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Antioxidant capacity, phenol, anthocyanin and ascorbic acid contents in raspberries, blackberries, red currants, gooseberries and Cornelian cherries

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Abstract

Raspberry (*Rubus idaeus*), blackberry (*Rubus fructicosus*), raspberry × blackberry hybrids, red currant (*Ribes sativum*), gooseberry (*Ribes glossularia*) and Cornelian cherry (*Cormus mas*) cultivars and native populations of varied pigmentation, originally from the Mediterranean area of Northern Greece, were assayed for antioxidant activity (determined as ferric reducing antioxidant power (FRAP) and deoxyribose protection), ascorbic acid, phenol, and anthocyanin contents. FRAP values ranged from 41 to 149 μmol ascorbic acid g^{-1} dry weight and protection of deoxyribose ranged from 16.1% up to 98.9%. Anthocyanin content ranged from 1.3, in yellow-coloured fruit, up to 223 mg cyanidin-3-glucoside equivalents 100 g^{-1} fresh weight in Cornelian cherry, whereas phenol content ranged from 657 up to 2611 mg gallic acid equivalents 100 g^{-1}dry weight. Ascorbic acid content ranged from 14 up to 103 mg 100 g^{-1} fresh weight. The present study outlines that the native Cornelian cherry population is an extremely rich source of antioxidants, demonstrating its potential use as a food additive.

Keywords: Berries; Antioxidants; Ascorbic acid; Anthocyanins; Phenols; Small fruit

1. Introduction

Small fruits constitute a good source of natural antioxidant substances. Extracts of fruits from various blackberry, raspberry and gooseberry cultivars act effectively as free radical inhibitors (Heinonen, Meyer, & Frankel, 1998; Wang & Lin, 2000; Wang & Jiao, 2000). In addition, the phenol, anthocyanin and ascorbic acid content of small fruits has been investigated (Kalt, Forney, Martin, & Prior, 1999; Wang, Cao, & Prior, 1996). Polyphenols comprise a wide variety of compounds, divided into several classes (i.e., hydroxybenzoic acids, hydroxycinnamic acids, anthocyanins, proanthocyanindins, flavonols, flavones, flavanols, flavanones, isoflavones, stilbenes and lignans), that occur in fruits and vegetables (Manach, Scalbert, Morand, Remesy, & Jimenez, 2004). Particularly, phenols contribute substantially to the antioxidant complement of many small fruit species, having potential health effects (Heinonen et al., 1998).

It has been already demonstrated that a wide diversity of phytochemical levels and antioxidant capacities exist within and across genera of small fruit (Moyer, Hummer, Finn, Frei, & Wrolstad, 2002). Furthermore, accumulating evidence exists, suggesting that genotype may have a profound influence on the content of bioactive compounds in berries (Anttonen & Karjalainen, 2005). However, to the best of our knowledge few data exist regarding the properties of small fruits originating from the Mediterranean area. In this paper we analysed raspberry, blackberry, raspberry × blackberry hybrids, red currant, gooseberry and Cornelian cherry cultivars, originating from Greece, for their antioxidant capacity, phenol, anthocyanin and ascorbic acid content.

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2. Materials and methods

2.1. Plant material

Samples of raspberry (*Rubus ideaus* L.), blackberry (*Rubus fructicosus*), raspberry × blackberry hybrids, red currant (*Ribes sativum*) and gooseberry (*Ribes grossularia*) cultivars were collected from a commercial farm (Thessaloniki, Northern Greece). Additionally, a native Cornelian cherry population with red colour (*Cornus mas* cv. Vermio) was collected from mount Vermio (altitude = 330 m, Veria, Northern Greece). The examined cultivars and their colour are shown in Table 1. In raspberry cultivars bearing fruit twice (cvs. Heritage, Autumn Bliss, Fallgold), samples were collected from both periods and examined separately. After harvest, the samples were immediately transferred to the laboratory of Horticulture at the Aristotle University of Thessaloniki and frozen at −20 °C, until needed.

2.2. Soluble solids content (SSC)

Samples of the examined cultivars were pooled to obtain a composite sample and analysed for SSC using a digital refractometer (Atago Model PR-1, Tokyo).

2.3. Ascorbic acid content

Ascorbic acid was quantified with the reflectometer set of Merck Co (Merck RQflex) according to their protocol for the juice of red fruit (Ascorbic Acid in Red Coloured Fruit Juices, Merck). Fruit sample (5 g) and 20 ml oxalic acid (1%) were mixed, homogenised for 1 min, and filtered. PVPP (polyvinylpolypyrrolidone) (500 g) was added to 10 ml of the filtered sample, to remove phenols, and 6–7 drops of H_2SO_4 (25%) were added, to reduce the pH to below 1. Results were expressed as mg ascorbic acid (AsA) 100 g^{-1} fresh weight (fw).

Table 1
The examined raspberry, blackberry, raspberry × blackberry hybrids, red currant, gooseberry and cornelian cherry cultivars and their colour

Cultivars	Colour
Rubus ideaus (raspberries)	
Heritage (Fallbearing)	Red
Autumn Bliss (Fallbearing)	Red
Fallgold (Fallbearing)	Yellow
Meeker (Junebearing)	Red
Rubus fructicosus (blackberries)	
Choctaw	Red-black
Thornless Evergreen	Red-black
Chester Thornless	Red-black
Hull Thornless	Red-black
Rubus ideaus × *Rubus fructicosus*	
Tayberry	Red
Sunberry	Red
Silvan	Black
Ribes sativum (red currants)	
London Market	Red
Rovada	Red
White Versailles	Yellow
Ribes grossularia (goosberries)	
Whinham's Industry	Red
White Smith	Yellow
Cornus mas (Cornelian cherry)	
Vermio	Red

2.4. Anthocyanins

Total anthocyanin content was measured with the pH differential absorbance method, as described by Cheng and Breen (1991). Briefly, absorbance of the extract was measured at 510 and 700 nm in buffers at pH 1.0 (hydrochloric acid–potassium chloride, 0.2 M) and 4.5 (acetate acid–sodium acetate, 1 M). Anthocyanin content was calculated using a molar extinction coefficient of 29,600 (cyanidin-3-glucoside) and absorbance of $A = [(A_{510} - A_{700})_{\text{pH 1.0}} - (A_{510} - A_{700})_{\text{pH 4.5}}]$. Results were expressed as mg cyanidin-3-glucoside equivalents 100 g^{-1} fw.

2.5. Total phenol content

Fruit samples were air-dried at 55 °C and homogenised. Dry sample (1 g) was placed in a test tube with 10 ml of extraction solution (50% methanol/H_2O) according to Vinson, Su, Zubik, and Bose (2001). The mixture was placed in the dark at 4 °C for 24 h. The supernatant was collected and replaced with an equal quantity of extraction solution, then placed in the dark at 4 °C for a further 48 h. The two supernatants were mixed and extraction solution was added until a total volume of 25 ml was obtained. This extract was used for determination of phenol content and FRAP assay.

The amount of total phenolics in extracts was determined according to the Folin–Ciocalteu's procedure (Singleton & Rossi, 1965). Briefly, 0.05 ml of diluted extract and 0.45 ml water were mixed with 2.5 ml of 1:10 diluted Folin–Ciocalteu's phenol reagent, followed by 2 ml of 7.5% (w/v) sodium carbonate. After 5 min at 50 °C, absorbance was measured at 760 nm. Phenol content was estimated from a standard curve of gallic acid and results expressed as mg gallic acid equivalents (GAE) 100 g^{-1} dry weight (dw).

2.6. Antioxidant activity

The FRAP assay was developed to measure the ferric reducing ability of plasma at low pH (Benzie & Strain, 1996). A sample containing 3 ml of freshly prepared FRAP solution (0.3 M acetate buffer (pH 3.6) containing 10 mM 2,4,6-tripyridyl-s-triazine (TPTZ) and 40 mM $FeCl_3 \cdot 6H_2O$) and 100 μl of extract (prepared as for phenol determination) was incubated at 37 °C for 4 min and the absorbance was measured at 593 nm. An intense blue colour is formed when the ferric-tripyridyltriazine (Fe^{3+}-TPTZ)

complex is reduced to the ferrous (Fe^{2+}) form at 593 nm. A standard solution of 1 mM L-ascorbic acid in distilled water was prepared. The absorbance change was converted into a FRAP value, by relating the change of absorbance at 593 nm of the test sample to that of the standard solution of L-ascorbic acid (AsA) and results were expressed as μmol AsA g^{-1} dw.

In addition, non-site specific $^{\cdot}OH$ radical scavenging activity was determined according to the deoxyribose method in the presence of 100 μM EDTA (Halliwell, Gutteridge, & Aruoma, 1987). $FeCl_3 \cdot 6H_2O$ and ascorbic acid solutions were prepared in degassed water prior to use. The reaction tube contained 1.5 mM deoxyribose, 1.5 mM H_2O_2, 450 μM L-ascorbic acid, 50 μM $FeCl_3 \cdot 6H_2O$ in 10 mM phosphate buffer (pH 7.4), 1.0 ml total volume. Following incubation at 38 °C for 30 min, 100 μl 100 mM EDTA, 1.0 ml 1.0% thiobarbituric acid + 0.02% butylated hydroxyanisole in 0.05 M NaOH and 1.0 ml 2.8% trichloroacetic acid were added to the reaction mixture, which was then heated in a boiling water bath for 15 min. Once samples were cooled, the absorbances were measured at 532 nm. The percent inhibition of hydroxyl radical was calculated as follows:

$$\%\ \text{Inhibition} = (\text{A Control} - \text{A Sample}) \times 100/\text{A Control}(\text{Abs. 532 nm Control}).$$

Prooxidant activity was determined, using a modification of the deoxyribose assay (Moran, Klucas, Grayer, Abian, & Becana, 1997).

2.7. Statistical analysis

At least three analyses were run for each cultivar for SSC, ascorbic acid, anthocyanin, phenol, total antioxidant and pro oxidant activity. Each analysis consisted of triplicate measurements of each sample and data were averaged over the three measurements. Data were treated for multiple comparisons by analysis of variance (ANOVA), followed by the Duncan's Multiple Range test with significance level $P < 0.05$. Data in percentages were subjected to arcsine transformation prior to statistical analysis. ANOVA was performed using the statistical software SPSS (SPSS Inc., Chicago, USA). Correlation coefficients (r) were also calculated.

3. Results and discussion

3.1. Soluble solids content

Great variability existed among the examined berry fruits, regarding their content in SSC. The highest SSC was in the Cornelian cherry cultivar (14.4%), followed by the blackberry (9.8–11.5%) and raspberry cultivars (7.1–10.8%). The lowest content of soluble solids was recorded in the tayberry hybrid (6.1%) (Table 2).

Table 2
Soluble solids content (%) of the examined cultivars after harvest

Cultivar	SSC (%)
Heritage[a,*]	10.0 ± 0.1def
Heritage[b]	8.0 ± 0.5abc
Autumn Bliss[a]	9.0 ± 1.2bcde
Autumn Bliss[b]	7.1 ± 1.5ab
Fallgold[a]	8.6 ± 2.0bcd
Fallgold[b]	10.8 ± 2.6ef
Meeker	7.3 ± 0.1ab
Tayberry	6.1 ± 0.8a
Sunberry	7.6 ± 0.9ab
Silvan	11.3 ± 1.9 f
Choctaw	11.5 ± 1.5f
Thornless Evergreen	11.5 ± 1.6f
Chester Thornless	10.6 ± 1.6ef
Hull Thornless	9.8 ± 2.2cdef
London Market	7.4 ± 1.2ab
Rovada	10.7 ± 0.8ef
White Versailles	8.4 ± 1.1bcd
Whinham's Industry	8.5 ± 1.4bcd
White Smith	8.5 ± 2.1bcd
Vermio	14.4 ± 2.1 g

[a] June harvest.
[b] Autumn harvest.
[*] Data are the means of three replications ± standard error. Values within column followed by the same letter are not significantly different at $P = 0.05$ (Duncan's Multiple Range test).

3.2. Ascorbic acid

Significant differences in ascorbic acid content among the different species were recorded (Table 3). Cornelian cherry had the highest content of ascorbic acid (103 mg 100 g^{-1} fw) which was up to 7.2-fold higher than the blackberry and blackberry × raspberry cultivars. The red currant cultivars and the autumn raspberry cultivars 'Heritage' and 'Autumn Bliss' had the next highest in ascorbic acid content (31.0–40.0 mg 100 g^{-1} fw), whereas June bearing raspberry and blackberry cultivars contained 16.8–37.7 and 14.3–17.5 mg 100 g^{-1} fw, respectively. These data are in agreement with those reported for other raspberry (21.2–31.1 mg 100 g^{-1} fw) (de Ancos, Gonzalez, & Cano, 2000) and blackberry cultivars (12.3–16.4 mg 100 g^{-1} fw) (Deighton, Brennan, Finn, & Davies, 2000).

The native Cornelian cherry population of the present study showed higher ascorbic acid content compared to other cornelian cherry cultivars (48.4–73.1 mg 100 g^{-1} fw) (Demir & Kalyoncu, 2003). In addition, its content was significantly higher than other fruits well known for their high ascorbic acid content, such as strawberries (46 mg 100 g^{-1} fw) (Roberts & Gordon, 2003), oranges (31 mg 100 g^{-1} fw) (Roberts & Gordon, 2003) and kiwi fruits (29–80 mg 100 g^{-1} fw) (Nishiyama et al., 2004).

3.3. Anthocyanins

Significant differences in anthocyanin content were recorded, since these pigments are responsible for the red and blue colour. The Cornelian cherry cultivar contained

Table 3
Ascorbic acid, anthocyanin and phenol contents of the examined cultivars

Cultivar	Ascorbic acid (mg 100 g^{-1} fw)	Anthocyanin (mg cyanidin-3-glucoside equivalents 100 g^{-1} fw)	Phenol (mg GAE 100 g^{-1} dw)
Heritage[a,*]	32.4 ± 2.1def	49.1 ± 7.8c	1280 ± 39de
Heritage[b]	31.0 ± 1.0cde	48.2 ± 6.4c	1905 ± 58i
Autumn Bliss[a]	37.7 ± 0.7fg	35.1 ± 2.6b	1052 ± 75b
Autumn Bliss[b]	31.0 ± 0.8cde	39.1 ± 6.8bc	2494 ± 77m
Fallgold[a]	18.5 ± 2.0a	1.3 ± 0.4a	1489 ± 33f
Fallgold[b]	16.8 ± 0.2a	3.4 ± 0.3a	1459 ± 66f
Meeker	20.1 ± 1.1ab	42.6 ± 5.3bc	2116 ± 44k
Tayberry	19.7 ± 1.6ab	103.5 ± 7.8d	1891 ± 76i
Sunberry	28.0 ± 2.3cd	175.8 ± 11.3g	2611 ± 69n
Silvan	18.4 ± 2.9a	197.8 ± 18.3h	2016 ± 89j
Choctaw	14.6 ± 1.2a	125.6 ± 1.6e	1703 ± 71h
Thornless Evergreen	17.5 ± 2.7a	146.8 ± 10.0f	2061 ± 148jk
Chester Thornless	14.3 ± 0.9a	134.6 ± 16.3e	2008 ± 99j
Hull Thornless	14.5 ± 1.3a	152.2 ± 8.4f	2349 ±153l
London Market	35.6 ± 2.2efg	7.8 ± 0.8a	1115 ± 42bc
Rovada	40.0 ± 2.3g	7.5 ± 1.6a	1193 ± 64cd
White Versailles	38.1 ± 5.2fg	1.4 ± 0.3a	657 ± 34a
Whinham's Industry	25.4 ± 2.6bc	43.3 ± 2.5bc	1257 ± 65de
White Smith	20.3 ± 1.5ab	2.4 ± 0.3a	1321 ± 69e
Vermio	103.3± 12.6h	223.0 ± 4.2i	1592 ± 132g

[a] June harvest.
[b] Autumn harvest.
[*] Data are the means of three replications ± standard error. Values within column followed by the same letter are not significantly different at $P = 0.05$ (Duncan's Multiple Range test).

the highest anthocyanin content expressed as cyanidin-3-glucoside (223 mg 100 g^{-1} fw), followed by the blackberry and raspberry × blackberry cultivars (104–198 mg 100 g^{-1} fw), whereas raspberry and red gooseberry cultivars contained lower amounts of anthocyanins (35–49 mg 100 g^{-1} fw) (Table 3). The yellow raspberry (cv. Fallgold) and gooseberry (cv. White Smith) cultivars, as well as the red currant cultivars, were characterised by the lowest anthocyanin content (1.3–7.8 mg 100 g^{-1} fw).

Similar results for anthocyanin content have been reported by others researchers, both in raspberry (de Ancos et al., 2000) and blackberry (Wang & Lin, 2000) cultivars, and therefore anthocyanins are regarded as important antioxidants in berry fruits (Mullen et al., 2002). However, in humans the bioavailability of dietary anthocyanins is low(-Mazza, Kay, Cottrell, & Holub, 2002; Wu, Cao, & Prior, 2002).

3.4. Phenol content

Red currant cultivars contained small quantities of phenols expressed as gallic acid equivalents (GAE) (657–1193 mg 100 g^{-1} dw), followed by the gooseberry cultivars (1257–1321 mg 100 g^{-1} dw) (Table 3). Significantly higher phenol content was recorded in the second harvest of the autumn bearing red raspberries, whereas no differences between the harvest period were detected in the yellow raspberry cultivar bearing fruit twice. Our data indicated, besides the fact that raspberry genotype influence of total phenol content (Anttonen & Karjalainen, 2005), that late harvest in particular cultivars significantly increased their phenol content. Blackberry and the raspberry × blackberry cultivars were characterised by the highest phenol, content compared to other species, with values up to 2611 mg 100 g^{-1} dw. Similar results have been reported by other researchers in blackberries (1786–2310 mg 100 g^{-1} dw) and raspberries (1137–2112 mg 100 g^{-1} dw), whereas lower contents in other red currant cultivars have been observed (290–450 mg 100 g^{-1} dw) (de Ancos et al., 2000; Deighton et al., 2000; Prior et al., 1998; Wang & Lin, 2000).

However, even when good experimental evidence exists, results need to be interpreted with caution in relation to human health benefits, as polyphenols may have limited bioavailability and may also be extensively metabolised (Duthie, Gardner, & Kyle, 2003). Bioavailability differs greatly between the various polyphenols, and the most abundant polyphenols are not necessarily those that have the best bioavailability profile, either because they have a lower intrinsic activity or because they are poorly absorbed from the intestine, highly metabolised, or rapidly eliminated.

3.5. FRAP values

Red currant and gooseberry cultivars had the lowest FRAP values (40.7–65.1 μmol AsA g^{-1} dw) (Table 4). The highest antioxidant activity was recorded in blackberry and in raspberry × blackberry cultivars (113.6–169.0 μmol AsA g^{-1} dw). The raspberry cultivars had FRAP values in the range 77.7–145.4 μmol AsA g^{-1} dw. However, the autumn bearing red raspberry cultivars 'Autumn bliss' and 'Heritage' recorded higher FRAP values in fruits of the second harvest, the same as for phenol content (Table 3), whereas no differences between the two harvest periods of the yellow-coloured cultivar 'Fallgold' were observed.

Table 4
Antioxidant capacity of the examined cultivars expressed as FRAP values (μmol g^{-1} dw) and % deoxyribose protection

Cultivar	μmol Ascorbic acid g^{-1} dw	% Deoxyribose protection
Heritage[a,*]	86.5 ± 5.8c	65.2 ± 2.0g
Heritage[b]	118.2 ± 4.8d	66.4 ± 1.0g
Autumn Bliss[a]	77.7 ± 6.7c	53.0 ± 1.5e
Autumn Bliss[b]	145.4 ± 10.9ef	70.5 ± 1.4h
Fallgold[a]	87.2 ± 4.0c	57.1 ± 1.0f
Fallgold[b]	88.8 ± 7.7c	65.8 ± 1.5g
Meeker	133.3 ± 4.6e	92.2 ± 0.5jk
Tayberry	149.3 ± 11.2f	93.7 ± 0.4k
Sunberry	169.7 ± 18.2g	86.7 ± 0.5i
Silvan	135.6 ± 12.4ef	91.1 ± 0.6j
Choctaw	113.6 ± 7.2d	96.4 ± 0.2l
Thornless Evergreen	146.6 ± 17.1ef	95.9 ± 0.5l
Chester Thornless	147.7 ± 18.4f	95.9 ± 0.3l
Hull Thornless	169.0 ± 22.4g	98.9 ± 0.1m
London Market	60.2 ± 2.9b	18.4 ± 2.7b
Rovada	63.3 ± 2.2b	27.0 ± 2.3c
White Versailles	40.7 ± 1.4a	16.1 ± 4.2a
Whinham's Industry	62.8 ± 2.6b	34.1 ± 3.4d
White Smith	65.1 ± 3.1b	35.3 ± 2.7d
Vermio	83.9 ± 5.4c	98.6 ± 0.3m

[a] June harvest.
[b] Autumn harvest.
[*] Data are the means of three replications ± standard error. Values within column followed by the same letter are not significantly different at $P = 0.05$ (Duncan's Multiple Range test).

FRAP values were highly correlated with phenol content ($r = 0.947$), whereas a less linear correlation between total antioxidant capacity and anthocyanin content was recorded ($r = 0.635$) (Table 5). Inversely, ascorbic acid content was negatively correlated with FRAP values ($r = -0.363$).

Similar results have been reported by other researchers (Wang & Lin, 2000), who found a linear correlation between total antioxidant capacity and phenol content both in blackberries ($r = 0.961$) and raspberries ($r = 0.911$). In addition, Deighton et al. (2000) reported that there were apparent linear relationships between antioxidant capacity (assessed FRAP) and total phenols ($r = 0.965$), whereas anthocyanin content had a minor influence on antioxidant capacity ($r = 0.588$) and ascorbic acid contributed only minimally to the antioxidant potential of Rubus juices.

Cornelian cherry, which was characterised by the highest ascorbic acid and anthocyanin content and one of the highest phenol contents, possessed a relatively low FRAP value (83.9 μmol AsA g^{-1} dw), which may be due to the fact that during the air-drying of the sample at 55 °C for the FRAP assay, a significant part of the ascorbic acid and anthocyanin content was destroyed. Piga, del Caro, and Corda (2003) found losses in ascorbic acid of 55% and in anthocyanins of 90% in plum fruits after drying at 60 °C.

Table 5
Correlation coefficients (r) of antioxidant capacity with ascorbic acid, anthocyanin and phenol contents

	Correlation coefficient (r)	
	FRAP	Deoxyribose assay
Ascorbic acid	−0.363	−0.082
Anthocyanins	0.635	0.789
Phenols	0.947	0.773
FRAP	–	0.838
Deoxyribose protection	0.838	–

The assessment of antioxidant activity can be done by using different *in vitro* methods. The FRAP assay is one of the most rapid tests and very useful for routine analysis, since a lot of samples can be analysed within a short time, although it has the limitation that it is conducted at non-physiological pH values. FRAP assay works employing metals ions for oxidation, measuring the formed ferrous ions by increased absorbance, instead of the use of organic radical producers (Schlesier, Harwat, Bohm, & Bitsch, 2002). The same authors strongly suggested the application of at least two methods for determination of antioxidant activity, due to differences between the test systems.

3.6. Deoxyribose protection

Red currants (16.1–27.0%) and gooseberry (34.1–35.3%) cultivars showed the lowest deoxyribose protection compared to other species (Table 4). Among red currant cultivars, the red-coloured had a higher percentage of deoxyribose protection, compared to the yellow-coloured, whereas non significant differences were detected among gooseberry cultivars. The deoxyribose protection among raspberry cultivars was in the range 65.2–92.2%, with the June bearing cultivar 'Meeker' possessing the highest percentage. The raspberry × blackberry and the blackberry cultivars showed higher deoxyribose protection compared

to raspberry, gooseberry and red currant cultivars, whereas the Cornelian cherry cultivar showed the highest deoxyribose protection (98.6%), along with the blackberry cultivar 'Hull Thornless' (98.9%). It has been reported that blackberries had the highest antioxidant capacity for the inhibition of free radicals (Wang & Jiao, 2000), and our findings agree with these data.

Deoxyribose protection had a relatively high correlation with FRAP values ($r = 0.838$), anthocyanin ($r = 0.789$) and phenol content ($r = 0.773$). Considerable data suggest that higher contents of total phenolics, flavonoids, and anthocyanins in red raspberry fruits contribute to their higher antioxidant activity (Wang & Lin, 2000). Our data are in agreement with those reported by other researchers (Kalt et al., 1999) who postulated that antioxidant capacity was strongly correlated with the total phenol ($r = 0.830$) and anthocyanin ($r = 0.900$) content in other small fruits. Inversely, ascorbic acid made only a small contribution (0.4–9.4%) to the total antioxidant capacity of the fruit (Kalt et al., 1999). In addition, when Kalt et al. (1999) made a comparative study, examining the antioxidant properties of small fruits, they divided them into two distinct groups: (a) those with high phenolics, anthocyanins, and antioxidant capacity (measured as oxygen radical absorbing capacity) and low ascorbate; and (b) those with low phenolics, anthocyanins, and antioxidant capacity and high ascorbate. These data strengthen the hypothesis that no direct correlation between ascorbic acid content and total antioxidant capacity can be established. A strong correlation ($r = 0.930$–0.960) between total phenolics and antioxidant activity has been also reported in stone fruits (Gil, Tomäs-Barberän, Hess-Pierce, & Kader, 2002).

In most samples, a close correlation of antioxidant capacity, as measured by the two methods, was recorded, except for the Cornelian cherry fruit. This might be attributed to different phenol compositions among different species. It is well documented that deoxyribose protection varies among different phenolic substances (Moran et al., 1997). Therefore, deoxyribose protection is highly dependent, not just on total phenol content, but on phenol type, and antioxidant capacity. A multitude of phenolic compounds have been detected in berries, including flavanols (kaempferol, quercetin, myricetin) and phenolic acids (ellagic, gallic, *p*-hydroxybenzoic, ferulic, caffeic, *p*-coumaric acid), and great differences among berry species exist, with regard to their phenolic profiles (Hakkinen et al., 1999).

3.7. Prooxidant activity

Prooxidant activity was monitored in gallic acid (50 μM) and ascorbic acid (50 μM) solutions, for comparative studies. Results indicated that their absorbance were 132% and 228%, respectively, compared to the control (100%). Prooxidant activity was recorded solely in the second harvest of the raspberry cultivar 'Autumn bliss' (103%), in the red currant cultivars 'London Market' (102%) and 'Rovada' (106%), and in the two gooseberry cultivars (101%). No prooxidant activity was observed in any of the other cultivars. These results indicate that the extracts of almost all the examined cultivars possessed antioxidant capacity greater than their ability to degrade deoxyribose. Furthermore, the Cornelian cherry samples showed the lowest prooxidant activity. Rødtjer, Skibsted, and Andersen (2006) monitored the antioxidant and prooxidant activities of pure phenolic compounds and illustrated the very different properties that these compounds can have in oxidation reactions. Therefore, prooxidant activity cannot be correlated with antioxidant capacity and especially with ascorbic acid and anthocyanin content (see Table 6).

Table 6
Prooxidant activity expressed as % absorbance compared with control (not containing sample)

Cultivar	% Absorbance
Heritage[a]	84.7 ± 1.0ef
Heritage[b]	92.3 ± 2.1gh
Autumn Bliss[a]	80.1 ± 2.5bc
Autumn Bliss[b]	103.1 ± 1.4l
Fallgold[a]	95.3 ± 1.6ij
Fallgold[b]	94.2 ± 2.0hi
Meeker	97.0 ± 2.2j
Tayberry	79.8 ± 1.5bc
Sunberry	90.8 ± 0.7g
Silvan	74.6 ± 1.6a
Choctaw	79.4 ± 5.5b
Thornless Evergreen	86.0 ± 3.3f
Chester Thornless	81.8 ± 0.5cd
Hull Thornless	82.5 ± 1.5de
London Market	101.8 ± 1.7kl
Rovada	106.0 ± 1.4m
White Versailles	93.8 ± 0.3hi
Whinham's Industry	100.8 ± 0.1kl
White Smith	100.9 ± 0.9kl
Vermio	76.3 ± 0.6a
Control[*]	100.0 ± 0.0k
Gallic acid, 50 μM	131.5 ± 2.1n
Ascorbic acid, 50 μM	227.6 ± 0.4o

[a] June harvest.
[b] Autumn harvest.
[*] Data are the means of three replications ± standard error. Values within column followed by the same letter are not significantly different at $P = 0.05$ (Duncan's Multiple Range test).

4. Conclusions

Small fruits are a significant source of phenolic compounds and ascorbic acid. Antioxidant activity varied greatly among the berry cultivars used in this study and was highly correlated with their contents of phenolic compounds. The present study indicates that the Cornelian cherry is an extremely rich source of ascorbic acid, anthocyanin, phenols and antioxidants, demonstrating its potential use as a food additive.

Cornelian cherry is found at relative high altitude, only in the Mediterranean area and to the best of our knowledge, few data exist regarding their quality attributes (Demir & Kalyoncu, 2003). Since commercial Cornelian cherry cultivars do not exist, further studies should be con-

ducted among native populations, in order to determine those high in antioxidant properties, which could be used as breeding material.

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