

*Invited Review***Antioxidants in Potato**

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**ABSTRACT**

The content of compounds in potato that may act as antioxidants in the human diet is not widely appreciated. Carotenoids are present in the flesh of all potatoes. The contents mentioned in the literature range from 50 to 100  $\mu\text{g}$  per 100 g fresh weight (FW) in white-fleshed varieties to 2000  $\mu\text{g}$  per 100 g FW in deeply yellow to orange-fleshed cultivars. The carotenoids in potato are primarily lutein, zexanthin, and violaxanthin, all of which are xanthophylls. There is just a trace of either alpha- or beta-carotene, meaning that potato is not a source of pro-vitamin A carotenes. In potatoes with total carotenoids ranging from 35 to 795  $\mu\text{g}$  per 100 g FW, the lipophilic extract of potato flesh presented oxygen radical absorbance capacity (ORAC) values ranging from 4.6 to 15.3 nmoles  $\alpha$ -tocopherol equivalents per 100 g FW. Potatoes contain phenolic compounds and the predominant one is chlorogenic acid, which constitutes about 80% of the total phenolic acids. Up to 30  $\mu\text{g}$  per 100 g FW of flavonoids are present in the flesh of white-fleshed potatoes with roughly twice the amount present in red- and purple-fleshed potatoes. The predominant flavonoids are catechin and epicatechin. Red and purple potatoes derive their color from anthocyanins. The skin alone may be pigmented, or the flesh may be partially or entirely pigmented. Whole unpeeled with complete pigmentation in the flesh may have up to 40 mg per 100 g FW of total anthocyanins. Red-fleshed potatoes have acylated glucosides of pelargonidin while purple potatoes have, in addition, acylated glucosides of malvidin,

petunidin, peonidin, and delphinidin. The hydrophilic antioxidant activity of solidly pigmented red or purple potatoes is comparable to brussels sprouts or spinach. In red and purple potatoes with solidly pigmented flesh with levels of total anthocyanin ranging from 9 to 38 mg per 100 g FW, ORAC ranged from 7.6 and 14.2 umole per g FW of Trolox equivalents. Potato contains on average 20 mg per 100 g FW of vitamin C, which may account for up to 13 % of the total antioxidant capacity. Potatoes should be considered vegetables that may have high antioxidant capacity depending on the flesh composition.

**INTRODUCTION**

The potato tuber is an underground stem providing an opportunity for the potato plant to propagate itself vegetatively. Domestication by human beings and selection as a food-stuff provided for higher yield and characteristics suitable for fresh market and processing. As a result the potato has become an exceptionally high-yielding carbohydrate-rich crop. Other notable features are a high-quality protein and a significant level of vitamin C (Woolfe 1987). Less well known are the carotenoids and phenolics found in potato, which are potent antioxidants. The purpose of this review is to place the antioxidant status of potato into perspective in terms of genetic variation available in germplasm and in relation to its place in the human diet.

Diets rich in antioxidant flavonoids and carotenoids have been associated with a lower incidence of atherosclerotic heart disease, certain cancers, macular degeneration and severity of cataracts (Cao et al. 1998a, 1999; Hertog et al. 1993;

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ABBREVIATIONS: AAPH, 2,2'-azobis(2-amidinopropane) dihydrochloride; DPPH, 2,2-Diphenyl-1-picrylhydrazyl; FRAP, ferric reducing ability of plasma; ORAC, oxygen radical absorbance capacity

Knekt et al. 1996; Kruezer 2001; Wang et al. 1999). Arguments for the health benefits of antioxidants are largely correlated to diet composition vs disease and morbidity in populations. The consumption of antioxidant-rich foods results in the maintenance of higher antioxidant levels in blood serum (Cao et al. 1998a, 1998b; Mazza et al. 2002; Prior and Cao 2000). Reduction of atherosclerotic heart disease in association with antioxidant rich diets is hypothesized to be related to a reduction in the oxidative polymerization of low-density lipoproteins and consequent lesion formation and plaque build up in key coronary arteries (Buring and Hennekens 1997). Cancer reduction is further hypothesized to be due to protection of DNA from destruction by reactive oxidative species (Wargovich 2000). Lutein supplementation in the diet has been correlated with improvement in visual function in patients suffering from macular degeneration and cataracts (Olmedilla et al. 2001). Consumption of diets high in fruits and vegetables increased the antioxidant levels in blood serum in human subjects (Cao et al. 1998a, 1998b). Although no studies have yet measured bioavailability of antioxidants from potato sources, there is limited information from small fruit consumption studies. Anthocyanins from elderberry juice were detected in blood serum and urine of subjects who consumed juice containing 500 mg of anthocyanins. The yield in the urine was 0.03% of the ingested amount suggesting a very low absorption through the gastrointestinal tract and excretion as the intact form (Murovic et al. 2001). Mazza et al. (2002) found that anthocyanins from a blueberry extract were absorbed in their intact glycosylated and acylated forms and were associated with an increase in serum antioxidant status.

## GENETICS OF ANTHOCYANINS AND CAROTENOIDS IN POTATO

The natural variation of cultivated potato germplasm includes types that are red and purple pigmented due to the presence of flavonoids in the skin and/or flesh. Anthocyanins are among the many flavonoids that may be found in potato tubers. A series of single genes controls presence and absence of red and blue pigments. Different genetic systems controlling pigment expression have been identified for diploid cultivated vs tetraploid cultivated potatoes (Dodds and Long 1955, 1956; Lunden 1960). De Jong (1991) and Van Eck et al. (1994) have argued that the genes appear to be syntenic and should be

regarded as belonging to the same genome. In other words, the genes coding for similar phenotypes in diploids and tetraploids are the same genes. The symbol *D* denotes a single gene controlling synthesis of red pigment, located on chromosome 2; the symbol *P* stands for a single gene on chromosome 11 controlling blue pigment synthesis; while *I*, of undetermined location, epistatically controls presence and absence of tuber skin and flesh pigmentation even when *P* and *D* are present. Gebhardt et al. (1989) reported a locus controlling purple skin color, *Psc*, on chromosome 4. The single gene *Pf*, linked to *I*, determines whether pigment is present beyond the periderm in the interior tissues of the tuber (DeJong 1987, 1991; Van Eck et al. 1994). The pigments have been determined to be various types of acylated anthocyanidin glucosides (Harbourne 1960; Rodriguez-Saona et al. 1998). The gene *Ac* is imputed to control acylation of anthocyanins. Diploid cultivated potatoes display both acylated and non-acylated forms while only acylated anthocyanins are present in the tetraploid cultivars (Swaminathan and Howard 1953). Potatoes have acylated glucosides of several aglycons (pelargonidin, petunidin, malvidin, and peonidin) and mostly xanthophyll type carotenoids, including predominantly lutein, violaxanthin and zeaxanthin (Brown et al. 2003; Fossen and Andersen 2000; Fossen et al. 2003; Iwanzik et al. 1983; Mazza and Miniati 1993; Rodriguez-Saona et al. 1998).

Outside of the center of origin of cultivated potato in the Andes of South America, it is rare to find varieties with anthocyanin pigments conferring red or purple flesh. However, much of the world's production is occupied by yellow-fleshed potatoes, which have higher total carotenoid than the white-fleshed varieties of North America and Great Britain. Although genetic control of presence and absence of anthocyanins is monogenic, the completeness of anthocyanin distribution in pigmented flesh may be under complex genetic control (Brown et al. 2003; De Jong 1991). White vs yellow flesh is thought to be under single gene control, while gene maps agree on the placement of this yellow-flesh factor (*Y/y*) on homolog 3 (Bonierbale et al. 1988; Gebhardt et al. 1989). White- and yellow-fleshed potatoes have similar composition of carotenoids; however, the yellow color of the latter group is due to higher concentrations of certain xanthophylls (Brown et al. 1993; Gross 1991).

## ANTIOXIDANT MEASUREMENT METHODS

There are numerous antioxidant assays in the literature. A description of three in some detail will provide a base of knowledge. Antioxidants are compounds that, when in the presence of an oxidizable substrate and an oxidizing agent, delay the oxidation of the substrate. Oxygen radical absorbance capacity (ORAC) is a measure of the capacity of an antioxidant to delay oxidation of a target molecule. In ORAC this is measured by detecting the loss of luminescence of  $\beta$ -Phycoerythrin (PE) due to oxidation. The loss of PE fluorescence in the presence of free radicals is an index of oxidative damage to the protein. The assay uses 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) as a free-radical-generating system and an area-under-curve technique for quantitation of antioxidant capacity. AAPH undergoes spontaneous decomposition and produces peroxy radicals with a rate dependent on temperature. Thus, the ORAC assay measures the capacity of an antioxidant to directly quench free radicals. The ORAC method is considered to have the advantage of combining both inhibition percentage and the length of inhibition time of free radical action by an antioxidant into a single quantity (Cao and Prior 1998).

The ferric reducing ability of plasma (FRAP) assay (Benzie and Strain 1996) is a measure of the ferric-to-ferrous iron reduction followed by the formation of colored ferrous-tripyridyltriazine complex in the presence of antioxidants. It is easier and less expensive to carry out than ORAC, but presents only a single time point percentage inhibition of oxidation.

The 2,2-Diphenyl-1-picrylhydrazyl (DPPH) assay for total antioxidant activity determines antioxidant activity based on the analysis described by Brand-Williams et al. (1995). DPPH, a stable radical, absorbs at 515 nm, and upon reduction by an antioxidant species, a decrease in absorbance is observed. The change in color (from purple to yellow) provides an easy and rapid way to evaluate the antiradical activities of extracts. DPPH can be used as a broad screen to identify the ranges of antioxidant activity.

Prior and Cao (1999) reviewed antioxidant measurement techniques. They emphasized the difficulty of comparing studies due to the large number of different techniques. However, they favored the ORAC assay because it takes the reaction between substrate and free radicals to completion using an area-under-the-curve technique compared to single measure-

ment during the lag phase. Ideally several different measurements should be used.

## ANTHOCYANINS

Anthocyanin contents of potatoes with pigmented flesh have been studied recently by several workers. Rodriguez-Saona et al. (1998) reported anthocyanin contents of partially and solidly red-fleshed potatoes ranging from 3 to 40 mg per 100 g fresh weight (FW). The major pigments were identified by HPLC and mass spectroscopy analysis to be acylated glucosides of pelargonidin. The potential commercial value of pelargonidin derivatives intended as natural colorants from red-fleshed radish and red-fleshed potato were compared by Wrolstad et al. (2001) and found to be promising from the standpoint of stability relative to artificial colorants, attractiveness, intensity of red hue, and stability.

Lewis et al. (1998a) found much higher concentrations of anthocyanins in certain cultivars extending up to 368 mg per 100 g FW in the purple-fleshed cv Urenika and up to 22 mg per 100 g FW in red-fleshed types. Concentrations are considerably higher in skin, approaching 900 mg in purple-fleshed and 500 mg in red-fleshed types per 100 g FW (of the skin alone). Red- and purple-fleshed potatoes always have red- and purple-pigmented skin, respectively. Pelargonidin and peonidin were in nearly equal amounts in the red flesh, while petunidin and malvidin were predominant in the purple flesh. Wild species had no anthocyanins in the flesh but up to 27 mg per 100 g FW in the skin (Lewis et al. 1998b). The cv Urenika, thought to have been directly transferred to the Maori by 18th century European visitors to New Zealand was identified by Cambie and Ferguson (2003) as an important functional food in the Maori diet due to the presence of anthocyanins. Fossen and Anderson (2000) determined the anthocyanins of the purple-fleshed cv Congo to consist of ferulyl gluco- and rhamno-pyransides of malvidin and petunidin, novel anthocyanins. Fossen et al. (2003) further reported the new finding of acylation with caffeic acid in extracts from an unnamed purple-fleshed Norwegian cultivar. Naito et al. (1997) similarly identified acylated glucopyranosides of pelargonidin as the primary anthocyanins in a red-fleshed potato produced from hybridization between *S. tuberosum* ssp *tuberosum* and *S. tuberosum* ssp *andigena*. Alcalde-Eon et al. (2003) reported acylated glucosides of anthocyanidins. The aglycons were pelargonidin, malvidin,

petunidin, peonidin, and delphinidin acylated with hydrocinamic acids in the skin and flesh of pigmented cv Pinta Boca, a variety in the taxon *Solanum stenotomum* from Bolivia. Anthocyanin content of red- and purple-fleshed potato derived from a breeding program conducted by the USDA/ARS at Prosser, WA, ranged from 7 to 35 mg in red-fleshed and 6 to 17 mg in purple-fleshed potato (Brown et al. 2003).

Anthocyanins were predominantly acylated glucosides of pelargonidin in the red-fleshed potato and acylated glucosides of predominantly petunidin and peonidin with smaller amounts of delphinidin and malvidin in the purple-fleshed potato. Antioxidant values (ORAC) for red-fleshed types ranged as high as 300% of the white flesh, while for purple-fleshed antioxidant values reached 250% of the white flesh. Hale (2003) found a range of 104 to 565  $\mu\text{g}$  per 100 g FW (DPPH test) among highly diverse materials. The purple-fleshed clones were among the top, presumably due to the high anthocyanins. One of the more interesting outcomes of this work is the measurement of high antioxidant values in cv Norkotah Russet (NR) and a series of intracloonal variants derived from NR. The DPPH test values ranged from 161 to 452 spanning significant differences statistically. This kind of result in a white-fleshed variety and its variants suggests that colorless compounds that are probably either flavonoids or phenolic acids are potentially very potent as antioxidants. Brown et al. (2004a) surveyed a number of breeding lines with solidly pigmented flesh reporting levels of the anthocyanin ranging from 9 to 38 mg per 100 g FW. ORAC values ranged from 7.6 and 14.2  $\mu\text{mole}$  per g FW of Trolox equivalents. The highest antioxidant value, a red-fleshed breeding line, was approximately 330% that of the average of the white-fleshed breeding lines and varieties tested. Pietta (2000) presented evidence that cyanidin is up to three times more effective than pelargonidin as an antioxidant. Kähkönen and Heionan (2003) have determined that malvidin is the most potent antioxidant of the anthocyanidins. Reyes and Cisneros-Zevallos (2003) found that the location of cultivation of the potato crop affected anthocyanin concentration of a purple-fleshed cultivar. Also they found that certain storage conditions simulating stress increased anthocyanin concentration by 60% in tubers harvested from environments that resulted in the lowest out-of-field concentrations. A method to extract red pigment from red-fleshed potato for use as a natural colorant was developed by Wrolstad and Rodriguez-Saona (2001).

## OTHER PHENOLIC COMPOUNDS

Lewis et al. (1998a) found that cultivated potato tuber skin contained 2000-5000  $\mu\text{g}$  per g FW phenolic acids and 200-300  $\mu\text{g}$  of flavonoids. Purple- and red-skinned tubers contained twice the concentration of phenolic acids as white-skinned tubers. Tuber flesh contained lower concentrations ranging from 100-600  $\mu\text{g}$  of phenolic acids and 0 to 30  $\mu\text{g}$  of flavonoids. They also found that purple- or red-fleshed cultivars had twice the flavonoid concentration of white-fleshed cultivars and three to four times the concentration of phenolic acids. Examples of flavonoids in order of abundance were catechin, epicatechin, erodictyol, kaempferol, and naringenin. The predominant phenolic acids were chlorogenic acid, protocatechic acid, vanillic acid, and p-coumaric acid. In wild *Solanum* species (Lewis et al. 1998b) phenolic acids ranged from 600 to 2700 in skin and 100 to 600  $\mu\text{g}$  per 100 g FW in the flesh. Similar types of phenolics acids were found with the exception of that caffeic acid concentrations increased to be the second most abundant after top-ranking chlorogenic acid. Flavonoids ranged from 20 to 170  $\mu\text{g}$  in the skin and 0 to 25  $\mu\text{g}$  per 100 g FW in the flesh, with the identities basically following the pattern found in cultivated potato. Pietta (2000) has shown that flavonoids differ greatly in their antioxidant capacity. Quercetin is, for instance, more than three times more effective as an antioxidant than kaempferol and erodictyol, and is twice as effective as catechin. Interestingly, Lewis et al. (1999) found that the total anthocyanin, phenolic acids, and flavonoid content increased during cold storage (at 4 C) in the skin and flesh of purple-fleshed New Zealand variety Urenika. Chu et al. (2000) found that the flavonoids and flavone extracts had high scavenging activities toward oxygen radicals. Potatoes showed 94% scavenging activity towards hydroxyl radicals, and, along with onions, almost complete inhibition of superoxide radicals.

## VITAMIN C

Potatoes have levels of vitamin C that contribute substantially to the Recommended Daily Allowance (in the USA) of 60 mg for adults (Augustin 1975). In two recent surveys of potato genotypes, concentrations varied between 11 and 30 mg per 100 g FW in North American varieties and breeding lines (Love et al. 2003) and 18 to 36 mg in six European varieties and 27 breeding lines (Dale et al. 2003). Recent reports of genetic vari-

ability report a high heritability for vitamin C content,  $h^2 = 0.96$ , and measured progeny clones from crosses that had 40 mg vitamin C per 100 g FW (Pavek and Corsini 2003). The presence of high vitamin C in the South American cultivated species *Solanum phureja* has been noted. In crosses of *S. phureja*, a diploid, with tetraploid parents relatively high levels of vitamin were noted in the progeny (Davies et al. 2002). Dale et al. (2003) also documented the large reduction in vitamin C content that occurs during storage, averaging 45%. Vitamin C was found to decrease more rapidly at 1 C storage compared to 20 C in two Japanese varieties, Danshaku and Kataakari (Kawakami et al. 2000). Relatively little is known of the contribution of vitamin C in potato to antioxidant value. However, one study (Chu et al. 2002) has estimated that vitamin C extracted from an unidentified potato obtained from a grocery store contributes 13.3% of the total antioxidant activity. Although a modest value, it remains to be determined what the higher concentrations available in breeding materials might contribute to total antioxidant value.

Relatively little is known of the affects of handling, storage, and processing of carotenoids, anthocyanins, phenolics, or flavonoids. There is, however, a body of knowledge surrounding the fate of vitamin C. Besides the decrease during storage already noted, vitamin C content is known to rise during crop development, but decrease during late season maturation of the crop (Shekhar et al. 1978). Bruising of potatoes during handling results in an initial increase in vitamin C followed by a 30% to 40% reduction relative to unbruised potatoes after 12 weeks in storage regardless of the storage temperature (Mondy et al. 1987). Vitamin C was in greater concentration in the pith than in the cortex in this study. Sweeney et al. (1969) noted higher concentrations in the apical end ("bud end") vs the basal end ("stem end") of tubers of cvs Pungo, Rosemount Cobbler, and Russet Burbank over 5 months storage at 55 F (12.8 C) and 70 F (21.1 C). The apical-basal differences persisted while whole tuber assays showed an overall decline in concentration of between 40% and 55%. Zinc fertilization (using zinc sulfate) resulted in a 40% increase in vitamin C content in the variety Katahdin (Mondy et al. 1993).

A number of studies have charted the loss of vitamin C during diverse cooking and processing steps. The processing of potato into flakes almost totally eradicated vitamin C (Sullivan et al. 1985). An important part of pre-cooked French fry production involves a blanching step. It has been found that 20% to 45% of vitamin C is lost due to diffusion into the water

bath during this process and that losses are mitigated best by reducing time of blanching at higher temperatures (Artz et al. 1983; Luna and Garrote 1987). Retention of vitamin C in processed commercial products, which included a blanching step, was 69%, 61%, and 53% in large-sized french fries, small-sized french fries, and pre-formed patties, respectively (Augustin et al. 1979). Vitamin C may decrease during chilling and brief refrigerated storage followed by microwave reheating; however, these decreases are smaller than reductions caused by extended storage or those due to the blanching step in commercial processing (Augustin et al. 1979). In experiments designed to mimic home preparation, vitamin C losses were between 20% and 25%. The least loss was found in unpeeled boiled potato. Unpeeled and boiled Russet Burbank lost much less vitamin C (5%) than Katahdin (34%) (Augustin et al. 1978). Cooking by boiling decreased vitamin C by 30% in European cvs Bintje, Van Gogh, and Nicola and keeping the potatoes hot for 1 h after cooking reduced it a further 10% (Hägg et al. 1998).

## ANTIOXIDANT ACTIVITY DUE TO PHENOLIC AND OTHER COMPOUNDS

The antioxidant capacity of tuber components was examined by Al-Saikhan et al. (1995). Patatin, the major tuber storage protein, and chlorogenic acid were the most potent antioxidants. Antioxidant activity appeared to be correlated with total phenolic acids. Of four potato cultivars tested (two white flesh and two yellow flesh), Norkotah Russet presented the highest total phenolic acid content and was among the two highest in antioxidant activity. As mentioned above Hale (2003) also found Norkotah Russet and intraclonal variants to be among the highest in antioxidant values.

Velioglu et al. (1998) compared a large group of fruits and vegetables as well as plant-derived products for antioxidant activity of the phenolic acid extracts. White-fleshed potato (Russet Burbank) was ranked among the top in antioxidant values of the phenolic acid fraction while harboring a comparatively low amount of total phenolic acids, 437  $\mu\text{g}$  per 100 g FW. Dao and Freidman (1992) reported a range of 10 to 19 mg per 100 g FW of chlorogenic acid in different white-fleshed potato genotypes. In the ranking of different phenolic acids for oxidation potential, caffeic acid, and chlorogenic acid were the lowest with values at one-third of those compounds with the highest oxidation potential (e.g., 4-hydroxybenzoic acid).

Hale (2003) reported total phenolic acid concentrations of white-fleshed varieties ranging between 60 and 394  $\mu\text{g}$  per 100 grams FW. Most of the variation was explained by differences in chlorogenic acid, which varied between 26 and 329  $\mu\text{g}$ . One aberration was the presence of more than 300  $\mu\text{g}$  per 100 g FW of rutin hydrate in cv Ranger Russet. This is a good example of possible genetic variation in phenolic acid composition in potato. An examination of hydrophilic extracts of white-fleshed wild species revealed a range as great as that found in cultivars and breeding lines including those with pigmented flesh. Although not clear which compounds were responsible for the high values, two wild species were consistently high, *S. jamesii* and *S. pinnatisectum* (Hale 2003). In addition, Hale (2003) found that the concentration of phenolic acids accounted for relatively little of the antioxidant activity ( $R^2 = 0.18$ ). Reyes and Cisneros-Zevallos (2003) found that slicing increased the total phenolic acids content in the flesh of a purple-fleshed potato in storage while it did not increase the anthocyanin content. Clearly, however, the phenolic acids in greatest abundance in potato (chlorogenic being foremost on this list as 80% of total) are potent antioxidants in raw flesh (Dao and Friedman 1992).

## CAROTENOIDS

White- and yellow-fleshed potatoes are very familiar to people around the world. The intensity of yellow color varies greatly and those at the far end of the continuum may be described as orange. Despite the common belief in earlier studies that the most intensely colored yellow-fleshed potatoes contained beta-carotene it may be true that there is no beta-carotene, or just a trace (Gross 1991). Rather, *Solanum* potato, in contrast to the sweet potato (*Ipomoea* spp.), contains xanthophylls of various sorts. Total carotenoid measurements from mid-20th century exist in the literature. Caldwell et al. (1945) reported 14 to 54 and 110 to 187  $\mu\text{g}$  per 100 g FW for white- and yellow-fleshed potatoes, respectively. Brunstetter and Wiseman (1947) reported 60  $\mu\text{g}$  and included beta-carotene as a minor component of the total carotenoid mixture. It is likely that the specific extraction methods, exposure to light during the process, rapidity of completion of each step, and oxidation intervene to change the carotenoid spectrum originally present in the tuber flesh. Kasim (1967) reported values for total carotenoid between 199 and 560  $\mu\text{g}$ , identifying lutein, violaxanthin, and lutein 5,6 epoxide as the components.

Granado et al. (1992) reported 17 and 65  $\mu\text{g}$  in raw and cooked potato, respectively. Tevini et al. (1984) and Tevin and Schoenecker (1986) reported a range of 102 to 219  $\mu\text{g}$  in yellow-fleshed potato, listing lutein, beta-carotene, neoxanthin, violaxanthin, and lutein 5,6 epoxide as components. Iwanzik et al. (1983), in one of the most complete studies, compared potatoes with various degrees of yellow intensity finding a range of total carotenoids from 27 to 329  $\mu\text{g}$ . They listed lutein, neoxanthin, violaxanthin, and lutein 5,6 epoxide as components and found a strong correlation between carotenoid concentration and colorimetric measurements of yellowness. Heinonan et al. (1989) reported 13 and 60  $\mu\text{g}$  from summer and spring potatoes, respectively, identifying the xanthophyll as lutein. A number of studies have measured levels in potato with intensely yellow flesh that derive these high levels from *S. phureja*, a diploid cultivated species endemic to the Andean Cordillera. Brown et al. (1993) found levels exceeding 2000  $\mu\text{g}$  in breeding materials segregating for orange-, yellow-, and white-fleshed phenotypes derived from a diploid population originating from *S. phureja* and *S. stenotomum* originally developed by Frank Haynes, North Carolina State University, NC, USA. The orange-fleshed types contained predominantly zeaxanthin, which is redder in color than lutein, conferring a dark yellow to orange appearance depending on concentration in the flesh. Hale (2003) found a range of 97 to 536  $\mu\text{g}$  per 100 g FW in a series of cultivars and breeding lines. Carotenoid content did not appear to be related to color of flesh. Brown et al. (2004a) divided cultivars into white, yellow, and dark yellow categories on the basis of color which corresponded to 50 to 100, 150 to 250, and 500 to 700  $\mu\text{g}$  per 100 g FW groupings. The last category, dark yellow, is not commercially available except as *Papa Amarilla* in South America; however, it is present in breeding lines in North America at this writing. Römer et al. (2002) produced an increase of zeaxanthin in yellow-fleshed potato by transformation of sense and antisense constructs of neoxanthin epoxidase. This inhibited conversion of zeaxanthin into violaxanthin. Increases in zeaxanthin over wild type ranged between four- and 130-fold. The highest levels of zeaxanthin reached 40  $\mu\text{g}$  per g dry weight (approximately 1000  $\mu\text{g}$  per 100 g FW). Lu et al. (2001) found high levels, in their most highly pigmented materials, 1435 and 2200 of total carotenoids, respectively, listing lutein, zeaxanthin, neoxanthin, violaxanthin, and lutein 5,6 epoxide as components. Breithaupt and Bamedi (2002) reported values of 58-175 and 38-62  $\mu\text{g}$  for yellow and white flesh, respectively, indicat-

ing that esterified xanthophylls made up a substantial portion of the total carotenoid content. Nesterenko and Sink (2003) reported the carotenoid levels and xanthophyll identities of white-, yellow-, and orange-fleshed potato. They reported values ranging 48 to 879  $\mu\text{g}$ . Of the yellow-fleshed types, the highest values were 265  $\mu\text{g}$  while the single orange-fleshed type had 879  $\mu\text{g}$ . Interestingly, the orange-fleshed type (derived from genetic materials described in Brown et al. [1993]) was the only one containing more than a trace of zeaxanthin, which constituted about one-half of the total carotenoid. Beside the ubiquitous lutein, which is always present in white-fleshed potato, violaxanthin was the second most common xanthophyll reported in abundance in yellow-fleshed potatoes. Brown et al. (2004a) is the only published study to date to report antioxidant values attributable to a chloroform soluble fraction of the tuber flesh. The ORAC values ranged from 2 to 7  $\mu\text{g}$  per 100 g FW  $\alpha$ -tocopherol equivalents. Total carotenoid concentration was correlated with the ORAC values,  $r = 0.77$ , and also had a statistically significant positive regression coefficient. Various studies have compared purified samples of carotenoids for antioxidant values. There is agreement that lycopene, the red carotenoid abundant in tomato, displays the highest value while lutein and zeaxanthin are approximately half as effective (Bohm et al. 2002; Miller et al. 1996). Clevidence et al. (2000) determined in their review article that consumption of dietarily realistic amounts of carotenoid-rich vegetables raised plasma and colon cell levels of several carotenoids by significant amounts.

## EFFECTS OF COOKING

There is almost no published information on the effects of cooking on the functional properties of constituents of potato other than vitamin C. One study found that the anthocyanin in red- and purple-fleshed potatoes survives in large part various cooking methods including frying in oil. Further the antioxidant properties of the anthocyanins persist at levels equal to or greater than 75% of the raw potato (Brown et al. 2004b). Blessington et al. (2004) reported that frying and microwaving increased antioxidant activity as measured in a hydrophilic extract using the DPPH assay. Interestingly, in this study, irradiation increased both carotenoid concentration and DPPH antioxidant activity.

## CONCLUSIONS

Potato is not ordinarily considered a food rich in antioxidants. However, a consideration of the genetic variability in concentrations of anthocyanins, phenolic acids, flavonoids, and carotenoids, including cultivars from the center of origin in South America invites re-orientation of preconceptions. Friedman (1997) listed imputed health benefits of diets rich in phenolic acids as antimutagenic, anticarcinogenic, glucose-lowering, and cholesterol-lowering. Many studies suggest beneficial effects in human health based on consumption of antioxidants as supplements or in the diet. However, information is still too preliminary to speak with unguarded authority. At least one popular book advocates very deliberately choosing diets with highly pigmented foods based primarily on the salutary effects of antioxidants and includes red-, purple-, and yellow-fleshed potatoes in the list of especially healthy foods (Joseph et al. 2002). Official dietary recommendations on antioxidants do not yet exist. Nonetheless, studies in the bioavailability and physiological parameters associated with the protective function of antioxidants contributed by potato to the diet would be very useful to the potato industry.

Furthermore, the genetic variability reported in this review provides impetus for future breeding work directed specifically at enhancing the antioxidative matrix by directed selection for higher concentrations of compounds having these properties. The identification and quantification of compounds in the potato tuber and attribution of antioxidative values as well as other properties is still in its infancy. Even more tantalizing is the lack of knowledge in terms of identification of new compounds and the differences between genotypes in terms of predominating types in each class. There is ample room for much experimentation on the effect of cultural and storage conditions on the concentrations of all classes of compounds. Lastly, the effect of different modes of cooking on stability of these compounds has hardly been touched, despite the obvious importance of this. Preliminary results, however, appear to indicate that major categories of antioxidants (anthocyanins and carotenoids) withstand the usual modes of cooking and retain their antioxidant capacity after cooking in large part. Potato is always cooked before consumption in the human diet. There is reason to expect that carotenoids survive cooking to a considerable extent based on studies in other foods (Clevidence et al. 2000). The persistence of vitamin C is documented after diverse cooking methods, yet there is

always some loss. It would appear that the antioxidative value of phenolic acids is mostly nullified by cooking (Friedman 1997). The effects of cooking on the properties of antioxidants in potato is therefore a field deserving of considerable effort in the future. The anthocyanin pigments of potato may be of interest as natural food colorants. The intensity of hue and the stability would be attractive in natural processed foods or for homeopathic medicines. The co-elution of anthocyanins and glycoalkaloids would be a technical problem requiring special separation steps to avoid the presence of glycoalkaloids in natural pigment product (Rodriguez-Saona et al. 1998). A method to extract red anthocyanin pigment from red-fleshed potato for use as a natural colorant was developed and patented by Wrolstad and Rodriguez-Saona (2001).

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