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Changes in Antioxidant Content of Tomato Fruits in Response to Cultivar and Nutrient Solution Composition

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The aim of this study was to investigate the effect of cationic proportions (K/Ca/Mg) in the nutrient solution on fruit quality (quality attributes and antioxidant content) using a high-pigment, 'Lunarossa', tomato cultivar and a standard tomato cultivar ('Corfù') grown in soilless culture. Treatments were defined by a factorial combination of three nutrient solutions having different cationic proportions and two indeterminately growing round tomato cultivars. A high proportion of K in the nutrient solution increased the quality attributes (fruit dry matter, total soluble solids content) and the lycopene content of tomato fruit, whereas a high proportion of Ca improved tomato fruit yield and reduced the incidence of blossom-end rot (BER). The highest total antioxidant activity was observed in the treatment with a high proportion of Mg in the Lunarossa cultivar. The high-pigment hybrid has provided a higher antioxidant content (lycopene and α-tocopherol content) than the commercial hybrid, but it was more susceptible to BER and consequently less productive.

KEYWORDS: Tomato; antioxidant activity; carotenoids; tocopherols; minerals; nutrients

INTRODUCTION

The nutritional quality of vegetables is becoming increasingly important for greenhouse growers who want to meet the ever-increasing demand of consumers in the highly competitive fresh vegetable market. Over the past 15 years, several researchers have shifted toward quality that is related to antioxidants that are active in preventing widespread human diseases (*1*, *2*). Worldwide, the tomato (*Lycopersicon esculentum* Mill.) constitutes an important agricultural crop and an integral part of the human diet and represents a convenient source of different classes of antioxidants such as carotenoids, ascorbic acid, phenolic compounds, and α-tocopherol (*3*). In particular, carotenoid intake reduces the risk of certain types of cancer, cardiovascular pathologies, and xerophthalmia (*4*−*6*).

The antioxidant content of fresh tomato can be affected by many pre- and postharvest factors (*7*). The management of mineral nutrition is a key preharvest factor that determines the yield and fruit quality of tomato plants. In this perspective the soilless culture represents an important tool, because it permits a precise control of plant nutrition (*8*). Several authors (*9*, *10*) have shown a significant influence of cationic ratio on tomato yield and quality attributes, but no information is available on the interaction effect of K, Ca, and Mg on the biosynthesis and accumulation of antioxidant compounds. Moreover, Trudel and Ozbun (*11*) have reported a 40% increase in lycopene concentration when potassium concentration in the nutrient solution has been increased from 0 to 8 mM, whereas a 26% depression of β-carotene concentration has been observed. Paiva et al. (*12*) showed a 29% decrease in lycopene concentration when calcium concentration was increased from 0.2 to 20 mM, obtaining a minimum of level of lycopene (21.5 $\mu g\ g^{-1}$) with calcium concentration in the nutrient solution being 13.7 mM. Actually, a lack of information is available on the influence of magnesium on the biosynthesis of antioxidants in tomato.

Tomato is represented by several hundred cultivars and hybrids in response to consumer requests for fresh use. Recently, the breeding programs have given more attention to the constitution of cultivar that is defined by "high pigment". These hybrids have shown contradictory performances for lycopene contents, from values similar to those for control hybrid to those 2-fold higher than those of commercial varieties (*13*).

Taking into account that tomato is one of the most important horticultural crops grown in hydroponics, where the use of appropriate nutrient solution is a crucial factor for obtaining high fruit quality, it is of great interest to understand the effect of cationic proportions (K, Ca, and Mg) in the nutrient solution and their interaction to improve fruit quality and antioxidant content in tomato.

The objective of this work was to assess the effect of cationic proportions (K/Ca/Mg) on yield and fruit quality (quality attributes and antioxidant content) using a high-pigment tomato cultivar and a standard tomato cultivar grown in soilless culture.

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MATERIALS AND METHODS

Plant Material and Growing Conditions. The experiment was conducted in a 300 m^2 polyethylene greenhouse situated at the experimental farm of Tuscia University, Italy (latitude 42° 25′ N, longitude 12° 08′ E, altitude 310 m). Plants were grown under natural light conditions, and automatic ventilation was provided when the air temperature in the greenhouse exceeded 25 °C. The greenhouse was maintained at daily temperatures between 15 and 35 °C. Treatments were arranged in a complete block design with four replicates. Treatments were defined by a factorial combination of three nutrient solutions having different cationic proportions (S_K = 0.68 K/0.16 Ca/0.16 Mg; S_{Ca} = 0.16 K/0.68 Ca/0.16 Mg; S_{Mg} = 0.16 K/0.16 Ca/0.68 Mg) and two indeterminately growing round tomato cultivars ('Corfù' and 'Lunarossa'). The Lunarossa cultivar (high-pigment hybrid, De Ruiter, The Netherlands) is characterized by a medium-size fruit (100−130 g), three or four lobes, and seven to nine fruits per truss, whereas Corfù (standard hybrid, SAIS, Italy) has an average fruit weight between 130 and 150 g (large-medium size), three or four lobes, and six to eight fruits per truss. Both cultivars are harvested at the full ripening stage (red) and are widely cultivated under greenhouse conditions in Italy. The experimental unit consisted of three plants.

At the two true-leaf stage tomato plants were transplanted (March 17, 2004) in pots containing 3.8 L of quartziferous sand. Plant rows were 1.3 m apart, and the space between plants within a row was 0.5 m. The distance between the centers of double rows was 1.9 m, resulting in a plant density of 2.1 plants m^{-2}. The nutrient solution was pumped from an independent tank through a drip-irrigation system with one emitter flow rate of 2 L h^{-1}. The irrigation scheduling was performed using low tension tensiometer. Three to 15 fertigations were applied per day at 1−3 min each. The timing of irrigation was increased to have 30% or more of the solution draining from the pots.

In all nutrient solutions, the macroanion proportions were 0.67 NO_3/0.26 SO_4/0.07 H_2PO_4, and the ratio between anions (NO_3^- + SO_4^{2-} + $H_2PO_4^-$) and cations (K^+ + Ca^{2+} + Mg^{2+}) was equal to 1. The total macronutrients concentration was 42 mequiv L^{-1}. In all treatments, the concentrations of macroanions (proportion × total concentration) were NO_3^-, 14.1 mequiv L^{-1}; SO_4^{2-}, 5.5 mequiv L^{-1}; and $H_2PO_4^-$, 1.5 mequiv L^{-1}); the concentrations of macrocations were K^+, 14.2 mequiv L^{-1}; Ca^{2+}, 3.4 mequiv L^{-1}; and Mg^{2+}, 3.4 mequiv L^{-1}, for the S_K treatment; K^+, 3.4 mequiv L^{-1}; Ca^{2+}, 14.2 mequiv L^{-1}; and Mg^{2+}, 3.4 mequiv L^{-1}, for the S_{Ca} treatment; and K^+, 3.4 mequiv L^{-1}; Ca^{2+}, 3.4 mequiv L^{-1} ; and Mg^{2+}, 14.2 mequiv L^{-1} for the S_{Mg} treatment. In all treatments, the micronutrients concentrations were Fe, 40.0 μequiv L^{-1}; Mn, 18.0 μequiv L^{-1}; Cu, 3.0 μequiv L^{-1}; Zn, 6.0 μequiv L^{-1}; B, 60.0 μequiv L^{-1}; and Mo, 1.8 μequiv L^{-1}. The electrical conductivity (EC) and pH of the nutrient solutions were 2.0 ± 0.2 dS m^{-1} and 6.0, respectively. Demineralized water was used in the preparation of all nutrient solutions. Crop management followed commercial practices used in Italy. Fully ripe fruits were harvested at day 79 after transplanting (DAT) and continued until the end of the experiment. During the harvest period, the number and weight of total, marketable, and unmarketable yields were measured on three plants per plot.

Chemicals and Standards. The organic solvents used for the separation of carotenoids, α-tocopherol, ascorbic acid, and polyphenols were of HPLC grade and purchased from Carlo Erba, Milan, Italy. Other organic solvents and chemicals used in the extraction procedures were of analytical grade (Sigma). For standard regression lines pure purchased from Sigma were used.

Determination of Analytical and Productive Parameters. These determinations were performed on the third truss. To mediate the effects of ripening stage, the fruits were harvested at the same red/yellow component (*a*/*b* ratio = 1.1−1.2) and measured by a tristimulus color analyzer (Minolta Chroma Meter CR-200, Minolta Camera Co. Ltd., Osaka, Japan) as described by McGuire (*14*). Total soluble solids (TSS) were measured by a refractometer (Atago CN 1, Tokyo, Japan) and expressed as °Brix at 20 °C. Titratable acidity (TA) was measured on samples titrated to pH 8.1 with 0.1 N NaOH and expressed as grams of citric acid per 100 g of fresh fruit weight. The fruit juice EC (dS m^{-1}) and pH were also measured.

Mineral Analyses. To obtain the fruit dry matter (DM), fruits were dried in a thermoventilated oven at 80 °C for 72 h. Dry fruits were ground in a Wiley mill to pass through a 20-mesh screen and analyzed for N, P, K, Ca, and Mg. The nitrogen concentration was determined after mineralization of vegetative material with sulfuric acid according to the regular Kjeldahl method (*15*); P, K, Ca, and Mg were determined by dry ashing method at 400 °C for 24 h. Subsequently, ash was dissolved in HCl (1:25 v/v), and the supernatant was assayed using an inductively coupled plasma emission spectrophotometer (*16*).

Sample Preparation. A representative sample (15 fruits) from each treatment was homogenized in a Waring blender for 1 min. Three replicates were prepared from each sample. The analyses of carotenoids, vitamin C, and antioxidant activity were performed immediately, and aliquots of the samples were stored at −80 °C until the polyphenols analysis was conducted.

Total Antioxidant Activity Determinations. The total antioxidant activity was measured by total radical-trapping antioxidant parameters (TRAP) and ferric reducing-antioxidant power (FRAP) assays. The extraction method followed the procedure reported by Pellegrini et al. (*17*).

To obtain tomato extracts for TRAP and FRAP analyses, the edible portion of tomato was homogenized in a blender. One gram of the homogenized sample was extracted with 4 mL of water under agitation for 15 min at room temperature and centrifuged at 1000*g* for 10 min, and the supernatant (water-soluble fraction) was collected. The extraction was repeated with 2 mL of water. The two supernatants were combined and used directly for TRAP and FRAP assays. The residue was extracted using 4 mL of acetone under agitation for 15 min at room temperature and centrifuged at 1000*g* for 10 min, and the supernatant (liposoluble fraction) was collected. The extraction was repeated with 2 mL of acetone. The two supernatants were combined and used directly for TRAP and FRAP assays.

TRAP and FRAP values of tomatoes were obtained by summing the values of the water-soluble and liposoluble fractions.

The TRAP was determined according to the method of Ghiselli et al. (*18*) that was based on the protection provided by antioxidants on the fluorescence decay of R-phycoerythrin (lag-phase) during a controlled peroxidation reaction. Ghiselli et al. (*18*) found that the mean SMP had a CV = 8.7%, without variation of TRAP value (CV = 0.96%). The reproducibility of the method was high (CV < 3%). Briefly, 120 μL of diluted tomato extract sample was added to 2.4 mL of phosphate buffer (pH 7.4) with 375 μL of double-distilled water and 75 μL of 2,2-azobis(2-amidinopropane)dihydrochloride (ABAP), and then the reaction kinetics was studied at 37 °C for 45 min by a Perkin-Elmer LS-50 B luminescence spectrometer. Antioxidant activity was expressed as equivalent millimolar Trolox (6-hydroxy-2,5,7,8-tetramethylchlorman-2-carboxylic acid) per kilogram of fresh weight (FW).

The FRAP method followed that of Benzie and Strain (*19*) through the use a Beckman DU 7400 spectrophotometer equipped with a thermostatically controlled cell holder. The method is based on the reduction of a Fe^{3+}-TPTZ (2,4,6-tripyridyl-*s*-triazine) complex to ferrous at low pH. Benzie and Strain (*19*) found that the precision and sensitivity of FRAP assay were very high: within-run coefficients of variations (CV_s) were <1.0% at FRAP values of 100, 200, and 900 μM and the between-run CV was <3.0% at 960 μM. The limit of detection of the FRAP assay is <2 μM reducing/antioxidant power.

Briefly, 900 μL of working FRAP reagent prepared daily was mixed well with 30 μL of diluted sample, and the absorbance was recorded at 595 nm after 30 min of incubation at 37 °C. Antioxidant activity was expressed as equivalent millimolar Fe^{2+} per kilogram of FW.

Extraction and Quantification of Vitamin C. Total ascorbic acid (AA+DHAA) was extracted and quantified by HPLC system according to the method of Margolis et al. (*20*). We performed a validation study to verify the method suitability. Precision was estimated as the CV of intra- and interday replicate analyses. CVs of <2.8 and 6.2 were found for intra- and interday precision, respectively. A recovery of 101 ± 2.2% was calculated at each concentration.

Briefly, 1 g of sample was suspended in 5 mL of water. To the sample was added 1 mL of 0.5 mol/L of dibasic potassium phosphate containing 100 g/L of 1,4-dithiothreitol (DTT). The sample was vortex-

mixed for 15 s and kept at room temperature for 30 min, and 1 mL of aqueous MPA (400 g/L metaphosphoric acid) was added. After the suspension had been centrifuged (1000*g*, 30 min, 5 °C), the clear phase was transferred to 1.8-mL vials. Chromatographic separation was carried on a 250 × 4.6 mm Capcell Pak NH_2 column (Shiseido, Tokyo, Japan), using ESA series HPLC, equipped with an eight-channel coulometric electrode array detector and an ESA coularray operating software that controls the equipment and performs data processing (ESA, Chemsford, MA). The setting potentials were 0, 100, 200, 300, and 400 mV. The column was equilibrated at 40 °C at a flow rate of 0.8 mL/min with a solvent composed of 0.680 g of monobasic potassium phosphate, 200 mL of water, 800 mL of acetonitrile, and 7.5 mL of concentrated phosphoric acid. The injection volume was 30 μL.

Extraction and Quantification of Polyphenols. Phenolics were hydrolyzed to obtain total free forms and extracted as described by Hertog et al. (*21*). The method used for polyphenols determination was validated by Serafini et al. (*22*) on lettuce. For both hydroxycinnamic acids and quercitin, a CV of <8 ($n = 10$) or <10% ($n = 20$) was found for intra- and interday precision, respectively. A recovery of >90% was calculated at each concentration for both hydroxycinnamic acids and quercetin.

Briefly, polyphenols were extracted from 3 g of homogenized tomatoes with ethyl acetate after acidic hydrolysis with HCl/methanol (1:1 v/v) at 90 °C for 2 h. Quantitative analysis was performed using an ESA series (model 580) HPLC solvent delivery module, an ESA 5600 eight-channel coulometric electrode array detector, and an ESA coularray operating software that controlled the equipment and performed data processing. A Supelcosil LC-18 column (25 × 4.6 cm, 5 μm) with a Perisorb Supelguard LC-18 (Supelco, Milan, Italy) was used. The volume injected was 30 μL. Chromatography was performed at 30 °C and 1 mL/min flow rate using 0.02 M sodium phosphate adjusted with 85% ortophosphoric acid to pH 2.8 (solvent A) and methanol (solvent B). Eluent flow rate was maintained at 1 mL min^{-1}, and the setting potentials were set at 60, 120, 200, 340, 480, 620, 760, and 900 mV. The linear gradient was started at 13% solvent B and then increased to 40% within 13.5 min, then to 90% within 25.5 min, and reaching the final conditions of 100% within 3 min and then returned to 13% solvent B within 3 min and maintained at that condition for 4 min.

Extraction and Quantification of Carotenoids and α-Tocopherol. Tomato carotenoids and α-tocopherol were determined as described by Sharpless et al. (*23*). This method is used by the National Institute of Standards and Technology (NIST). We performed a validation study to verify the method suitability. Precision was estimated as the CV of intra- and interday replicate analyses. CVs of 7.5, 6.8, and 4.8, respectively, for lycopene, β-carotene, and lutein were found for intraday precision. CVs of 11.2, 9.9, and 8.3, respectively, for lycopene, β-carotene, and lutein were found for intraday precision. A recovery of 96% was calculated at each concentration.

Briefly, ≈1 g of sample was combined with 3 mL of tetrahydrofuran (THF) and 2.7 mL of methanol. The mixture was saponified for 30 min in a 40 °C water bath after the addition of 0.3 mL of a 40% (w/v) methanolic KOH solution, and then ≈0.15 g of ascorbic acid was added to neutralize the KOH. The analytes were extracted with three 15-mL portions of hexane/diethyl ether (50+50). The organic phase were combined and evaporated under a stream of nitrogen and the residue redissolved in 10 mL of ethanol. For the analysis 0.1 mL of the sample was re-evaporated and reconstituted in 0.5 mL of mobile phase (50% methanol, 45% acetonitrile, and 5% THF). Fifty microliters of reconstituted extract was injected on a Waters Nova Pack C18 column (3.9 × 150 mm), 4 μm, at a flow rate of 1 mL min^{-1}. The extracts were analyzed by a Perkin-Elmer ISS 200 series HPLC system. The eluents were methanol/acetonitrile/THF (50:45:5). The peaks were detected with a variable spectrophotometric detector (Perkin-Elmer LC-95, Norwalk, CT) connected to a personal computer PeNelson model 1020 (Perkin-Elmer). The detection wavelengths were 450 and 292 nm, respectively, for carotenoids and α-tocopherol.

Statistical Analysis. Data were statistically analyzed by ANOVA using the SPSS software package (SPSS 12.0). Duncan's multiple-range test was performed when $P = 0.05$ for each of the significant variables.

Table 1. Effects of Nutrient Solution Composition and Cultivar on the Total (T), Marketable Yield (M, Expressed in Kilograms per Plant), Percentage of Blossom-End Rot (BER), Marketable Mean Weight (MW, Expressed in Grams per Fruit), and Number (N, Expressed in Number per Plant) of Tomato Fruits (Interaction Values Are the Mean of Four Replicates)

		yield			marketable fruit	
nutr solution	cultivar	T	M	BER	MW	N
S_K[a]	Corfù	5.59	4.23	21.7 c	154.9	27.5
	Lunarossa	4.34	2.48	39.9 a	114.0	21.7
	mean	*4.96 b*	*3.36 c*	*30.8*	*134.4*	*24.6 c*
S_{Ca}	Corfù	6.56	6.09	5.0 e	132.4	46.2
	Lunarossa	5.90	5.16	7.3 d	110.6	46.5
	mean	*6.23 a*	*5.62 a*	*6.1*	*121.5*	*46.4 a*
S_{Mg}	Corfù	5.62	4.73	13.6 de	140.9	33.5
	Lunarossa	5.19	3.43	32.3 b	122.3	28.2
	mean	*5.40 b*	*4.08 b*	*22.9*	*131.6*	*30.9 b*
significance[b]						
nutr solution (S)		***	***	***	ns	***
cultivar (C)		**	***	***	***	*
S × C		ns	ns	*	ns	ns

[a] S_K, S_{Ca}, S_{Mg}, nutrient solution with high proportion of K, Ca, and Mg, respectively. [b] ns, *, **, ***, nonsignificant or significant at $P \leq 0.05$, 0.01, and 0.001, respectively. Different letters within each column indicate significant differences according to Duncan's multiple-range test ($P = 0.05$).

RESULTS AND DISCUSSION

Yield Components. Total and marketable yields and fruit number were significantly affected by nutrient solution composition and cultivar but not by their interaction, whereas the incidence of blossom-end rot (BER) was significantly influenced by nutrient solution composition, cultivar, and their interaction. Moreover, the marketable mean fruit weight was significantly affected by cultivar but not by solution composition and their interaction (**Table 1**). The highest total and marketable yields were observed in the nutrient solution containing the high proportion of Ca (S_{Ca}), followed by S_{Mg} and S_K treatments. The highest incidence of BER was observed in Lunarossa cultivar with S_K treatment followed by 'Lunarossa' with S_{Mg} treatment and by 'Corfù' in S_K treatment. The lowest marketable yield on S_K and S_{Mg} in comparison to S_{Ca} treatment was due to a higher incidence of BER, leading to lower number of marketable fruits. The total and marketable yields of Corfù cultivar (respectively, 5.92 and 5.02 kg $plant^{-1}$) were higher in comparison to 'Lunarossa' (respectively, 5.14 and 3.69 kg $plant^{-1}$). The highest marketable yield recorded on 'Corfù' in comparison to 'Lunarossa' was due to an increase in both fruit mean weight (142.7 vs 115.6) and number (35.7 vs 32.2) and lower BER incidence. The results obtained in the current study confirm the importance of Ca in the nutrient solution to reduce BER incidence (*24*, *25*). Moreover, the antagonism in the root zone among K, Ca, and Mg affected Ca uptake and Ca translocation to the fruit, leading to a high BER incidence and hence to a reduction in marketable yield (*25*). Several authors (*9*, *10*) have shown that increasing the K:Ca ratio while reducing the Ca:Mg ratio reduces tomato marketable yield.

Quality Attributes. The fruit DM and the TSS content were significantly affected by the nutrient solution composition and cultivar and not by their interaction, whereas the fruit juice EC was affected only by the solution composition. The TA content was significantly influenced by solution composition and solution composition × cultivar interaction, but not by cultivar (**Table 2**). The highest DM and TSS contents were recorded

Table 2. Effects of Nutrient Solution Composition and Cultivar on Dry Matter (DM), Total Soluble Solids (TSS), Titratable Acidity (TA), and Electrical Conductivity (EC) of Tomato Fruits (Interaction Values Are the Mean of Four Replicates)

		quality attributes			
nutr solution	cultivar	DM (%)	TSS (°Brix)	TA (g 100 g^{-1} of FW)	EC (dS m^{-1})
S_K[a]	Corfù	6.13	6.56	0.32 a	5.27
	Lunarossa	6.32	6.99	0.22 b	5.67
	mean	*6.22 a*	*6.78 a*	*0.27*	*5.47 a*
S_{Ca}	Corfù	5.45	5.50	0.20 b	4.36
	Lunarossa	6.09	6.63	0.22 b	3.83
	mean	*5.77 ab*	*6.06 b*	*0.21*	*4.09 b*
S_{Mg}	Corfù	5.46	6.25	0.25 b	5.48
	Lunarossa	5.76	6.50	0.24 b	5.07
	mean	*5.61 b*	*6.37 ab*	*0.25*	*5.27 a*
significance[b]					
nutr solution (S)		*	*	*	***
cultivar (C)		*	**	ns	ns
S × C		ns	ns	*	ns

[a] S_K, S_{Ca}, S_{Mg}, nutrient solution with high proportion of K, Ca, and Mg, respectively. [b] ns, *, **, ***, nonsignificant or significant at $P \leq 0.05$, 0.01, and 0.001, respectively. Different letters within each column indicate significant differences according to Duncan's multiple-range test ($P = 0.05$).

on fruits from plants grown in nutrient solutions with a high proportion of K (S_K) followed by S_{Mg}, whereas the lowest value was recorded for the S_{Ca} treatment. The Corfù cultivar showed a lower DM (6.10 vs 6.71%) and TSS content (5.68 vs 6.06 °Brix) in comparison to the Lunarossa cultivar. The fruit juice EC followed a trend similar to that of the DM and TSS contents. Moreover, the highest TA value was also recorded on S_K treatment with Corfù cultivar. It is well established that K plays a key role in the metabolism of carbohydrates and photosynthesis in tomato fruits (*26*), leading to a higher concentration in TSS content and titratable acidity (*24*, *27*).

Mineral Content. Some of the world's most widespread and debilitating nutritional disorders are caused by diets lacking in vitamins and minerals. Fruits and vegetables usually contribute 35, 24, and 11% total K, Mg, and P to the dietary intake of humans, respectively (*28*). Differences among the concentrations of fruit mineral elements are mainly due to nutrient solution composition and to a lesser degree to the effect of cultivar (**Table 3**). No significant differences were recorded on total nitrogen concentration in fruit tissue (av = 2.0 g 100 g^{-1} of DW). A significant nutrient solution composition × cultivar interaction was observed for P and K concentration. The highest concentration of P was recorded on 'Lunarossa' treated with high proportions of Mg (S_{Mg}) and Ca (S_{Ca}) and on 'Corfù' in S_{Ca} treatment, whereas the highest concentration of K was observed in both cultivars treated with a high proportion of K (S_K). The Ca fruit concentration was negatively affected by an increase in K and Mg in nutrient solution due to the antagonism in the root zone between the largely hydrated Ca^{2+} ion and the other cations that are smaller and easier to carry and transport, especially K^+. Similar results were observed for Mg and K fruit contents that were negatively affected by using nutrient solutions with high proportions of K or Ca and high proportions of Ca or Mg, respectively. Finally, the lower fruit concentration of Ca observed in the S_K and S_{Mg} treatments could explain the high BER incidence recorded in these treatments.

Total Antioxidant Activity (TAA). The TAA of fruits and vegetables is an important parameter in assessing the quality of products. In addition, levels of single antioxidants in fruits and vegetables do not necessarily reflect their total activity. In the current study TRAP and FRAP assays were applied to compare results with those of the literature (*18*, *19*). The antioxidant activity values observed in the current experiment were 2.48−5.86 mM Fe^{2+} kg^{-1} of FW using the FRAP assay and 1.05−1.80 mM Trolox kg^{-1} of FW using the TRAP assay, and that was in the range reported by Pellegrini et al. (*17*).

No significant differences among treatments were observed for TAA that was 1.47 mM Trolox kg^{-1} of FW when the TRAP assay was used. The TAA was significantly affected by nutrient solution, cultivar, and their interaction when the FRAP assay was used. The highest TAA was observed in Lunarossa cultivar when a high proportion of Mg was used, followed by the Lunarossa cultivar when a high proportion of Ca and Mg in the nutrient solution was used. The lowest values were observed in Corfù cultivar with S_K, S_{Ca}, and S_{Mg} treatments (**Figure 1**).

Hydrophilic Antioxidants. Phenolic compounds and ascorbic acid represent the main water-soluble antioxidants in tomatoes. Several epidemiological studies have shown the importance of vitamins in preventing cancer and heart diseases (*29*, *30*).

Table 3. Effects of Nutrient Solution Composition and Cultivar on the Mineral Composition of Tomato Fruits (Interaction Values Are the Mean of Four Replicates)

		mineral element (g 100 g^{-1} of DW)				
nutr solution	cultivar	N	P	K	Ca	Mg
S_K[a]	Corfù	1.98	0.46 c	3.70 a	0.07	0.37
	Lunarossa	1.99	0.52 b	3.49 ab	0.08	0.35
	mean	*1.98*	*0.49*	*3.59*	*0.07 b*	*0.36 b*
S_{Ca}	Corfù	2.04	0.53 ab	3.23 c	0.18	0.33
	Lunarossa	1.94	0.54 ab	2.71 d	0.19	0.31
	mean	*1.99*	*0.52*	*2.97*	*0.18 a*	*0.32 b*
S_{Mg}	Corfù	1.90	0.46 c	3.04 c	0.07	0.42
	Lunarossa	2.27	0.58 a	3.34 bc	0.10	0.47
	mean	*2.08*	*0.52*	*3.19*	*0.08 b*	*0.44 a*
significance[b]						
nutr solution (S)		ns	ns	***	***	***
cultivar (C)		ns	***	ns	ns	ns
S × C		ns	*	**	ns	ns

[a] S_K, S_{Ca}, S_{Mg}, nutrient solution with high proportion of K, Ca, and Mg, respectively. [b] ns, *, **, ***, nonsignificant or significant at $P \leq 0.05$, 0.01, and 0.001, respectively. Different letters within each column indicate significant differences according to Duncan's multiple-range test ($P = 0.05$).

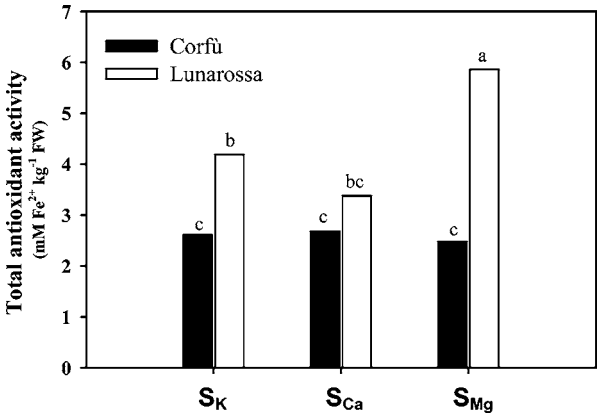

Figure 1. Effects of nutrient solution composition and cultivar on total antioxidant activity (mM Fe^{2+} kg^{-1} of FW) by FRAP assay. Different letters indicate significant differences according to Duncan's test ($P = 0.05$). Values are the mean of four replicates.

Vitamin C content observed in the current experiment was not affected by nutrient solution composition, cultivar, and their interaction (**Table 4**). Vitamin C levels ranged from 37 to 54 mg 100 g^{-1} of FW, and these levels agree with the range of 84−590 mg kg^{-1} of FW reported in a review by Dumas et al. (*7*). The structure of phenolic compounds makes them very efficient scavengers of peroxyl radicals. Moreover, the action of phenolic compounds may be related to their capacity to reduce and chelate ferric iron that catalyzes lipid peroxidation. Caffeic acid content was significantly affected by nutrient solution composition and cultivar but not by solution × cultivar interaction. Caffeic acid content was higher in 'Lunarossa' compared to 'Corfù' (0.42 vs 0.27 mg 100 g^{-1} of FW) when averaged across nutrient solution composition. No significant differences were observed for the other phenolic compounds. Ferulic acid, naringenin, and quercetin contents were 1.29, 1.17, and 1.24 mg 100 g^{-1} of FW, respectively. The *p*-coumaric acid content was found to be below the detection limit. The positive effect of high Mg proportion in the nutrient solution on caffeic acid content may be attributed to the high Mg request for activity of glutamine synthetase, which is an important enzyme that regulates ammonia assimilation within the chloroplasts (*26*). In fact, the importance of nitrogenous compounds such as phenylalanine in the pathway of hydroxycinnamic acids is widely recognized (*31*). Therefore, the positive influence of nutrient solution with a high proportion of Mg on TAA can be explained by the increment of caffeic acid in S_{Mg} treatment. A positive correlation ($r = 0.81$*) between the caffeic acid content and water-soluble fraction of TAA was observed; similar results were also reported by Raffo et al. (*32*). Finally, it is widely known that Mg is an essential element that activates glutathione synthase with glutathione being readily soluble in water and a powerful antioxidant in plants (*26*).

Lipophilic Antioxidants. The concentration of lycopene may be increased by genetic engineering, but the improvement of cultural practices may provide comparable results (*33*). Lycopene content was significantly affected by nutrient solution composition amd cultivar but not by their interaction, whereas only cultivar significantly affected α-tocopherol content. No significant differences were recorded for β-carotene and lutein in all treatments (**Table 5**). The highest lycopene content was recorded on plants grown in nutrient solution with a high proportion of K followed by Mg, whereas the lowest value was recorded for S_{Ca} treatment. Trudel and Ozbun (*11*) reported that the K effect on lycopene content is related to the importance of that element in protein synthesis and the activity of acetic thiokinase. That enzyme is involved in the formation of acetyl CoA, a molecule implied in the biosynthesis of isopentenyl diphosphate (IPP), the first precursor of carotenoids, and the mevalonic acid pathway. More recent studies have shown that plants use the 1-deoxy-D-xylulose-5-phosphate (DOXP) pathway to synthesize carotenoids rather than the mevalonic acid pathway (*34*). In addition, K may be involved in the process of carotenoid biosynthesis by its action on the activity of enzymes that regulate carbohydrate metabolism such as pyruvate kinase and phosphofructokinase as well as on precursors of IPP (pyruvate and glyceraldehyde 3-phosphate). The effect of Ca concentration confirms the data reported by Paiva et al. (*12*) that showed that an increase in Ca concentration of the nutrient solution results in a decrease in lycopene content due to the antagonism between Ca and K or the possible Ca influence on ethylene biosynthesis. Finally, the S_{Mg} treatment gave an intermediate lycopene content. When averaged across nutrient concentrations, the high-pigment cultivar (Lunarossa) exhibited the higher lycopene content compared to Corfù cultivar (2982 vs 2206 μg 100 g^{-1} of FW).

To distinguish between the concentration and metabolism effects, it is fundamental to express lycopene concentration on a dry weight basis (*32*). Lycopene content expressed on a dry weight basis followed a similar trend as those expressed on a fresh weight basis. When averaged across cultivar, the S_K treatment gave a higher lycopene content (526.8 mg 100 g^{-1} DW) in comparison to the S_{Ca} treatment (349.2 mg 100 g^{-1} of DW), whereas the S_{Mg} treatment had an intermediate value (440.6 mg 100 g^{-1} of DW). Lycopene content when averaged across nutrient concentrations was higher in 'Lunarossa' than in 'Corfù' (491.07 vs 386.7 mg 100 g^{-1} of DW).

Table 4. Effects of Nutrient Solution Composition and Cultivar on Vitamin C, Ferulic Acid, Narigenin, Caffeic Acid, and Quercetin Contents of Tomato Fruits (Interaction Values Are the Mean of Four Replicates)

		hydrophilic antioxidants (mg 100 g^{-1} of FW)				
nutr solution	cultivar	vitamin C	ferulic acid	narin-genin	caffeic acid	quer-cetin
S_K[a]	Corfù	43.10	1.51	0.99	0.25	1.10
	Lunarossa	44.44	1.40	1.39	0.35	1.36
	mean	*43.77*	*1.45*	*1.19*	*0.30 b*	*1.23*
S_{Ca}	Corfù	37.88	1.50	1.06	0.24	1.36
	Lunarossa	54.77	1.38	0.88	0.39	1.12
	mean	*46.32*	*1.44*	*0.97*	*0.32 b*	*1.24*
S_{Mg}	Corfù	44.15	1.05	1.12	0.30	1.26
	Lunarossa	48.26	0.90	1.56	0.52	1.24
	mean	*46.21*	*0.97*	*1.34*	*0.41 a*	*1.25*
significance[b]						
nutr solution (S)		ns	ns	ns	**	ns
cultivar (C)		ns	ns	ns	**	ns
S × C		ns	ns	ns	ns	ns

[a] S_K, S_{Ca}, S_{Mg}, nutrient solution with high proportion of K, Ca, and Mg, respectively. [b] ns, **, nonsignificant or significant at $P \leq 0.01$, respectively. Different letters within each column indicate significant differences according to Duncan's multiple-range test ($P = 0.05$).

Table 5. Effects of Nutrient Solution Composition and Cultivar on Lycopene, β-Carotene, Lutein, and α-Tocopherol Contents of Tomato Fruits (Interaction Values Are the Mean of Four Replicates)

		lipophilic antioxidants (μg 100 g^{-1} of FW)			
nutr solution	cultivar	lycopene	β-caro-tene	lutein	α-tocoph-erol
S_K[a]	Corfù	2796	570	128	1020
	Lunarossa	3749	559	176	1250
	mean	*3272 a*	*538*	*152*	*1135*
S_{Ca}	Corfù	1859	385	152	1020
	Lunarossa	2159	411	143	1230
	mean	*2009 c*	*397*	*147*	*1125*
S_{Mg}	Corfù	1964	511	135	1120
	Lunarossa	3039	481	114	1220
	mean	*2501 b*	*496*	*124*	*1170*
significance[b]					
nutr solution (S)		**	ns	ns	ns
cultivar (C)		**	ns	ns	*
S × C		ns	ns	ns	ns

[a] S_K, S_{Ca}, S_{Mg}, nutrient solution with high proportion of K, Ca, and Mg, respectively. [b] ns, *, **, nonsignificant or significant at $P \leq 0.05$ and 0.01, respectively. Different letters within each column indicate significant differences according to Duncan's multiple-range test ($P = 0.05$).

The lycopene levels detected in the fruits were in the range (880−4200 μg 100 g^{-1} of FW) reported by Mangels et al. (*35*), but they were relatively low when compared to values of different typologies of tomato fruits (*36*). The low lycopene content reported in the current experiment could be due to climatic conditions inside the greenhouse, especially air temperature that exceeded 30 °C during the harvest period, leading to a reduction in lycopene biosynthesis (*37*).

The Lunarossa cultivar contained 15% more α-tocopherol content than the Corfù cultivar (1237 vs 1055 μg 100 g^{-1} of FW). The α-tocopherol content observed in the current experiment (1020−1250 μg 100 g^{-1} of FW) was similar to the value reported by Abushita et al. (*36*).

As a summary, a high proportion of K in the nutrient solution increased the quality attributes and antioxidants content (especially lycopene) of tomato fruit, whereas a high proportion of Ca improved tomato fruit yield and reduced BER incidence. The high proportion of Mg in the solution improved the TAA of 'Lunarossa'. Furthermore, the high-pigment hybrid of tomato has guaranteed an antioxidant content higher than that of the standard hybrid, but it has resulted in higher susceptibility to BER and a consequent lower productivity.

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