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Antioxidant Composition in Cherry and High-Pigment Tomato Cultivars

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Fourteen cultivars of cherry tomatoes and four cultivars of high-pigment tomato hybrids were cultivated in southern Italy, and the red-ripe fruits were analyzed for their content in different classes of antioxidants and for their antioxidant activity. Among the different cultivars, significant differences were found between lycopene, β-carotene, α-tocopherol, vitamin C (ascorbic acid and dehydroascorbic acid), and total phenolic and flavonoid contents. LS203 and Corbus appear to be the cultivars with the highest content of lipophilic and hydrophilic antioxidants among cherry tomatoes, respectively. All cultivars of high-pigment tomato hybrids showed an expected exceptionally high lycopene content. Among them, the highest content of lipophilic and hydrophilic antioxidants was found in cv. HLY 13. Hydrophilic and lipophilic antioxidant activities were both significantly influenced by genotype. Such results highlight an existing unexploited variability in tomato germplasm and stress the need to evaluate the biodiversity and to support conventional breeding programs to improve tomato nutritional value.

KEYWORDS: ***Lycopersicon esculentum*; tomato; antioxidants; lycopene; β-carotene; vitamin C; AsA/DHA; phenols; flavonoids**

INTRODUCTION

The awareness of harmful effects of free radicals for human health has recently increased. Free radicals are very unstable molecules arising physiologically during cellular aerobic metabolism (∼2−3% of oxygen consumed by a cell is converted into free radicals) (*1*). They react quickly with other compounds, beginning chain reactions. Once the process is started, it can cascade, finally resulting in disruption of a living cell or in molecular and cellular DNA damage (*2*). Normally, the human body can handle these compounds, but if their amount becomes excessive, damage can occur. Free radicals have been indicated as probable pathogenesis determinants of many degenerative and chronic diseases that develop with age, such as cancer, cardiovascular disease, cataract, and immunity system dysfunctions (*2*). For their potential role in preventing such diseases, natural compounds with antioxidant activity have gained the attention of researchers and nutritionists. Estimation of the antioxidant activity is becoming, in fact, an evaluation parameter for the nutritional quality of food.

A large number of fresh fruits and vegetables are primary sources of antioxidants. As such, a high intake of fresh fruits and vegetables has been demonstrated to be protective against both heart disease and certain types of cancer (*3*). Tomatoes (*Lycopersicon esculentum* Mill.), commonly used in the Mediterranean diet, are a major source of antioxidants and contribute to the daily intake of a significant amount of these molecules. They are consumed fresh or as processed products (canned tomatoes, sauces, juice, ketchup, soup). The consumption of fresh tomatoes and tomato products has been inversely related to the development of some types of cancer (*3*) and to plasma lipid peroxidation (*4*, *5*).

Tomatoes contain different classes of substances with antioxidant properties such as carotenoids, vitamin C, phenolics, and tocopherols. Lycopene is the major carotenoid present in tomatoes, accounting for >80% of the total tomato carotenoids in fully red-ripe fruits, where it is responsible for their characteristic color (*6*). Lycopene shows strong antioxidant activity both in vitro and in vivo (*7*). It has the highest antioxidant activity among all dietary antioxidants (*8*, *9*), and it is fairly stable to storage and cooking. In addition, heat processing such as cooking, required for the preparation of tomato sauces, is recommended because it increases the bioavailability of lycopene in the human body (*10*).

Tomatoes also contain moderate amounts of α- and β-carotenes and lutein. β-Carotene is known for its provitamin A activity and lutein for its association with a reduced risk of lung cancer (*11*). In addition, tomatoes have gained the attention also as source of vitamins C and E (*12*) and phenolics (*13*). Phenolic compounds are important secondary metabolites in plants commonly substituted by sugar moieties. Many phenolic compounds exhibit antioxidative, anticarcinogenic, antimicrobial, antiallergic, antimutagenic, and anti-inflammatory activities (*13*). Among phenolic compounds, flavonoids reduce low-

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density lipoprotein (LDL) oxidation and quench reactive oxygen radicals, thereby decreasing the risk of cardiovascular diseases and cancer (*14*, *15*).

It has been shown that a single compound or class of compounds cannot determine their positive effect on health even associated with the consumption of fresh fruits and vegetables; rather it is exerted by the whole pool of antioxidants, with noticeable synergistic effects. Lycopene synergizes with other natural compounds, such as α-tocopherol and 1,25-dihydroxy-vitamin D_3, in inhibiting prostate carcinoma cell proliferation (*16*), HL-60 leukemic cell differentiation (*17*), and LDL oxidation (*5*). Evidence for the interaction between vitamins C and E in defending lipoproteins against oxidative damage has been recently suggested in a study on young men (*18*). Therefore, to assess the nutritional quality of fresh tomatoes, it is important to use a multifactorial approach analyzing all of the main compounds having antioxidant activity.

It is known that the amount of each antioxidant in the vegetables is strongly influenced by varietal differences in addition to agronomical, geographical, and environmental factors (*9*, *19*, *20*). The aim of this study was to highlight variations in the nutritional value of 14 different cultivars of fresh uniformly ripe cherry tomatoes (red-ripe stage) and 4 industrial tomato cultivars characterized by a high content of lycopene (hereafter named high-pigment tomato hybrids), by evaluating different classes of antioxidants. Insight into various antioxidant components of tomatoes would aid in the selection of high added nutritional value cultivars.

MATERIALS AND METHODS

Tomato Sampling. Seeds of 14 different cultivars of cherry tomatoes (Cherubino, Cherelino, Corallino, Corbus, LS203, Lycorino, Minired, Naomi, Piccadilly, Rubino Top, Sakura, Salentino, Sharon, and Shiren) and 4 cultivars of high-pigment tomato hybrids (HLY 02, HLY 13, HLY 18, and Kalvert) were germinated in alveolar boxes at the beginning of April 2005. One-month-old tomato seedlings were transplanted in a field in the province of Lecce (southern Italy) and grown to maturity. Standard agronomical techniques were used for plant nutrition and pathogen prevention. Briefly, the field was deep ploughed (60−70 cm) and 1000 kg/ha of a basic organomineral fertilizer (Fertil agreste start, Scam) was spread. Post-transplant nitric nutrition with ammonium nitrate (fertilizer Leon, Hydro Agri), 600 kg/ha, was given when required. Propamocarb hydrochloride, a fungicide, Confidor Supra (Bayer), an insecticide, and metallic copper were used for pest control.

Uniformly ripe healthy fruits, at the red-ripe stage, were harvested and immediately analyzed for antioxidant content [lycopene, β-carotene, ascorbic acid (AsA), dehydroascorbic acid (DHA), α-tocopherol, and total phenolics and flavonoids] as well as for hydrophilic and lipophilic antioxidant activities.

Sample Preparation. Three uniform fruits for each cultivar were cut into small pieces and sequentially homogenized in a Waring blender for 2 min and in a 100 mL glass potter in 1:1 w/w cold homogenization buffer [40 mM Hepes (Na^+), pH 7.5, containing 10 mM imidazole (as glucosidase inhibitor), 1 mM benzamidine, 5 mM 6-amino-*n*-hexanoic acid, and 1 mM phenylmethanesulfonyl fluoride (as proteinase inhibitors), and 10 mM dithiothreitol]. The homogeneous suspension was used for analyses.

Dry Weight Determination. The dry weight of each sample was determined on 1 g triplicate aliquots of the homogenate suspension by using a Büchi TO-50 infrared dryer at 70 °C. The weight was recorded at 1 day intervals until it remained unchanged.

Lycopene and β-Carotene Assay. Lycopene and β-carotene contents were determined on triplicate aliquots of the homogenate suspension (0.5 g) according to the method of Sadler et al. (*21*) as modified by Perkins-Veazie et al. (*22*). Carotenoids were extracted with 0.05% (w/v) butylated hydroxytoluene (BHT) in acetone and 95% ethanol (1:1 v/v). Lycopene and β-carotene were separated by partition into hexane and directly assayed. A Dionex HPLC instrument with an AD 25 UV−vis detector was used, and the separation was performed at 31 °C on an Acclaim HPLC column C_{18} (5 μm, 250 × 4.6 mm). The separation was performed by using a linear gradient of acetonitrile (A), hexane (B), and methanol (C), as follows: from 70% A, 7% B, 23% C to 70% A, 4% B, 26% C within 35 min, with a flow rate of 1.5 mL/min. Concentration of standard solutions was calculated using the molar extinction coefficients of 17.2×10^4 for lycopene and 13.9×10^4 for β-carotene in hexane. Peaks were detected at 503 nm.

α-Tocopherol Assay. The content of α-tocopherol was determined by HPLC as described by Fryer et al. (*23*), slightly modified. One gram of the homogenate suspension (three replicates) was treated with 13.5 mL of extraction buffer (2 mM AsA, 5 mM $MgCl_2$, 80 mM H_2SO_4), and tocopherols were partitioned by their solubility in hexane. The hexane was taken to dryness, and the resulting dry sample was resuspended in 1 mL of absolute ethanol. The separation was performed by using a linear gradient of acetonitrile (A), hexane (B), and methanol (C), as follows: from 70% A, 7% B, 23% C to 70% A, 6% B, 24% C within 15 min, with a flow rate of 1.5 mL/min. α-Tocopherol was detected at 280 nm.

Ascorbic Acid (AsA) and Dehydroascorbic Acid (DHA) Assay. AsA and DHA content was determined as reported by Kampfenkel et al. (*24*) on triplicate aliquots of homogenate suspension (0.1 g). AsA and DHA were extracted by using 6% metaphosphoric acid and detected at 525 nm in a Beckman DU 650 spectrophotometer.

Total Phenols Assay. Total phenols were extracted as described by Martinez-Valverde et al. (*13*) on triplicate aliquots of homogenate suspension (0.3 g). Briefly, 5 mL of 80% aqueous methanol and 50 μL of 37% HCl were added to each sample. The extraction was performed at 4 °C, for 2 h, under constant shaking (300 rpm). Samples were centrifuged at 10000*g* for 15 min. The total phenols assay was performed by using the Folin−Ciocalteu reagent as described by Spanos and Wrolstad (*25*) on triplicate 50 μL aliquots of the supernatant. The absorbance was read at 750 nm using a Beckman DU 650 spectrophotometer. Results were expressed as milligrams of gallic acid equivalents (GAE).

Flavonoid Assay. The flavonoid content was measured using the colorimetric assay described by Zhishen et al. (*26*) on triplicate aliquots of homogenate suspension (0.3 g). Fifty microliter aliquots of the absolute methanol extract were used for flavonoids determination. Samples were diluted with distilled water to a final volume of 0.5 mL, and 30 μL of 5% $NaNO_2$ was added. Sixty microliters of 10% $AlCl_3$ and 200 μL of 1 M NaOH plus 210 μL of distilled water were added, respectively, after 5 min and after a further 6 min. Absorbance was read at 510 nm using a Beckman DU 650 spectrophotometer, and flavonoid content was expressed as milligrams of rutin equivalents (RE).

Measurement of Antioxidant Activity. Hydrophilic and lipophilic antioxidants were extracted from 0.3 g homogenate aliquots (three replicates) with absolute methanol or hexane at 4 °C, under constant shaking (300 rpm), overnight. Samples were centrifuged at 10000*g*, and supernatants were used for analysis. Antioxidant activity was measured in both hydrophilic and lipophilic fractions using the FRAP assay method (*27*). Fifty microliters of hydrophilic or lipophilic tomato extract was added to 1.5 mL of FRAP reagent [1 mM 2,4,6-tripyridyl-2-triazine (TPTZ) and 20 mM ferric chloride in 0.25 M sodium acetate buffer, pH 3.6] and mixed thoroughly. After 4 min at 20 °C, absorbance at 593 nm was measured against water. A calibration curve (50−1000 μM ferrous ion) was produced with freshly prepared ammonium ferrous sulfate. Values were obtained from three replicates and expressed as millimolar FRAP per gram of fresh weight.

Statistical Analysis. Results are presented as mean value ± standard deviation. Statistical analysis was based on Student's *t* test. Significant difference was statistically considered at $P < 0.001$.

RESULTS AND DISCUSSION

There is increasing evidence that the consumption of fresh tomatoes could play an important role in enhancing the antioxidant intake in the human diet, leading to an improvement in the protection of the organism against free radicals, which are important causative agents of a number of human diseases.

Many epidemiological studies indicate that the regular consumption of tomatoes may lead to a lower risk of various forms of cancer (*3*, *7*).

In this study we report variations in the nutritional value of 14 different cultivars of cherry tomatoes and 4 cultivars of high-pigment tomato hybrids. The comparison was done by evaluating all major compounds having antioxidant properties, as well as the antioxidant activity of the hydrophilic and lipophilic fractions.

Cherry tomatoes are characterized by relatively high levels of antioxidants such as vitamin C, tocopherols, total phenols, and carotenoids, particularly lycopene. These tomatoes are usually consumed raw in salad dressed with olive oil, which increases the bioavailability of such molecules and consequently their salutary effects on human health (*10*). High-pigment tomato hybrids are relatively new selections obtained by conventional plant-breeding programs finalized to increase lycopene content. The increase of lycopene amount is of particular importance in tomatoes subjected to industrial processing to compensate for the loss of antioxidant activity due to chemical, physical, and biological factors (*28*).

It has been well established that the total antioxidant content of fresh tomatoes can be affected by many pre- and postharvest factors such as agronomic and cultural practices, ripening stage at harvest, and storage conditions (*9*, *19*, *29*). To minimize the influence of such factors on genotype-related variability of field-grown tomatoes, all cultivars under analysis were grown simultaneously in the same field and subjected to identical cultural practices and, of course, environmental conditions. Only fully ripe tomatoes (red-ripe stage) were harvested and analyzed. The ripening stage of tomatoes can, in fact, affect their lycopene as well as other antioxidants content (*19*, *20*, *29*).

It has been demonstrated that the highest amount of lycopene accumulates in the tomato skin and that the skin and the seeds are important contributors to the major antioxidants of tomatoes (*30*). Therefore, our analyses were performed on whole tomatoes for a real estimation of the total antioxidant content.

The different cultivars of cherry tomatoes showed a high variation in the content of lycopene (**Figure 1**). A variation between 1- and 3-fold was found expressing the data on either a fresh weight (fw) or a dry weight (dw) basis. In both cases, the highest lycopene content was found in cv. LS203 (120 mg/kg of fw; 1.3 g/kg of dw) and the lowest in cv. Rubino Top (43 mg/kg of fw; 0.5 g/kg of dw). Similar variations in lycopene content, ranging from 50 to 110 mg/100 g of fw, have been reported in Hungarian varieties of tomatoes (*19*). Variations between 20 and 70 mg/kg of fw have also been reported in Indian cultivars (*9*, *31*). Kuti and Konuru (32) have been recently reported a content of lycopene ranging between 74 and 117 mg/kg of fw in other cultivars of field-grown cherry tomatoes. A less extended variability in lycopene content was found in high-pigment tomato hybrids ranging from 253 mg/kg of fw (2.7 g/kg of dw), found in Kalvert, to 175 mg/kg of fw (2.2 g/kg of dw) in HLY 13, which was found to be the cultivar with the lowest content of lycopene. When data were expressed on a dw basis, HLY 02 was determined to be the richest cultivar in lycopene (3.2 g/kg of dw) with a content 2.4−7-fold higher than that of cherry tomatoes. Our values are comparable with those reported for field-grown tomatoes by Abushita et al. (*19*), Gomez et al. (*33*), and Takeoka et al. (*34*), ranging from 52 to 236 mg/kg of fw, and confirm that field-grown tomatoes generally present higher levels of lycopene with respect of greenhouse-grown tomatoes, in which it ranges between 1 and 108 mg/kg of fw (*20*, *35*).

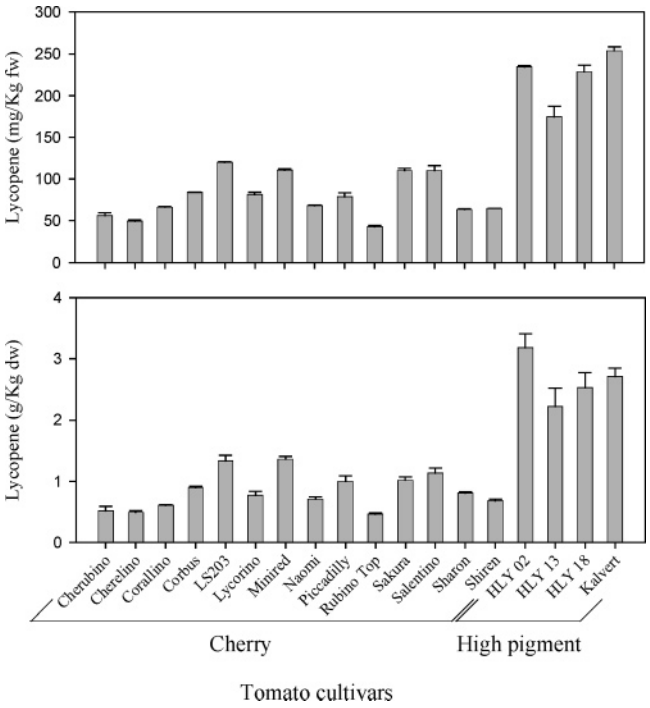

Figure 1. Content of lycopene in various cultivars of cherry and high-pigment tomatoes. Data are means ± standard deviation of three replicates.

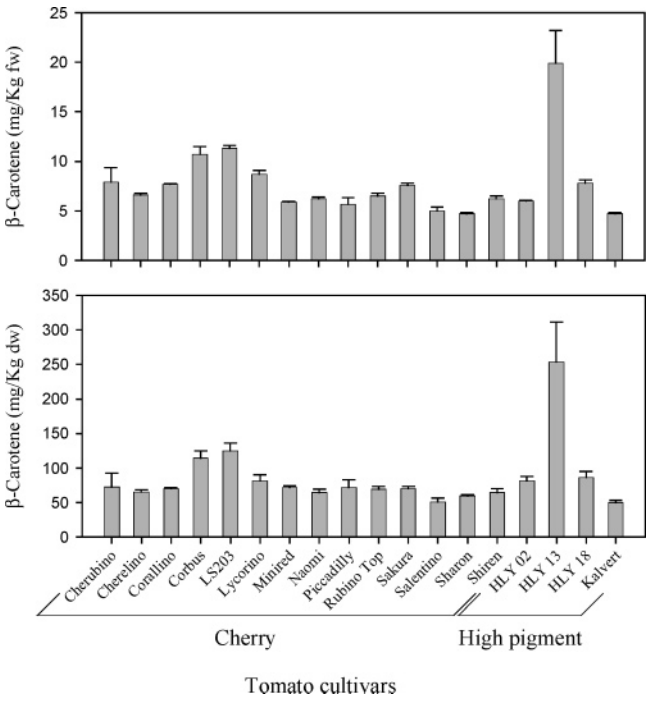

Figure 2. Content of β-carotene in various cultivars of cherry and high-pigment tomatoes. Data are means ± standard deviation of three replicates.

Although lycopene represents the most abundant carotenoid in red-ripe tomatoes, approximately from 80 to 90% of the total pigments, we have also measured the amount of β-carotene (**Figure 2**). Other carotenoids such as α-carotene, phytoene, and phytofluene, which have been reported to accumulate during ripening in tomato fruit and to account, all together, for ∼6.8% of the total carotenoids (*20*), were not detectable in all analyzed cultivars. β-Carotene accounted for 4.3−12.2% of the total carotenoids in cherry tomatoes and for 1.8−3.3% in three (HLY 02, HLY 18, Kalvert) of the four analyzed high-pigment cultivars. A significantly high content of β-carotene was found

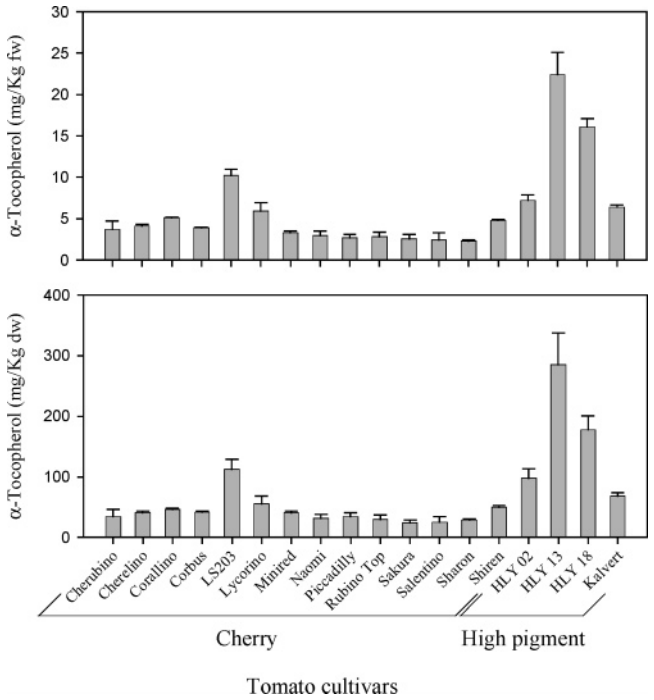

Figure 3. Content of α-tocopherol in various cultivars of cherry and high-pigment tomatoes. Data are means ± standard deviation of three replicates.

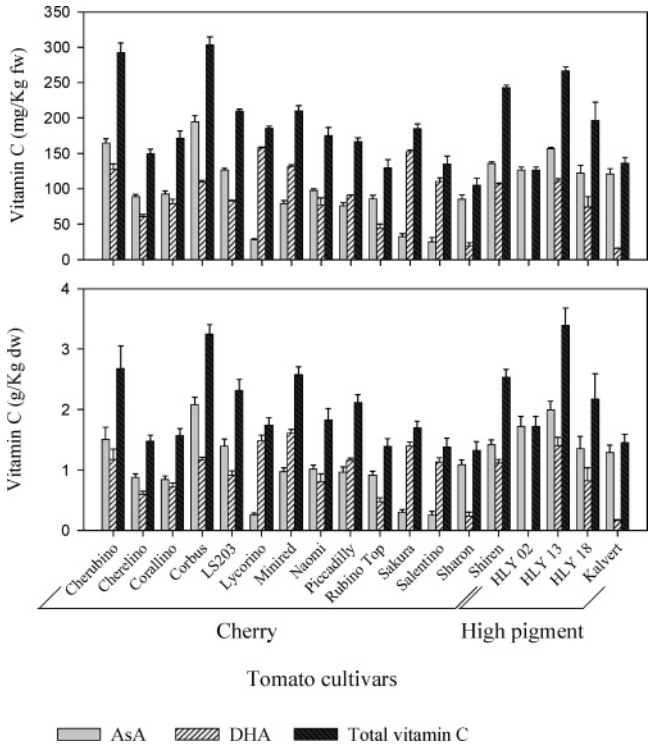

Figure 4. Content of ascorbic (AsA) and dehydroascorbic acid (DHA) in various cultivars of cherry and high-pigment tomatoes. Data are means ± standard deviation of three replicates.

in HLY 13, in which it represented 10.2% of the total carotenoids, indicating that in this hybrid the high amount of lycopene was also associated with a high amount of β-carotene. LS203 (11 mg/kg of fw; 125 mg/kg of dw) and HLY 13 (20 mg/kg of fw; 253 mg/kg of dw) were found to be the cultivars with the highest contents of β-carotene among cherry and high-pigment tomato hybrids, respectively. On the contrary, the lowest amount of β-carotene was found in Sharon and Salentino (approximately 5 mg/kg of fw; <60 mg/kg of dw) and in Kalvert (5 mg/kg of fw; 50 mg/kg of dw) cultivars among cherry and high-pigment tomato hybrids, respectively.

R,*R*,*R*-α-Tocopherol is the most biologically active form of vitamin E. It is essential for normal growth and development of the human body, and its deficiency often leads to clinical abnormalities (*36*). It has also been recently proposed that α-tocopherol enhances some biological properties of lycopene such as inhibition of cell proliferation (*16*) and LDL oxidation, and reduction of aortic valve lesion (*5*). **Figure 3** shows the results obtained from the determination of α-tocopherol content in the 14 cultivars of cherry tomato and in the 4 high-pigment tomato hybrids under investigation. The highest values (10 mg/kg of fw; 113 mg/kg of dw) were obtained with LS203, in this cultivar the amount of α-tocopherol appeared to be exceptionally higher than that observed in the other cherry cultivars analyzed in this study and also with respect to other cultivars of tomatoes (0.96−3.15 mg/kg of fw) (*37*). The lowest values of α-tocopherol were estimated in Salentino (2 mg/kg of fw, 25 mg/kg of dw) and Sharon (2 mg/kg of fw, 29 mg/kg of dw) cultivars. A very high content of α-tocopherol was also found in high-pigment tomato hybrids (22 mg/kg of fw, 285 mg/kg of dw in HLY 13; 16 mg/kg of fw, 43 mg/kg of dw in HLY 18; 7 mg/kg of fw, 98 mg/kg of dw in HLY 02; 6 mg/kg of fw, 68 mg/kg of dw in Kalvert), which could somehow be correlated with high lycopene levels. In mature tomato fruits, naturally occurring mutations that increase carotenoid content, including lycopene, are also characterized by a dramatic increase in plastid biogenesis and in the production of other compounds such as vitamin C and flavonoids (*38*).

It has been reported that tomato fruit has a moderate amount of vitamin C (20 mg/100 g of fw) (*39*). Both AsA and its oxidized form, DHA, contribute to vitamin C content. Changes between cultivars have been observed; AsA and DHA contents evidenced the highest variability among tomato antioxidants (**Figure 4**). The oxidized form accounted for between 0 and 85% of the total vitamin C, a range larger than that observed by Raffo et al. (*20*), which was between 22 and 54%. It is well-known that the amount of DHA acid is strongly affected by experimental procedures (*40*). Cv. Corbus showed the highest amount of AsA (194 mg/kg of fw; 2.1 g/kg of dw) and also a considerable amount of DHA (109 mg/kg of fw; 1.2 g/kg of dw); Salentino, Lycorino, and Sakura had a low content of AsA (<33 mg/kg of fw) but a high content of its oxidized form (from 110 to 158 mg/kg of fw). The amounts of AsA and DHA in high-pigment tomato hybrids were similar to that observed in cherry tomatoes, ranging from 157 mg/kg of fw (2.0 g/kg of dw) in HLY 13 to 121 mg/kg fw (1.3 g/kg of dw) in Kalvert for AsA and from 110 mg/kg of fw (1.4 g/kg of dw) in HLY 13 to 0 mg/kg in HLY 02 for DHA. Differences were also evidenced in the redox state of the system AsA/DHA of the different tomato cultivars. Because many environmental conditions change the redox state of this system, it has been proposed that it could function as a sensor modulating cellular metabolism and hormone sensitivity in response to exogenous factors (*40*). This suggests that tomato cultivars can perceive the surrounding environment in a different way, according to their genotype.

Tomatoes have been identified as the most important suppliers of phenols in the human diet, followed by corn and beans (*41*). Although it has been reported that some phenols occurring in large amount in the cuticular membrane of ripe tomato fruits, such as the flavonoid chalcone chalconaringenin and the flavanone naringenin, may express a pro-oxidative effect, that is, they promote rather than limit the oxidation of LDL by copper (*42*, *43*), some other phenols, such as epicatechin, often

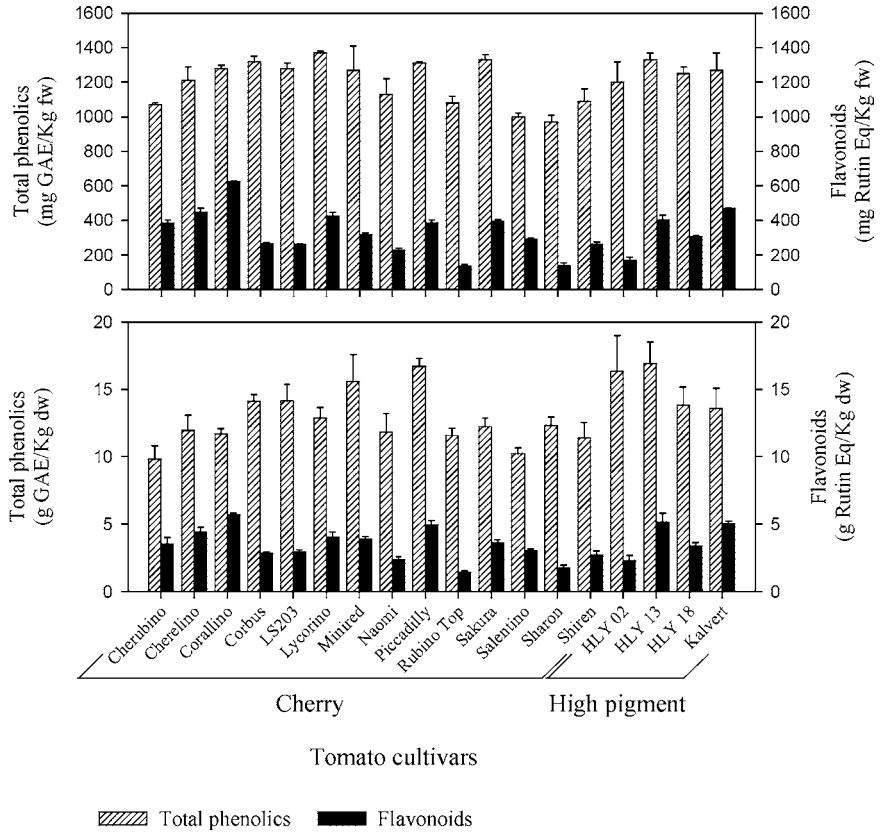

Figure 5. Content of total phenolics and flavonoids in various cultivars of cherry and high-pigment tomatoes. Data are means ± standard deviation of three replicates.

surpass the antioxidant effect of well-known vitamins C and E, suggesting a protective role in reducing oxidative stress (*13*). For this reason, cherry and high-pigment tomatoes were also analyzed for phenolic content (**Figure 5**). The amount of total hydrophilic phenolics, as determined by the Folin−Ciocalteu assay, was considerably higher in comparison with those reported in the literature for tomatoes (190−670 mg of catechin equiv/kg of fw) (*9*). Although genetic control is the primary factor in determining phenolic compound content in fruits and vegetables, variations may be also caused by environmental factors, such as light and temperature (*44*). High solar irradiance, typical of southern Italy, could cause the increase of phenols, which tend to accumulate in the epidermal tissue because of their potential role in protection against ultraviolet radiation (*45*). Moreover, it has been proposed that the greater skin/volume ratio of cherry tomatoes could enhance their phenolic content, in particular, flavonols, because these compounds occur within the skin of the berry (*46*). In cherry tomatoes, the cv. Lycorino showed the highest total phenolic content (1370 mg of GAE/kg of fw), followed by Sakura (1330 mg of GAE/kg of fw) and Corbus (1320 mg of GAE/kg of fw). The former cultivar differed from Sharon and Salentino, which showed the lowest phenolic contents, 970 and 1000 mg of GAE/kg of fw, respectively. Concerning high-pigment tomato hybrids, phenol content ranges between 1330 mg of GAE/kg of fw in HLY 13 and 1200 mg of GAE/kg of fw in HLY 02, which is still a very high amount if compared with other cultivars. Differences were evidenced when data were expressed on a dw basis; in this case, Piccadilly was the cherry cultivar with the highest amount of phenols (16.7 g of GAE/kg of dw), whereas Kalvert was the cultivar with the lowest amount of phenols (13.6 g of GAE/kg of dw) among high-pigment tomato hybrids.

Flavonoids, which are the major components of the total phenolic content of tomatoes, were also analyzed and quantified. Tomatoes have been considered to be a relatively rich source of flavonoids, with an average of 5 mg/100 g of fw (*46*). In our analyses, flavonoids accounted for 12−49% of total phenols in tomatoes. Significant differences were observed in the total flavonoids of the different examined cultivars (**Figure 5**). Corallino was the cultivar with the highest content of flavonoids among cherry tomatoes (622 mg of RE/kg of fw; 5.7 g of RE/kg of dw), 4.6-fold greater than that measured in Rubino Top (134 mg of RE/kg of fw; 1.4 g of RE/kg of dw). Among the high-pigment tomato hybrids, Kalvert and HLY 13 were the cultivars with the highest contents of flavonoids (470 mg of RE/kg of fw, 5.0 g of RE/kg of dw; and 402 mg of RE/kg of fw, 5.1 g of RE/kg of dw, respectively), followed by HLY 18 (306 mg of RE/kg of fw; 3.4 g of RE/kg of dw) and HLY 02 (168 mg of RE/kg of fw; 2.3 g of RE/kg of dw), which was the poorest cultivar in flavonoid content.

The evaluation of total antioxidant activity is of great relevance in the field of nutrition and food technology. It represents a measure of the capacity of food extracts to delay oxidation processes in a controlled system (*9*), allowing an evaluation of the possible synergistic and/or antagonistic effects of bioactive compounds taken together in determining the antioxidant activity of such extracts (*47*). Cv. Corbus showed the highest total hydrophilic antioxidant activity, as evaluated by FRAP value (4.53 mM FRAP/g of fw) followed by Cherubino (3.52 mM FRAP/g of fw) and Corallino and Shiren (both 3.33 mM FRAP/g of fw) (**Figure 6**). The antioxidant activity of these cultivars was at least 1.5-fold greater than the FRAP values detected from cv. Sharon and cv. Salentino (2.16 and 2.19 mM FRAP/g of fw, respectively), which were the

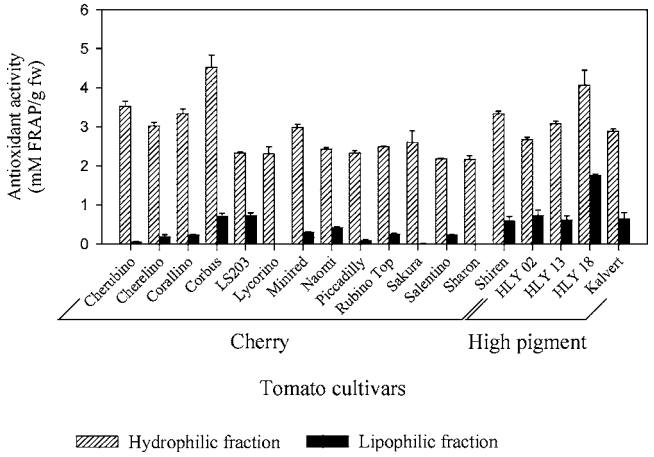

Figure 6. Total antioxidant activity in the hydrophilic and lipophilic extracts of various cultivars of cherry and high-pigment tomatoes. Data are means ± standard deviation of three replicates.

cultivars with the lowest hydrophilic antioxidant activity. Scalfi et al. (*48*) and, more recently, George et al. (*9*) reported similar values in other cultivars of cherry tomatoes. The authors also demonstrated a significantly higher antioxidant power of cherry tomatoes in comparison with normal size tomatoes in which the hydrophilic antioxidant activity was below 2.0 mM FRAP/g of fw. Total hydrophilic antioxidant activity ranged from 2.67 (HLY 02) to 4.07 (HLY 18) mM FRAP/g of fw in high-pigment tomato hybrids, still higher than that reported for normal size tomatoes.

The hydrophilic antioxidant activity has been attributed to the presence of phenolic compounds, such as caffeic and chlorogenic acid, in the methanolic fraction (*33*). After considering data from all tomato cultivars, no correlation ($R^2 = 0.02$) between FRAP and total phenolic content was evident. The antioxidant capacity might not always correlate with the amount of phenols (*49*). The lack of correlation could be due to the content of AsA, which may account for most of the FRAP value. There was in fact a good linear correlation ($R^2 = 0.49$; $P < 0.001$) between vitamin C content and FRAP. The total antioxidant hydrophilic activity was certainly correlated with the levels of all of the major antioxidants (vitamin C, total flavonoids, and hydrophilic phenolics), but it was not just the mere sum of their content. It is plausible that it depends also upon synergistic effects among all water-soluble antioxidants and their interactions with other constituents of the fraction.

It has been reported that evaluation of lipophilic antioxidant activity with the FRAP method is not reliable because of the inability of carotenoids to reduce ferric chloride (*9*). The lipophilic antioxidant activity measured in the lipophilic fraction was very low, with the exception of the HLY 18 cultivar, ranging from 0 to 0.71 mM FRAP/g of fw in cherry tomatoes and from 0.62 to 1.75 mM FRAP/g of fw in high-pigment tomato hybrids. Even though FRAP values are excessively low in comparison with the high amount of detected lipophilic antioxidants, a linear correlation with lycopene content ($R^2 = 0.45$) and with the sum of all lipophilic antioxidants ($R^2 = 0.46$) (**Figure 7**) was observed with a high significance level ($P < 0.001$).

This study has confirmed the important role played by genetic background in determining the antioxidant potential of fresh raw tomatoes. The variability detected among the 14 cultivated cherry tomato cultivars and among the 4 new advanced selections of high-pigment tomato hybrids highlighted an existing unexploited variability in the cultivated tomato germplasm. The lack of a cultivar with a high amount of all antioxidants emphasizes the need to mix characters from different genotypes in breeding programs. Among cherry tomatoes cv. LS203 seems to be the most suitable to enhance carotenoid and α-tocopherol contents, whereas cv. Corbus appears to be the best choice for breeding for hydrophilic antioxidant content. All high-pigment tomatoes represent obvious starting points for further increase in lycopene content. Cv. HLY 13 with its high levels of β-carotene, α-tocopherol, vitamin C, and phenolics appears to be interesting for breeding for hydrophilic as well as lipophilic antioxidant contents. Such results stress the need to evaluate the biodiversity and to support conventional breeding programs to improve the tomato nutritional value.

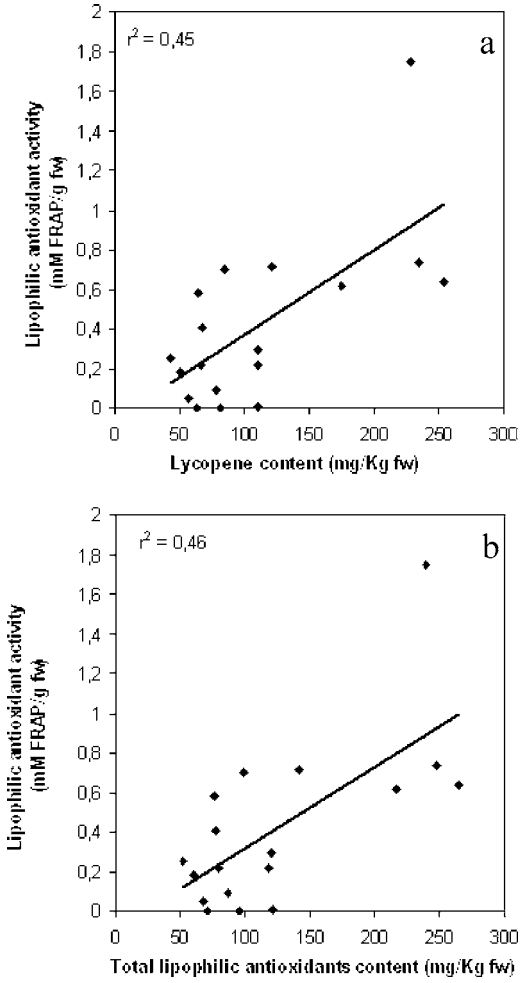

Figure 7. Relationship between lycopene and lipophilic antioxidant activity measured by the FRAP method (**a**) and between the sum of all analyzed lipophilic antioxidants (lycopene + β-carotene + α-tocopherol) and lipophilic antioxidant activity measured by the FRAP method (**b**). The correlation was calculated with a significance level of $P < 0.001$.

ABBREVIATIONS USED

AsA, ascorbic acid; DHA, dehydroascorbic acid; GAE, gallic acid equivalents; RE, rutin equivalents.

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