Antioxidant capacity of lipophilic fraction

Both hydrophilic and lipophilic phytochemicals can effectively scavenge free radicals and are essential in the prevention of oxidative stress. The level of lipophilic antioxidants in a protein free human plasma reaches 33.1 ± 1.5 to $38.2 \pm 1.9\%$ of the total antioxidant capacity (Prior et al., 2003). Therefore it is essential that food sources rich in lipophilic antioxidants are identified. Commonly consumed fruits are poor sources of lipophilic antioxidants and subsequently, the contribution of lipophilic fraction towards the total antioxidant capacity (ORAC-T) is low. For example, in blueberry and plum this contribution is 0.5%, apricot – 0.6%, apple – 0.8%, blackberry – 1.9%, kiwi and peach – 2.7%, pear – 2.9%, pineapple – 3.1%, banana – 7.5% (Wu et al., 2004; USDA database on Oxygen Radical Absorbance Capacity (ORAC) of selected foods, 2007). The contribution of lipophilic fraction towards the ORAC-T values of commercially grown native Australian fruits evaluated in this study varied from 5.8% (quandong) to 30.75% (riberry, Table 1). In this aspect native Australian fruits differ from the common fruits listed above. Kakadu plum is an important fruit for the Australian native food industry with the largest volumes of native fruit sold, reaching approximately 20000 kg per year. In this evaluation Kakadu plum displayed an outstanding ORAC-T value of 430.04 $\mu\text{M TEq/g FW}$, which is 6.6-fold higher than that of a blueberry (65.5 $\mu\text{M TEq/g FW}$, USDA database on Oxygen Radical Absorbance Capacity (ORAC) of selected foods, 2007), a fruit recognised for its high antioxidant capacity. The contribution of the lipophilic fraction towards ORAC-T in Kakadu plum was 26.66% (Table 1), which is comparable to avocado (28.6%, Wu et al., 2004). Similarly, high levels of oxygen radical scavenging capacity of lipophilic fractions were detected for riberry (30.7%), lemon aspen (28.8%) and Australian citrus (20.5–26.7%). Quandong was the fruit that exhibited the highest ORAC-T values; however, in this case the contribution of lipophilic compounds was 5.8% (Table 1). Quandong is sold currently in Australia predominantly in a dry form. A commercial sample of dry quandong, supplied by the industry, has also been evaluated. The total oxygen radical scavenging capacity of the dry quandong reached $2027.97 \pm 275 \mu\text{M TEq/g DW}$, which was 11.1% lower than that of a fresh quandong ($2281.41 \pm 221 \mu\text{M TEq/g DW}$). The ORAC-L values of

Table 1

Oxygen radical absorbance capacity of selected commercially grown native Australian fruits.

Fruit	ORAC-T ($\mu\text{M TEq/g FW}$)	ORAC-L ($\mu\text{M TEq/g FW}$)	ORAC-L (%)	ORAC-H (%) ^a
Kakadu plum ^b	430.04	114.64 \pm 13.89	26.66	73.34
Australian desert lime	56.78	11.90 \pm 0.17	20.96	79.04
Lemon aspen	184.78	53.29 \pm 0.50	28.84	71.16
Davidson's plum ^b	100.9	17.80 \pm 0.17	17.64	82.36
Finger lime (green)	57.81	11.86 \pm 1.25	20.51	79.49
Finger lime (pink)	88.82	23.73 \pm 0.75	26.72	73.28
Riberry	72.04	22.15 \pm 0.86	30.75	69.25
Quandong	531.73	30.77 \pm 0.30	5.79	94.21

Results are presented as means \pm standard deviation ($n=3$). ORAC-T: total oxygen radical absorbance capacity; $\mu\text{M TEq/g FW}$: micromole Trolox equivalent/g fresh weight; ORAC-L: oxygen radical absorbance capacity – lipophilic compounds; ORAC-H: oxygen radical absorbance capacity – hydrophilic compounds.

^a For ORAC-H values refer to: Food Chemistry (2010), 123, 1048–1054.

^b The weight of stone excluded.

the fresh and dry quandong were 132.02 ± 1.3 and $39.98 \pm 1.0 \mu\text{M TEq/g DW}$, respectively. This result indicates significant losses of lipophilic antioxidants in quandong during the commercial drying process.

3.2. Lipophilic phytochemicals

The main lipophilic phytochemicals detected with the help of a high performance liquid chromatography were components of vitamin E: α -tocopherol, γ -tocopherol and δ -tocopherol, and lutein. Chlorophylls were detected in Kakadu plum, Davidson's plum and Australian citrus (Table 2). Kakadu plum contained $1.041 \pm 0.118 \text{ mg/100 g FW}$ of vitamin E with α -tocopherol contributing 98.2%. Relatively high levels of total fat in Kakadu plum were reported earlier by Brand-Miller et al. (1993) (0.5 mg/100 g FW), with a high variability among samples collected from various sides. Avocado is among the richest sources of vitamin E with α -tocopherol as the main component. The levels of vitamin E in Australian grown Hass avocado varied from 1398 to 2646 $\mu\text{g/100 g FW}$ and the level of α -tocopherol from 1197 to 2151 $\mu\text{g/100 g FW}$ (Zabaras & Konczak, 2010). Similarly, the level of α -tocopherol in Californian grown Hass avocado varied from 1627 to 2757 $\mu\text{g/100 g FW}$, with higher levels detected in fruit harvested later in the season (Lu et al., 2009). The level of vitamin E in Kakadu plum equals approximately 50% of that in avocado. High level of vitamin E, combined with the high ORAC-T values and exceptionally high level of vitamin C reported previously (Konczak et al., 2010), represents a valuable characteristics of Kakadu plum from the nutritional point of view.

α -Tocopherol was the main component of vitamin E mixtures of riberry (98.7%), lemon aspen (96.6%) and quandong (90.4%). However, the composition of tocopherol mixture in Davidson's plums differed to all other fruits, with 44.6% of α -tocopherol, 21.7% of γ -tocopherol and 32.5% of δ -tocopherol. δ -Tocopherol was also present in quandong (Table 2). The levels of vitamin E components in Australian citrus varied from 2.4 to 0.5 mg/100 g FW, with the highest levels in pink finger lime. These levels were higher than reported for lemon (0.15 mg/100 g FW of edible portion, 0.25 mg/100 g FW of peels) and lime (0.22 mg/100 g FW of edible portion) (USDA National Nutrient Database for Standard Reference, Release 23, 2010).

Vitamin E is one of the most important lipid-soluble antioxidants that protect human cells against lipid peroxidation. In plant cells, the function of vitamin E components is the protection against photo-inhibition and photooxidative stress (Havaux, Eymery, Porfirova, Rey, & Dörmann, 2005). In comparison to other countries, due to its location in the Southern Hemisphere where the stratospheric ozone is depleted, Australia has higher level of solar UV radiation. It can be speculated that ongoing exposure of native Australian plants to this environment could positively affect the levels of accumulation of phytochemicals, such as vitamin E, protecting plant cell from damaging UV-B rays.

Table 2
Lipophilic phytochemicals in commercially grown native Australian fruits.

Fruit	Vitamin E components (mg/100 g FW)			Vitamin E (mg/100 g FW)	Lutein (mg/100 g FW)	Chlorophyll a (mg/100 g FW)	Chlorophyll b (mg/100 g FW)
	α -Tocopherol	γ -Tocopherol	δ -Tocopherol				
Kakadu plum ^a	1.022 ± 0.107	0.021 ± 0.009	ND	1.041 ± 0.118	0.260 ± 0.014	2.724 ± 0.08	0.536 ± 0.134
Australian desert lime	0.701 ± 0.177	0.081 ± 0.017	ND	0.783 ± 0.194	0.295 ± 0.013	T	1.350 ± 0.044
Lemon aspen	0.282 ± 0.047	0.010 ± 0.003	ND	0.292 ± 0.051	ND	ND	ND
Davidson's plum ^a	0.040 ± 0.003	0.030 ± 0.001	0.020 ± 0.002	0.092 ± 0.007	0.092 ± 0.009	ND	0.157 ± 0.012
Finger Lime (green)	0.517 ± 0.033	0.004 ± 0.0004	ND	0.521 ± 0.033	0.401 ± 0.027	T	T
Finger Lime (pink)	2.335 ± 0.233	0.025 ± 0.002	ND	2.360 ± 0.235	0.139 ± 0.011	T	T
Riberry	0.229 ± 0.044	0.001 ± 0.0005	ND	0.230 ± 0.040	ND	ND	ND
Quandong	1.165 ± 0.078	0.086 ± 0.005	0.038 ± 0.005	1.289 ± 0.082	ND	ND	ND

Results are presented as means ± standard deviation ($n = 3$). ND, not detected. T-traces (peak area less than 3% of the total peak area).

^a Weight of the stone excluded.

Lutein, a pigment which improves visual function and symptoms in atrophic age-related macular degeneration (ARMD) (Richer et al., 2004), was detected in the Kakadu plum, Davidson's plum and Australian limes (Table 2). The level of lutein in Kakadu plum was similar to that in kiwi fruit (0.259–0.316 mg/100 g FW) (Cano, 1991) and 5- to 2.5-fold that of acerola fruit (De Rosso & Mercadante, 2005). The level of lutein in Davidson's plum was equal to that in banana (0.084 mg/100 g FW) and approximately 2.5-fold of that of apple (0.029 mg/100 g FW) (USDA National Nutrient Database for Standard Reference, Release 23, 2010). Australian desert lime and finger limes (peels included) contained higher levels of lutein than lemon and grapefruit juice (approximately 0.010 mg/100 g FW) (USDA National Nutrient Database for Standard Reference, Release 23, 2010).

Chlorophylls were identified in green-coloured Kakadu plum (Table 2). Traces of chlorophyll b were also found in Davidson's plum, which however may suggest that this anthocyanin-rich fruit was harvested before reaching its full maturity. Chlorophyll b was also present in Australian citrus.

The extracts were analyzed for the presence of lycopene and β -carotene; however, these compounds were not detected in the evaluated samples (data not presented).

The correlation coefficient between the total level of identified lipophilic compounds and the ORAC-L activity indicates a low level positive correlation ($R^2 = 0.3637$). This study, aimed at identification for the first time of the major lipophilic antioxidants in commercially grown native Australian fruits, indicates that the fruits represent a valuable source of lipophilic antioxidants and further studies in depth towards complete identification of these phytochemicals are warranted.

3.3. Mineral composition

The mineral composition of commercially grown native Australian fruits evaluated in this study is presented in Table 3. Potassium (K) is a major mineral, required by humans at level higher than 100 mg/day (Ozcan, 2004). Quandong contained more potassium (K) per 100 g dry weight than any other plant source evaluated in this study. This level is comparable to K level in turnip, artichoke and carrot consumed in Finland, and higher than K level in any Finnish fruit (Ekholm et al., 2007) as well as

UK (510–2740 mg/100 g DW), German (910–1740 mg/100 g DW) and Mexican (710–2310 mg/g DW) fruits: apple, avocado, lime, mango, orange, papaya and pineapple (Sanchez-Castillo et al., 1998). The levels of K in other Australian fruits evaluated in this study were comparable to these in European fruits and vegetables (Ekholm et al., 2007). Quandong also contained the highest level of sodium (Na, Table 3). This fruit, being a semi-parasite plant, is one of a very few species successfully growing in the areas of a high soil salinity in the arid and semi-arid regions of Australia, and relies on water supply by the host plant. This characteristic of quandong explains the high content of sodium.

The majority of Australian fruits contained from 52.5 to 166.9 mg/100 g DW of phosphate (P) and in this respect were comparable to the fruits from UK (40–150 mg/100 g DW) and Mexico (60–190 mg/100 g DW) (Sanchez-Castillo et al., 1998). The content of P in fruits consumed in Finland was reported to vary from 30 to 360 mg/100 g DW (Ekholm et al., 2007).

Ca, Zn and Mg are required as cofactors in enzymatic processes that represent an integral part of the structure of DNA self-repair system. Ca is required for chromosome segregation, Zn – for DNA synthesis and repair and Mg – for DNA synthesis and chromosome segregation (Fenech, 2005). Australian citrus were the richest sources of Ca (above 330 mg/100 g DW), closely followed by riberry and Kakadu plum (307.7 and 282.4 mg/100 g DW, respectively). These fruits contained similar levels of Ca as the European red currant (Ekholm et al., 2007). The Ca content in the remaining Australian fruits was above 150 mg/g DW and was comparable to that in European berries and vegetables such as cauliflower, broccoli and onion (Ekholm et al., 2007).

With regards to Zn content, quandong and lemon aspen contained approximately twice as much Zn as raspberry (2.0 mg/100 g DW), identified as the richest source of Zn among berries grown in Finland (Ekholm et al., 2007). All other fruits contained similar levels of Zn to the European fruits (Ekholm et al., 2007).

Iron (Fe), a physiologically essential trace element, functions in the hemoglobin in red blood cells, which transports oxygen from the lungs to the body's tissues, including the muscles and the brain. The highest levels of Fe (above 10 mg/100 g DW) were present in lemon aspen and quandong (Table 3). All other samples contained from 1.24 to 7.29 mg/100 g DW and in this respect were comparable to fruits

Table 3
Mineral element contents (mg/100 g DW) of selected native Australian fruits.

Fruit	Fe	Cu	Mn	Zn	Ca	Mg	K	P	Se	Mo	Ni	Cd	Pb	Al	Co	Na
Australian desert lime	4.740	0.641	0.877	1.060	384.2	94.5	1287.8	127.8	<0.001	0.0077	0.048	0.0055	0.004	3.875	0.004	2.2
Kakadu plum	3.990	0.303	3.500	0.574	282.4	203.8	1905.5	52.45	<0.001	0.0185	0.036	0.010	0.007	0.521	0.005	10.4
Lemon aspen	13.25	0.834	10.02	3.925	133.3	147.6	1512.9	129.0	<0.001	0.0128	0.443	0.0435	0.008	2.670	0.008	45.0
Davidson's plum	1.240	0.638	19.55	0.426	217.3	138.1	1465.5	94.45	<0.001	0.0109	0.0160	0.0085	0.004	22.80	0.003	1.7
Quandong	16.55	0.100	0.288	4.240	133.3	217.9	3456.2	96.90	<0.001	0.0556	0.0153	0.0315	0.023	4.935	0.002	306.0
Riberry	4.320	1.135	22.75	1.315	307.7	189.0	1715.7	118.8	<0.001	0.0107	0.128	0.0245	0.208	1.665	0.008	47.1
Finger lime (green)	7.290	0.715	0.450	0.848	352.7	139.5	1459.6	166.9	<0.001	0.0104	0.0349	0.005	0.004	0.405	0.002	11.1
Finger lime (pink)	3.670	1.31	0.400	0.780	334.1	111.1	1242.6	141.7	<0.001	0.0083	0.0563	0.004	0.004	0.644	0.003	8.7

Results are based on three independent evaluations ($n = 3$).

and vegetables consumed in Finland (Ekholm et al., 2007) and richer in Fe than selected fruits consumed in UK (0.4–4.4 mg/100 g DW) and Mexico (1.1–4.1 mg/100 g DW) (Sanchez-Castillo et al., 1998).

The levels of Mg in Australian fruits were within the range of 94.5–217.9 mg/100 g DW (Table 1). These levels were similar to or slightly higher than those in berries consumed in Finland (strawberry, blackcurrant, redcurrant and raspberry, 100–160 mg/100 g DW) and within the same range as Finnish vegetables (80–265 mg/100 g DW) (Ekholm et al., 2007). Selected fruits evaluated in Germany contained from 10 to 330 mg/100 g DW of Mg (Sanchez-Castillo et al., 1998). Lower levels of Mg were reported for fruits consumed in UK (20–120 mg/100 g DW) and Mexico (30–170 mg/100 g DW) (Sanchez-Castillo et al., 1998).

Riberry, finger limes and lemon aspen contained the highest levels of copper (Cu) which were approximately twice the level of Cu in European fruits and vegetables with the exception of European squash (0.9 mg/100 g DW), celery root (1.2 mg/100 g DW) and artichoke (1.0 mg/100 g DW) (Ekholm et al., 2007).

Relatively high level of Mn (10.0–22.75 mg/100 g DW) was found in the fruits of Davidson's plums, riberry and lemon aspen (Table 3). Similar Mn levels were reported for bilberry, lingonberry and cranberry consumed in Finland (Ekholm et al., 2007). Other Australian fruits contained similar levels of Mn to those in other fruits consumed in Finland (Ekholm et al., 2007).

Co and Ni are required by humans in minute amounts and are toxic at high levels. Australian fruits contained from 0.0016 (green finger lime) to 0.0084 mg/100 g DW (riberry, Table 3) of cobalt. These levels were comparable to the Co levels in fruits consumed in Finland (0.002 to 0.011 mg/100 g DW) (Ekholm et al., 2007). The levels of Ni in Australian fruits varied from 0.0153 mg/100 g DW (quandong) to 0.0563 mg/100 g DW (pink finger lime) with the exception of lemon aspen that contained a higher level of 0.443 mg/100 g DW. The higher level of Ni in lemon aspen might be associated with the laterite deposits of Ni existing in areas of Queensland and NSW (Australian minerals, 2010). In fruits consumed in Finland the level of Ni varied from 0.007 mg/100 g DW (apple) to 0.088 mg/100 g DW (raspberry) (Ekholm et al., 2007) which indicates that, with the exception of lemon aspen, the levels of Ni in Australian fruits were within the same range as the levels of Ni in fruits consumed in Finland.

Lead (Pb) is best known for its toxicological properties. Australian native fruits contained from 0.004 mg/100 g DW (green finger lime) to 0.208 mg/100 g DW (riberry) of lead. Lower levels of Pb were reported for vegetables consumed in Finland: from 0.002 (tomato) to 0.036 mg/100 g DW (radish) and fruits: from 0.005 mg/100 g DW (strawberry) to 0.016 mg/100 g DW (cranberry) (Ekholm et al., 2007). In order to compare our results with these for Pb level in Mexican fruits, the levels of Pb in Australian native fruits were recalculated to $\mu\text{g}/100\text{ g FW}$ and the following values were obtained: Australian desert lime: 0.910; Kakadu plum: 0.919, lemon aspen: 1.252; Davidson's plum: 0.296, quandong: 5.408; green finger lime: 0.846; pink finger lime: 0.827 and riberry: 18.346 $\mu\text{g}/100\text{ g FW}$. In Mexican fruits the levels of Pb varied from 0 to 243 $\mu\text{g}/100\text{ g FW}$, with majority of fruits containing from 20 to 50 $\mu\text{g}/100\text{ g FW}$ (Sanchez-Castillo et al., 1998). This indicates that the levels of Pb in Australian fruits are higher than Pb levels in fruits consumed in Finland but lower than Pb levels in Mexican fruits.

With the exception of Davidson's plum and quandong, the levels of Al in Australian fruits were comparable to and slightly higher than these in Finnish fruits. The level of Al in Davidson's plum (22.8 mg/100 g DW) was higher than in other fruits grown in Australia and higher than in European fruits, but only half of that in vegetables capsicum and paprika produced in Turkey (Ozcan, 2004).

4. Conclusions

Composition of selected lipophilic phytochemicals and their contribution towards the total oxygen radical absorbance capacity of exotic Australian fruits were evaluated for the first time. Vitamin E

components were identified in all evaluated samples. Lutein was identified in Australian citrus, Kakadu plum and Davidson's plum. Lycopene and β -carotene were not detected. The levels of major minerals, such as potassium, phosphorus, calcium, magnesium, and trace elements such as iron, zinc, manganese, selenium and copper as well as cobalt, nickel, aluminium and lead in native Australian fruits are similar to the levels of these elements in a range of vegetables and fruits produced and consumed in Europe and Mexico.

References

- Australian minerals (2010). http://www.australianminerals.gov.au/aimr/commodity/nickel_09.jsp Retrieved February 12, 2010.
- Bertini, I., Sigel, A., & Sigel, H. (2001). *Handbook of metalloproteins*. New York: MarcelDekker Inc.
- Brand, J. C., Rae, C., McDonnell, J., Lee, A., Cherikoff, V., & Truswell, A. S. (1983). The nutritional composition of Australian Aboriginal bushfoods. *Food Technology in Australia*, 35, 293–298.
- Brand-Miller, J., James, K. W., & Maggiore, P. M. A. (1993). *Tables of composition of Australian Aboriginal foods*. Aboriginal Studies Press.
- Cano, M. P. (1991). HPLC separation of chlorophyll and carotenoid pigments of four kiwi fruit cultivars. *Journal of Agricultural and Food Chemistry*, 39, 1786–1791.
- Cooper, W. (2004). *Fruits of the Australian tropical forest*. Melbourne, Victoria, Australia: Nokomis Editions Pty Ltd.
- Cribb, A. B., & Cribb, J. W. (1981). *Wild medicine in Australia*. Sydney, NSW, Australia: Collins.
- De Rosso, V. V., & Mercadante, A. Z. (2005). Carotenoid composition of two Brazilian genotypes of acerola (*Malpighia punicifolia* L.) from two harvests. *Food Research International*, 38, 1073–1077.
- Ekholm, P., Reinivuo, H., Mattila, P., Pakkala, H., Koponen, J., Happonen, A., et al. (2007). Changes in the mineral and trace element content of cereals, fruits and vegetables in Finland. *Journal of Food Composition and Analysis*, 20, 487–495.
- Fenech, M. (2005). The genome health clinic and genome health nutrigenomics concepts: Diagnosis and nutritional treatment of genome and epigenome damage on an individual basis. *Mutagenesis*, 20, 255–269.
- Graham, C., & Hart, D. (1997). *Bushfoods*. In K. W. Hyde (Ed.), *The new rural industries. A handbook for farmers and investors* (pp. 225–234). Barton, ACT, Australia: Rural Industries Research & Development Corporation.
- Havaux, M., Eymery, F., Porfirova, S., Rey, P., & Dörmann, P. (2005). Vitamin E protects against photoinhibition and photooxidative stress in *Arabidopsis thaliana*. *The Plant Cell*, 17, 3451–3469.
- Huang, D., Ou, B., Hampsch-Woodill, M., Flanagan, J. A., & Deemer, E. K. (2002). Development and validation of oxygen radical absorbance capacity assay for lipophilic antioxidants using randomly methylated β -cyclodextrin as the solubility enhancer. *Journal of Agricultural and Food Chemistry*, 50, 1815–1821.
- Konczak, I., Zabarás, D., Dunstan, M., & Aguas, P. (2010). Antioxidant capacity and phenolic compounds in commercially grown native Australian fruits. *Food Chemistry*, 123, 1048–1054.
- Kong, K. W., Chew, L. Y., Prasad, K. N., Lau, C. Y., Ismail, A., Sun, J., et al. (2010). Nutritional constituents and antioxidant properties of indigenous kemayau (*Dacryodes rostrata* (Blume) H. J. Lam) fruits. *Food Research International*, doi:10.1016/j.foodres.2010.10.039.
- Kozłowski, H., Janicka-Klos, A., Brasun, J., Gaggelli, E., Valensin, D., & Valensin, G. (2009). Copper, iron, and zinc ions homeostasis and their role in neurodegenerative disorders (metal uptake, transport, distribution and regulation). *Coordination Chemistry Reviews*, 253(21–22), 2665–2685.
- Low, T. (1991). *Wild food plants of Australia*. Sydney: Collins, Angus & Robertson Publishers Pty Ltd.
- Lu, Q. Y., Zhang, Y., Wang, Y., Wang, D., Lee, R. P., Gao, K., et al. (2009). California Hass avocado: Profiling of carotenoids, tocopherol, fatty acid, and fat content during maturation and from different growing areas. *Journal of Agricultural and Food Chemistry*, 57, 10408–10413.
- Michael, D. (2000). *New pharmaceutical, nutraceutical & industrial products: The potential for Australian agriculture*. Barton, ACT, Australia: Rural Industries Research and Development Corporation.
- Mirdehghan, S. H., & Rahemi, M. (2007). Seasonal changes of mineral and phenolics in pomegranate (*Punica granatum* L.) fruit. *Scientia Horticulturae*, 111, 120–127.
- Ozcan, M. (2004). Mineral content of some plants used as condiments in Turkey. *Food Chemistry*, 84, 437–440.
- Prior, R. L., Hoang, H., Gu, L., Wu, X., Bacchiocca, M., Howard, L., et al. (2003). Assays for hydrophilic and lipophilic antioxidant capacity (Oxygen radical absorbance capacity (ORAC_{FL})) of plasma and other biological and food samples. *Journal of Agricultural and Food Chemistry*, 51, 3273–3279.
- Puente, L. A., Pinto-Munoz, C. A., Castro, E. S., & Cortes, M. (2010). *Physalis peruviana* Linnaeus, the multiple properties of a highly functional fruit: A review. *Food Research International*, doi:10.1016/j.foodres.2010.09.034.
- Richer, S., Stiles, W., Statkute, L., Pulido, J., Frankowski, J., Rudy, D., et al. (2004). Double-masked, placebo-controlled, randomized trial of lutein and antioxidant supplementation in the intervention of atrophic age-related macular degeneration: The Veterans LAST study (Lutein Antioxidant Supplementation Trial). *Optometry*, 75, 216–230.
- Robins, J. (2004). Native foods overview. In S. Salvin, M. Bourke, & T. Byrne (Eds.), *The new crop industry handbook* (pp. 417–426). Barton, ACT, Australia: Rural Industries Research & Development Corporation.

- Sanchez-Castillo, C., Dewey, P. J. S., Aguirre, A., Lara, J. J., Vaca, R., de la Barra, P. L., et al. (1998). The mineral content of Mexican fruits and vegetables. *Journal of Food Composition and Analysis*, 11, 340–356.
- USDA database on Oxygen Radical Absorbance Capacity (ORAC) of selected foods (2007). Retrieved: September 25, 2010 from: <http://www.ars.usda.gov/nutrientdata>.
- USDA National Nutrient Database for Standard Reference, Release 23 (2010). <http://www.ars.usda.gov/SP2UserFiles/Place/12354500> Retrieved: October 1, 2010.
- Wu, X., Beecher, G. R., Holden, J. M., Haytowitz, D. B., Gebhardt, S. E., & Prior, R. L. (2004). Lipophilic and hydrophilic antioxidant capacities of common foods in the United States. *Journal of Agricultural and Food Chemistry*, 52, 4026–4037.
- Zabaras, D., & Konczak, I. (2010). Potential physiological activities of lipophilic and hydrophilic fractions from Australian-grown fruits. In C.-T. Ho, C. Mussinan, F. Shahidi, & E. Tratras-Contis (Eds.), *Recent advances in food and flavour chemistry*. Royal Society of Chemistry. (pp. 361–368).