Phenolics and Antioxidant Capacity in Selected New York State Plums

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We dedicate this paper to Professor Robert Andersen who retired recently after a long and dedicated career in stone fruits breeding at Cornell University-Geneva.

Plums may be good sources of natural antioxidants due to their high levels of phenolic phytochemicals. The predominant phenolics in plums are hydroxycinnamic acids and anthocyanidin derivatives. When compared to other common fruits, plums have higher phenolic content and higher antioxidant capacity indicating that an increased consumption of plums through our diet is highly desirable for the associated health benefits.

Antioxidants are compounds that retard or inhibit the oxidation of molecules that can occur by the presence of reactive free radicals. Many phenolic phytochemicals, routinely consumed in our diet, have shown antioxidant properties by chelating metal ions, inhibiting lipid oxidation, inhibiting radical-forming enzymes, or quenching free radicals. In recent years, active research has been conducted on fruits and vegetables due to their biologically beneficial effects, which are derived from the antioxidant activities of phenolic phytochemicals.

Foods containing various molecules (proteins, lipids, vitamins, and carbohydrates) are vulnerable to attack by reactive free radicals. Free radicals such as superoxide radical anion, hydrogen peroxide, hydroxyl radical, and singlet oxygen, are normally generated during daily physiological metabolic activities. Damage mediated by free radicals results in the disruption of membrane fluidity, protein denaturation, lipid peroxidation, DNA oxidation, and alteration of platelet functions. Oxidative stress caused by an overwhelming amount of free radicals beyond normal defense capacity of antioxidant systems for oxidation, has been considered a link with aging and many degenerative diseases. Phenolics that quench reactive free radicals can prevent the oxidation of other molecules and may, therefore, have health-promoting effects in the prevention of degenerative diseases such as cancers and Alzheimer's disease.

Significant amounts of phenolic compounds (phenolics) are present in fruits, vegetables and beverages where diverse combinations of phenolics exist. Phenolics are found widely as secondary metabolites in the plant kingdom. Among phenolics, flavonoids frequently occur as glycoside forms, whereas hydroxycinnamic acids generally exist as ester forms. The sugars linked to flavonoid aglycons include arabinose, galactose, glucose, rhamnose, rutinose and xylose. The distribution and composition of phenolics in fruits and vegetables are affected by various factors such as maturity, cultivars, horticultural practices, geographic origin, growing seasons, postharvest storage conditions and processing procedures.

Phenolics are routinely consumed as part of our daily diet. They are the most important group among the phytochemicals and they influence the sensory qualities (color, flavor, taste) of fresh fruits, vegetables and their products. In addition, many phenolic phytochemicals possess important biochemical properties including antioxidative, anticarcinogenic, antimicrobial, antiallergic, antimutagenic and anti-inflammatory activities. Recently, interest in the research area of bioactive phenolics has been growing rapidly due to their many possible benefits to human health. Epidemiological observations suggest that dietary intake of natural bioactive compounds including flavonoids through fruits and vegetables may reduce the risk of cancers and heart disease (Potter, 1997; Hertog et al., 1997).

Various fruits such as grapes and apples are well investigated and are known to contain significant amounts of phenolics. Yet plums, which have very high concentrations of phenolic phytochemicals, remain underutilized in the average American diet and under-researched worldwide. We have been working on phenolics and antioxidant capacity of plums using spectrophotometric methods and reversed-phase high-performance liquid chromatography (HPLC). This article describes our results on total phenolics, antioxidant capacity, and identification of individual phenolics in 10 cultivars of fresh plums grown in NY State from the 2001 and 2002 harvest seasons. Phenolics in plums were extracted by the ultrasound-assisted method using aqueous methanol. The ultrasound-assisted method is rapid and efficient for the extraction of phenolics, during which a constant stream of nitrogen gas is introduced to provide an oxygen-free environment to prevent and minimize the browning reactions.

Total Phenolics in Plums

Total phenolics were analyzed by the colorimetric method using the Folin-Ciocalteu's phenol reagent. Total phenolics of 10 different fresh plum cultivars grown in NY State in 2001 and 2002 are presented in Table 1. The cultivars are categorized by skin color as follows: dark blue/purple plums (Beltsville Elite B70197, Castleton, Empress, Longjohn, NY 6, NY 9, and Stanley), red plum (Early Magic), and yellow plums (Mirabellier, and NY 101). There was a significant difference in total phenolics due to different plum cultivars and growing seasons (or crop years). The total phenolics in plums of the 2001 crop varied from 125.0 to 372.6 mg gallic acid equivalents (GAE)/100 g with an average of 192.1 mg GAE/100 g, whereas plums harvested in 2002 showed total phenolics at 138.1 to 684.5 mg GAE/100 g with an average of 285.8 mg GAE/100 g. Beltsville Elite B70197 was found to have the highest total phenolics among plums tested in 2001 and 2002, while NY 9 had the lowest. Plum cultivars with dark blue/purple skin had higher total phenolics compared to plum cultivars with yellow and red skin. There were greater differences in total phenolic content due to cultivar than different crop years. The cultivars having the highest total phenolics had 3.0 and 4.7 times higher levels than the cultivars with the lowest phenolic content in 2001 and 2002, respectively, whereas seasonal variation caused less than 2.1 times the difference of total phenolics for each of the cultivars between 2001 and 2002. Plums were previously shown to have a higher total phenolics content than apple, banana, and orange (Kim et al., 2003; Proteggente et al., 2002).

Antioxidant Capacity of Plums

Antioxidant capacity in plums was expressed as vitamin C equivalent antioxidant capacity (VCEAC). Vitamin C, which is an antioxidant standard, is naturally present as one of major nutrients in fruits and vegetables and has been shown to possess preventive effects on carcinogenesis (Lee et al., 2002). VCEAC was evaluated on the basis of a chemical reaction using blue/green ABTS (2,2¢-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) radicals.

The total phenolic content of plums was highly correlated to the VCEAC in fresh plums from 2001 and 2002 crops (Figure1). This suggests that phenolics in plums may play an important role in scavenging free radicals. A good correlation was previously observed between total phenolics and antioxidant capacity in fresh plums (Gil et al., 2002).

The VCEAC of 10 different fresh plum cultivars grown in NY State in 2001 and 2002 is shown in Table 1. Similarly to total phenolics in plums, there was a significant difference in average content of VCEAC due to cultivars and crop years (or growing seasons). Fresh plums in 2001 possessed antioxidant capacities broadly ranging from 204.9 to 567.0 mg/100 g VCEAC, where Beltsville Elite B70197

TABLE 1

Total phenolics and vitamin C equivalent antioxidant capacity (VCEAC) in various fresh plum cultivars grown in NY State in 2001and 2002[a]

Cultivars	Total phenolics (mg GAE/100 g)		VCEAC (mg vit. C equiv./100 g)	
	2001	2002	2001	2002
Beltsville Elite B70197	372.6 ± 7.5	684.5 ± 2.6	567.0 ± 17.6	889.6 ± 3.2
Castleton	176.4 ± 1.8	250.5 ± 1.6	264.3 ± 10.3	337.8 ± 13.2
Early Magic	143.1 ± 2.0	192.1 ± 5.6	204.9 ± 16.7	251.2 ± 6.5
Empress	187.0 ± 2.1	398.7 ± 8.8	269.8 ± 11.8	524.8 ± 3.9
Longjohn	216.2 ± 1.8	398.9 ± 8.4	289.8 ± 38.4	550.4 ± 11.1
Mirabellier	136.8 ± 2.3	215.7 ± 2.9	211.6 ± 20.2	171.1 ± 6.6
NY 6	162.8 ± 1.6	146.6 ± 1.0	262.3 ± 23.7	154.9 ± 6.6
NY 9	125.0 ± 2.3	138.1 ± 2.9	239.1 ± 21.2	144.4 ± 11.2
NY 101	181.9 ± 2.2	196.1 ± 1.5	289.6 ± 17.9	216.2 ± 3.2
Stanley	181.3 ± 4.6	236.7 ± 4.5	249.9 ± 12.5	308.0 ± 5.3

[a]The data are presented with mean ± standard deviation (n = 6). Total phenolics and VCEAC are expressed as gallic acid equivalent (GAE) and vitamin C equivalent, respectively.

TABLE 2

Hydroxycinnamic acids in various fresh plum cultivars grown in NY State in 2001 and 2002[a]

Cultivars	neochlorogenic acid(mg/100 g)		chlorogenic acid(mg/100 g)	
	2001	2002	2001	2002
Beltsville Elite B70197	215.4 ± 7.6	184.6 ± 12.0	9.5 ± 0.5	10.4 ± 0.7
Castleton	73.1 ± 8.5	66.8 ± 2.2	7.1 ± 1.0	8.0 ± 0.3
Early Magic	18.1 ± 5.4	19.1 ± 0.1	0.9 ± 0.5	3.0 ± 0.0
Empress	127.7 ± 13.7	155.7 ± 13.3	8.0 ± 1.0	7.3 ± 0.7
Longjohn	128.0 ± 19.9	121.8 ± 4.4	16.4 ± 1.3	11.5 ± 0.4
Mirabellier	63.9 ± 7.3	44.1 ± 2.4	16.4 ± 2.7	15.9 ± 0.9
NY 6	67.9 ± 11.1	35.5 ± 2.2	8.8 ± 1.4	4.3 ± 0.3
NY 9	49.7 ± 4.1	28.1 ± 1.7	3.7 ± 0.4	3.3 ± 0.3
NY 101	179.4 ± 20.2	78.8 ± 6.1	21.0 ± 2.6	5.8 ± 0.4
Stanley	104.2 ± 16.4	108.6 ± 4.3	7.8 ± 1.5	9.2 ± 0.3

[a]The level of hydroxycinnamic acids are reported as mean ± standard deviation (n = 6 for 2001; n = 4 for 2002). The concentration of neochlorogenic acid is described as chlorogenic acid equivalents.

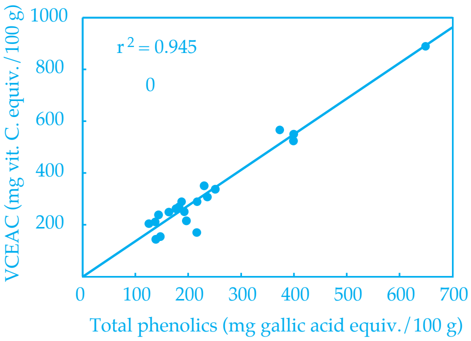

Figure 1. Relationship between total phenolics and vitamin C equivalent antioxidant capacity (VCEAC) in various fresh plum cultivars.

showed the highest VCEAC among 10 plum cultivars and carried 2.8 times higher VCEAC than Early Magic which had the lowest VCEAC. For the 2002 crop, VCEAC varied from 144.4 to 889.6 mg/100 g. Beltsville Elite B70197 also was found to have the highest VCEAC among plums tested in 2002, while NY 9 had the lowest. Compared to plums with yellow and red skins, plums with dark blue/purple skin showed higher antioxidant capacity. As with total phenolics, the difference due to cultivars was greater than the difference observed due to growing seasons. Plum cultivars having the highest antioxidant capacity had ~ 2.8 and 6.2 times higher level than cultivars with the lowest level for 2001 and 2002 respectively, whereas there was a difference of only 1.9 times between the 2001 and 2002 crops. Based on the results reported in Table 1, plums may be used as good sources of natural antioxidants. It was previously reported that plums possessed higher antioxidant capacity than apple, banana, lettuce, orange and tomato (Kim et al., 2003; Proteggente et al., 2002). Another use of plums would be their utilization in commercial food processing which may efficiently prevent lipid oxidation and therefore rancidity and production of undesirable by-products resulting in shelf life extension of foods. The antioxidant components in plums, mainly phenolics, could be a natural way to replace the use of synthetic antioxidants (BHA, BHT, etc.) by the addition of plum in food formulations.

Identification of Phenolics in Plums

Individual phenolic compounds in plums were tentatively identified and quantified using a High Pressure Liquid Chromatograph. Hydroxycinnamic acids in 10 plum cultivars grown in NY State in 2001 and 2002 are shown in Table 2. The main acids found were neochlorogenic and chlorogenic acids. There was a significant difference in the content of hydroxycinnamic acids due to plum cultivars and growing seasons. Irrespective of skin color, all the plum cultivars commonly had chlorogenic and neochlorogenic acids. For the 2001 crop, neochlorogenic acid ranged from 18.1 to 215.4 mg chlorogenic acid equivalents (CAE)/100 g, whereas chlorogenic acid values were between 0.9 and 21.0 mg/100 g. Plums harvested in 2002 had neochlorogenic acid content from 19.1 to 184.6 mg CAE/100 g and chlorogenic

TABLE 3

Flavonols in various fresh plum cultivars grown in NY State in 2001 and 2002[a]

Cultivars	rutin (mg/100 g)		quercetin 3-galactoside (mg/100 g)		quercetin 3-glucoside (mg/100 g)		quercetin derivatives (mg/100 g)	
	2001	2002	2001	2002	2001	2002	2001	2002
Beltsville Elite B70197	4.3 ± 0.3	6.1 ± 0.4	nd[b]	nd	nd	nd	nd	0.4 ± 0.0
Castleton	3.8 ± 0.5	3.8 ± 0.2	nd	nd	nd	0.8 ± 0.0	nd	nd
Early Magic	6.3 ± 0.6	8.3 ± 0.1	nd	1.2 ± 0.0	2.2 ± 0.3	1.5 ± 0.0	2.7 ±áf3 0.3	1.8 ± 0.0
Empress	3.3 ± 0.4	3.7 ± 0.5	nd	nd	nd	nd	nd	nd
Longjohn	7.7 ± 1.3	6.2 ± 0.3	nd	0.7 ± 0.0	nd	0.4 ± 0.0	nd	0.5 ± 0.0
Mirabellier	6.7 ± 0.5	7.2 ± 0.4	3.5 ± 0.4	0.6 ± 0.0	1.2 ± 0.1	0.5 ± 0.0	nd	nd
NY 6	2.8 ± 0.3	1.4 ± 0.1	nd	nd	nd	nd	nd	nd
NY 9	4.3 ± 0.3	2.7 ± 0.2	nd	nd	nd	nd	nd	nd
NY 101	5.0 ± 0.6	1.0 ± 0.1	nd	nd	nd	nd	nd	nd
Stanley	3.8 ± 0.6	3.3 ± 0.1	nd	nd	nd	nd	nd	nd

[a]The level of flavonols are reported as mean ± standard deviation (n = 6 for 2001; n = 4 for 2002). The concentration of quercetin derivatives is described as quercetin equivalents.
[b]nd = non detected

TABLE 4

Anthocyanins in various fresh plum cultivars grown in NY State in 2001 and 2002[a]

Cultivars	cyanidin derivative (mg/100 g)		cyanidin 3-glucoside (mg/100 g)		cyanidin 3-rutinoside (mg/100 g)		peonidin 3-glucoside (mg/100 g)		peonidin derivative (mg/100 g)	
	2001	2002	2001	2002	2001	2002	2001	2002	2001	2002
Beltsville Elite B70197	nd[b]	nd	3.9 ± 0.3	7.4 ± 0.4	25.7 ± 1.0	33.0 ± 1.9	nd	1.5 ± 0.2	11.5 ± 0.5	16.2 ± 1.0
Castleton	nd	nd	7.0 ± 0.9	14.2 ± 0.3	16.1 ± 1.9	22.1 ± 0.7	1.2 ± 0.2	2.3 ± 0.2	5.0 ± 0.7	6.9 ± 0.4
Early Magic	3.1 ± 0.3	nd	6.7 ± 0.6	4.1 ± 0.1	18.9 ± 1.9	23.4 ± 0.5	nd	0.3 ± 0.0	1.9 ± 0.3	3.1 ± 0.1
Empress	nd	nd	1.9 ± 0.8	1.4 ± 0.4	17.5 ± 2.2	22.4 ± 2.8	nd	nd	2.0 ± 0.3	3.1 ± 0.4
Longjohn	nd	nd	5.3 ± 0.9	7.2 ± 0.2	33.0 ± 2.0	41.1 ± 0.6	nd	0.7 ± 0.0	5.4 ± 0.8	9.1 ± 0.2
Mirabellier	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
NY 6	nd	nd	13.5 ± 2.0	3.8 ± 0.7	23.8 ± 3.5	8.9 ± 0.5	1.1 ± 0.2	0.3 ± 0.0	4.4 ± 0.6	2.1 ± 0.1
NY 9	nd	nd	3.9 ± 0.4	2.6 ± 0.2	24.2 ± 2.1	17.4 ± 1.1	nd	0.3 ± 0.0	8.3 ± 0.7	7.1 ± 0.4
NY 101	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Stanley	nd	nd	2.1 ± 0.3	3.4 ± 0.1	21.5 ± 3.9	25.5 ± 0.9	nd	0.3 ± 0.1	5.2 ± 0.9	6.1 ± 0.4

[a]The level of anthocyanins are reported as mean ± standard deviation (n = 6 for 2001; n = 4 for 2002). Concentrations of cyanidin and peonidin derivatives are described as cyanidin and peonidin equivalents, respectively.
[b]nd = non detected

acid from 3.0 to 15.9 mg/100 g. Beltsville Elite B70197, which had the highest content of neochlorogenic acid among various plums tested in 2001 and 2002, had more than 9.7 times higher neochlorogenic acid than Early Magic, which had the lowest. Longjohn, Mirabellier and NY 101 had chlorogenic acid at relatively high levels. Neochlorogenic acid was always in higher concentration than its isomer, chlorogenic acid, in all the cultivars of plums studied. There was no effect of crop year on hydroxycinnamic acid content. Neochlorogenic acid was previously reported to be the major hydroxycinnamic acid derivative, whereas chlorogenic acid the minor (Tomas-Barberan et al., 2001).

Flavonols in 10 plum cultivars grown in NY State in 2001 and 2002 are shown in Table 3. The flavonols found in plums were the derivatives of quercetin. Rutin (quercetin 3-rutinoside) was the most common and predominant among flavonols present in 10 plum cultivars tested, with concentrations ranging from 2.8 (NY 6) to 7.7 (Longjohn) mg/100 g for the 2001 crop, and from 1.0 (NY 101) to 8.3 (Early Magic) mg/100 g for the 2002 crop. Hyperoside (quercetin 3-galactoside) and isoquercitrin (quercetin 3-glucoside) were found in a few plum cultivars such as Castleton, Early Magic, Longjohn, and Mirabellier. One or two additional quercetin derivatives was present in Beltsville Elite B70197, Early Magic, and Longjohn.

Anthocyanins in 10 plum cultivars grown in NY State in 2001 and 2002 are presented in Table 4. Among flavonoids identified in fresh plums, anthocyanins were found to be the principal group. As expected, there were no anthocyanins found in yellow plums (Mirabellier and NY 101). A previous report (Tomas-Barberan et al., 2001) found no anthocyanins in the yellow plum Wickson. Anthocyanins of red and purple plum cultivars possessed the glycosides of cyanidin and peonidin such as keracyanin (cyanidin 3-rutinoside), kuromanin (cyanidin 3-glucoside) and peonidin derivatives. Keracyanin was the predominant anthocyanin in anthocyanin-containing plums. Longjohn had the highest amount of keracyanin among plum cultivars tested in both crop years. The highest level of peonidin derivative was found in Beltsville Elite B70197 among plums harvested in 2001 and 2002.

The average concentration of hydroxycinnamic acids (neochlorogenic and chlorogenic acids) in 10 plum cultivars was 112.7 mg/100 g for the 2001 crop and 92.2 mg/100 g for the 2002 crop. The common flavonol, rutin, in 10 plums was found at the average of 4.8 and 4.4 mg/100 g for 2001 and 2002 crops, respectively. For anthocyanin-containing plums, the sum of 3 common anthocyanins (keracyanin, kuromanin, peonidin derivative) averaged 33.6 and 36.4 mg/100 g for 2001 and 2002, respectively. Compared with the plums harvested in 2001, plums of the 2002 crop had 18.2% and 8.3% less hydroxycinnamic acids, and flavonol rutin while there was an 8.3% increase in three common anthocyanins. It indicates that the growing season may affect hydroxycinnamic acids content more than levels of flavonol rutin and common anthocyanins.

Conclusions

Plum cultivars showed significant differences in total phenolics and antioxidant capacity. There was a positive linear relationship between antioxidant capacity and total phenolics. Individual phenolics identified by reversed-phase HPLC analysis were neochlorogenic acid, chlorogenic acid, rutin, quercetin 3-glucoside, quercetin 3-galactoside, cyanidin 3-glucoside, cyanidin 3-rutinoside, peonidin 3-glucoside, and derivatives of cyanidin, peonidin, and quercetin. Plum cultivars exhibited diverse composition and different concentrations of phenolics. Plums contained copious amounts of phenolics and may be good sources of natural antioxidants through our diet, providing health-promoting effects in humans and preventing diseases. Plums are reported to have higher VCEAC than apples, the latter being one of the most commonly consumed fruit in our diet (Kim et al., 2003). Therefore, an increased consumption of plums is recommended in our diet.

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Dr. Chang (Cy) Lee is a professor and chair of the Food Science and Technology department at Geneva who specializes in food phytochemicals. This research was conducted in his lab. Dr. Dae-Ok Kim and Dr. Ho Jin Heo are postdoctoral research associates in Dr. Lee's lab. Dr. Young Jun Kim previously worked with Dr. Lee's group but is now an assistant professor at Korea University. Jay Freer is a research support specialist in the Department of Horticulture who works with Dr. Bob Andersen. Dr. Olga Padilla-Zakour is an Assistant Professor in the department of Food Science and Technology who leads Cornell's Food Venture Center.