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Impact of Different Distribution Scenarios and Recommended Storage Conditions on Flavor Related Quality Attributes in Ripening Fresh Tomatoes

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Supporting Information

ABSTRACT: Tomato (*Solanum lycopersicum*) fruits of three cultivars picked at different ripening stages were subjected to conditions in the laboratory simulating both short and long distribution chains as occurring in commercial practice and to recommended storage conditions. At the end of the postharvest experiments, a flavor quality profile of fruits was obtained by chemical determination of volatile compounds, sugars, and organic acids, and physical measurement of texture properties. In two of the three cultivars, the overall profile and many of the individual quality attributes was significantly affected by the distribution chain conditions, the effect being more pronounced in tomatoes marketed at full ripeness than in those marketed at an intermediate ripening stage. In these cultivars, tomatoes harvested at the Breaker stage, subjected to long chain conditions and then allowed to achieve full ripeness at room temperature, did not develop the same overall profile observed on fruits fully ripened on the vine and exposed to a simulated short chain. Fruits subjected to recommended commercial storage conditions, cold stored above the chilling range (10 or 13 °C) and at high relative humidity (95%), developed a different profile when compared to fruit exposed to the simulated long distribution chain (6 °C and 55−80% RH), suggesting that these changes in temperature and relative humidity may remarkably affect flavor formation in tomato fruits. Major drivers of profile differentiation between tomatoes subjected to different postharvest scenarios were the levels of some aroma compounds derived from aminoacids (1-nitro-2-phenylethane, 2-isobutylthiazole, phenylacetaldehyde, 2-phenylethanol, and 2- and 3-methylbutanal) and lipids ((*E,E*)- and (*E,Z*)-2,4-decadienal), and, among nonvolatile flavor compounds, of organic acids (citric and malic).

KEYWORDS: *Solanum lycopersicum, local food, postharvest, volatile, aroma, sugar, organic acid, texture, SBSE*

INTRODUCTION

In recent years, in many Western countries consumer demand for food that is locally produced and marketed is generating a growing interest in some forms of short food supply chains characterized by a more direct connection between the food consumer and producer.[1] Investigations on the attitudes of consumers who purchase local foods have highlighted that freshness and quality are among the main factors in determining their preferences.[2] However, in the debate on local food systems it has been pointed out that quite poor scientific evidence supports the claimed higher quality of locally produced fresh foods versus nonlocally produced foods.[3]

In this context, it is of interest to establish the extent to which the quality of fresh horticultural products subjected to a short distribution chain after harvest may be different from that of the same fresh products exposed to the longer distribution chains occurring in the current postharvest handling system and commonly involving refrigeration.

When addressing this issue, fresh tomato may represent an appropriate and significant case study based not only on the economic value of this crop but also on the several implications of the postharvest handling and marketing system for the quality of this product, as discussed in the literature.[4−6] The constraints of this system are considered among the main causes of the poor flavor quality of fresh tomatoes.[4,7] Detrimental effects on flavor formation are ascribed, in particular, to the practice of harvesting fruits at early ripening stages as well as to improper temperature management during postharvest handling.[4] In addition, commercial breeding programs, focusing on fruit size, firmness, and extended shelf life, have contributed to the decline in tomato flavor.[4,8]

In particular, a few experimental studies have shown that harvesting fruits at early ripening stages negatively affects their sensory profile with respect to fruits ripened on the vine.[9−11] In a few tomato cultivars, cold storage of fruits, both within and above the chilling range, has been observed to result in a significant alteration of the fresh fruit flavor, even before any visual symptoms of injury could be seen.[7,12−14] Changes in the levels of many aroma volatiles have also been associated with low temperature storage in several studies.[13−18] In addition, accumulation of organic acids has been repeatedly found to be enhanced as a result of cold storage.[7,19] Conversely, it has been noted that stored tomatoes can ripen to excellent edible quality if picked at the appropriate mature green stage and handled properly.[20] Whether harvesting at a later stage is a feasible

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Table 1. Conditions Adopted in the Postharvest Experiments[a]

Fruit group	Ripeness stage at harvest	Post harvest conditions: Days in simulated cold storage/transport and ripening at room temperature 0	1	2	4	6	7	9	12	Full ripeness
1st Experiment: Caramba and Rebelion tomatoes										
Short chain (harvest day)	P/R	H-**A**								
Short chain (1 day)	P/R	H RT	**A**							
Medium/Long chain at harvest	B/LR	H-**A**								
Medium chain	B/LR	H	6°C	**A**						
Long chain	B/LR	H	6°C		**A**					
Extended long chain	B/LR	H		6°C			**A**			
Extended long chain + ripening	B	H		6°C			|		RT	**A**
Recommended commercial storage conditions	B/LR	H	13°C Breaker – 10°C Light Red / 95% R.H.				**A**			
Recommended commercial storage conditions (extended time)	B/LR	H		13°C Breaker – 10°C Light Red / 95% R.H.					**A**	
2nd Experiment: Nerina tomatoes evaluated at full ripeness										
Short chain (harvest day)	R	H-**A**								
Short chain (1 day)	R	H RT	**A**							
Medium/Long chain at harvest	G	H-**A**								
Medium chain + ripening	G	H	6°C	|			RT			**A**
Long chain + ripening	G	H		6°C		|		RT	**A**
Extended long chain + ripening	G	H			6°C			|	RT	**A**
Recommended commercial storage conditions + ripening	G	H		13°C / 95% R.H.			|		RT	**A**
Recommended commercial storage conditions(extended time)+ripening	G	H				13°C / 95% R.H.			| RT	**A**
2nd Experiment: Nerina tomatoes marketed an intemediate ripening stage										
Short chain (harvest day)	T	H-**A**								
Short chain (1 day)	T	H RT	**A**							
Medium chain	T	H	6°C	**A**						
Long chain	T	H		6°C		**A**				
Extended long chain	T	H			6°C			**A**		
Recommended commercial storage conditions	T	H		10°C / 95% R.H.			**A**			
Recommended commercial storage conditions (extended time)	T	H			10°C / 95% R.H.				**A**	

[a]H: harvest. A: analyses. P: Pink. R: Red. B: Breaker. LR: Light Red. G: Green. T: Turning. RT: room temperature (21 ± 1°C).

option in order to achieve a better flavor quality is still a matter open to controversy. Some evidence has been given about the possibility to store red harvested tomatoes up to 7 days at ambient temperature without marked loss of flavor quality, as perceived by consumers.[21] On the whole, a thorough understanding of the influence of commercial postharvest handling practices on fresh tomato flavor quality is still lacking.

In the present study, the impact of different distribution scenarios and of recommended commercial storage conditions on some flavor related quality attributes in fresh tomatoes have been investigated by simulating in the laboratory distribution chain conditions occurring in the current postharvest handling system in Italy as well as reproducing recommended storage conditions. The flavor quality of fruits exposed to these conditions was evaluated by chemical determination of organic acids, sugars, and volatile compounds, and by physical measurement of texture properties.

■ MATERIALS AND METHODS

Tomatoes. Fresh tomatoes (*Solanum lycopersicum* cv. Caramba, Nerina, and Rebelion) were grown according to organic cultural practices in an unheated greenhouse in a commercial farm located at Maccarese, in proximity to Rome, during fall 2010 and spring 2011. The three cultivars were selected as widespread representatives of different fruit typologies (respectively, round-shaped, egg-shaped, and Marmande type), all characterized by medium to high susceptibility to postharvest handling.

First Postharvest Experiment. For the first experiment, Caramba and Rebelion fruits were harvested at the following ripening stages, defined on the basis of external color:[22] Breaker and Pink, for samples representing tomatoes marketed at an intermediate stage of ripeness; Light Red and Red, for samples corresponding to tomatoes marketed at full ripeness. Fruits were picked early in the morning, immediately transported to the laboratory, washed, dried, and sorted to eliminate defects.

Then they were grouped and subjected to the conditions reported in Table 1, simulating postharvest conditions corresponding to short, medium, and long distribution chains. For each treatment, a single group of 25 fruits was formed. In common commercial practice, fruits that have to sustain a long distribution chain are picked at an earlier ripening stage than the counterparts directed to a shorter distribution chain. Accordingly, in the case of tomatoes marketed at an intermediate stage of ripeness, fruits picked at the Pink stage were used for the simulation of short chain conditions, whereas fruits harvested at the Breaker stage were selected for the medium/long chain conditions. Similarly, in the case of tomatoes marketed at full ripeness, fruits picked at the Red and Light Red stages were subjected, respectively, to short and medium/long chain conditions. For the postharvest experiment, to mimic cold storage and transport, fruit samples were kept at a temperature of 6 ± 1 °C, the relative humidity ranging from about 55% to 80%. Tomato samples exposed to conditions of medium/long distribution chain were analyzed at the end of the simulated cold storage/transport period, 2, 4, and 7 days after the harvest. To evaluate the combined effect of harvesting at early ripening stages and refrigeration on fruit ability to develop the typical tomato flavor profile following ripening at room temperature, a group of fruits harvested at the Breaker stage and exposed to conditions of extended long chain

Table 2. Analytical Parameters and Abbreviations Used in PCA Plots[a]

compound name/analytical parameter	abbreviation	identification	m/z fragment
acetaldehyde	AcAl	ref comp.[1]	44
ethanol	Eth	ref comp.[1]	45
acetone	Ace	ref comp.[1]	58
ethylacetate	EtAc	ref comp.[1]	61
3-methylbutanal	3MeBAl	ref comp.[1]	58
2-methylbutanal	2MeBAl	tentatively[2]	58
isopropylacetate	IsAc	ref comp.[1]	61
1-penten-3-one	PeOne	ref comp.[1]	84
1-penten-3-ol	PeOl	ref comp.[1]	57
1-pentanal	PeAl	ref comp.[1]	58
3-pentanone	Int. std.		57
2-methyl-2-butenal	2MeBEAl	ref comp.[1]	84
3-methyl-1-butanol	3MeBOl	ref comp.[1]	70
2-methyl-1-butanol	2MeBOl	ref comp.[1]	57
(*E*)-2-pentenal	PeEAl	ref comp.[1]	84
1-pentanol	PeOl	ref comp.[1]	55
(3*Z*)-3-hexenal	ZHexe	ref comp.[1]	80
hexanal	Hexa	ref comp.[1]	72
(*E*)-2-hexenal	EHexe	ref comp.[1]	69
(*Z*)-3-hexenol	HeEol	ref comp.[1]	67
1-hexanol	HeOl	ref comp.[1]	56
1-nitro-3-methylbutane	NiBu	tentatively[3]	55
benzaldehyde	Ben	ref comp.[1]	106
2-heptenal	Hept	ref comp.[1]	83
1-octen-3-one	OcOne	tentatively[2]	70
6-methyl-5-hepten-2-one	6MeOne	ref comp.[1]	108
2-octanone	Int. std.		58
6-methyl-5-hepten-2-ol	6MeOl	ref comp.[1]	95
5-ethyl-2(5*H*)-furanone	EtFu	tentatively[2]	83
phenylacetaldehyde	PhAc	ref comp.[1]	91
2-isobutylthiazole	IsTh	ref comp.[1]	99
2-methoxyphenol	MePh	ref comp.[1]	109
2-phenylethanol	PhEt	ref comp.[1]	91
linalool	Lin	ref comp.[1]	93
camphor	Cam	ref comp.[1]	152
furaneol	Fur	ref comp.[1]	128
methylsalicylate	MeSa	ref comp.[1]	120
β-cyclocitral	BCyc	ref comp.[1]	137
neral	Ner	ref comp.[1]	69
geranial	Ger	ref comp.[1]	69
1-nitro-2-phenylethane	NiPh	tentatively[3]	104
tr-anethol	Int. std.		148
(*E*,*Z*)-2,4-decadienal	Zdec	tentatively[3]	81
(*E*,*E*)-2,4-decadienal	Edec	ref comp.[1]	81
eugenol	Eug	ref comp.[1]	164
vanillin	Van	ref comp.[1]	151
β-damascenone	BDam	ref comp.[1]	69
geranylacetone	GeAc	ref comp.[1]	69
β-ionone	BIon	ref comp.[1]	177
fructose	Fru	ref comp.[1]	
glucose	Glu	ref comp.[1]	
malic acid	Mal	ref comp.[1]	
citric acid	Cit	ref comp.[1]	
firmness	Firm		
deformation	Def		
stiffness	Stif		

[a]For all chemical compounds, details on identification are reported, and for volatiles, the *m/z* fragment used for quantification by GC-MS is also reported. 1, based on the reference pure compound; 2, based on a comparison with MS spectra reported in the NIST/EPA/NIH Mass Spectra Library 2005; 3, based on other spectral and chemical information as reported in the Materials and Methods section.

was transferred afterward to room temperature (21 ± 1 °C), allowed to achieve full ripeness (Red stage), and then analyzed. In addition, to examine the effect of recommended commercial storage conditions for extended times (up to 12 days), groups of fruits harvested at the Breaker and Light Red stage were kept in climatic cells at 13 and 10 °C, respectively, the optimal recommended temperature for cold storage being dependent on the maturity stage at harvest.[22] Relative humidity was set at 95%.

Second Postharvest Experiment. A second experiment was designed to also evaluate the effect of the duration of cold storage (combined with harvesting at an early ripening stage, Green) on fruit ability to develop the flavor profile of vine ripened fruits, when they were allowed to ripen at room temperature after the refrigeration period. For this experiment, cv. Nerina fruits were used. Fruits harvested at the Green stage were subjected to medium/long chain conditions or to recommended storage conditions for extended times, then allowed to fully ripen at room temperature, and finally evaluated at the Red stage (Table 1); these fruits were compared to tomatoes harvested at the Red stage and exposed to short chain conditions. To also consider the case of tomatoes marketed at an intermediate stage of ripeness, cv. Nerina fruits harvested at Turning and subjected to short, medium, and long chain conditions, as well as to recommended storage conditions for extended times, were evaluated just at the end of the simulated postharvest handling process, without following ripening at room temperature (Table 1).

Chemicals. All chemicals and reference compounds were obtained commercially. Calcium chloride, acetaldehyde, ethanol, acetone, ethyl acetate, isopropyl acetate, 3-methyl butanal, 3-methyl-1-butanol, 2-methyl butenal, 2-methyl-1-butanol, 1-penten-3-one, 1-penten-3-ol, 1-pentanal, (*E*)-2-pentenal, 1-pentanol, (*Z*)-3-hexenal, hexanal, (*E*)-2-hexenal, (*Z*)-3-hexenol, 1-hexanol, 2-heptenal, benzaldehyde, 6-methyl-5-hepten-2-one, 6-methyl-5-hepten-2-ol, phenylacetaldehyde, 2-isobutylthiazole, 2-methoxyphenol, 2-phenyl ethanol, linalool, camphor, furaneol, methyl salicylate, β-cyclocitral, neral and geranial isomer mixture (citral), (*E*,*E*)-2,4-decadienal, eugenol, vanillin, β-damascenone, β-ionone, geranylacetone, 2-octanone, 3-pentanone, *tr*-anethole, fructose, glucose, and malic and citric acid were purchased from Sigma Aldrich (Milan, Italy). Acetonitrile and metaphosphoric and orthophosphoric acid were purchased from Carlo Erba Reagenti (Milan, Italy).

Analytical Determinations. *Volatile Compounds.* Tomato sample treatment was carried out following the procedure developed by Buttery et al.[23] The whole tomato sample (200 g), formed by pieces cut from 8 different fruits, was blended for 30 s. The blended mixture was allowed to stand at room temperature for 180 s longer, then a saturated $CaCl_2$ solution (200 mL) was added and the mixture blended for 10 s. A standard solution (1 mL) containing 2-octanone (24.51 mg L^{-1}), 3-pentanone (24.45 mg L^{-1}), and *tr*-anethole (9.98 mg L^{-1}) in water was then added and the mixture blended again for 10 s. Then the mixture was centrifuged for 15 min at 12000 rpm and 4 °C and the resulting supernatant collected and filtered by Whatman filter paper n. 113. Isolation of volatile compounds from the obtained aqueous mixture was carried out in duplicate by the Stir Bar Sorptive Extraction technique (SBSE).[24,25] Fifteen milliliters of the mixture was stirred at 800 rpm with a PDMS-coated stir bar (1.0 mm thickness, 10 mm length, Gerstel GmbH, Mülheim and der Ruhr, Germany) for 90 min, at room temperature, in hermetically closed vials. To thermally desorb the extracted volatile compounds from the stir bar, a thermal desorption unit (TDU, Gerstel GmbH) mounted onto the GC injector was used. Before each analysis, the twisters were conditioned at 280 °C, for 7 min with a carrier gas flow of 75 mL min^{-1}. The thermal desorption unit was installed on an Agilent 6890 GC 5973N MS system (Agilent Technologies Inc., Palo Alto, CA). Desorption conditions were as follows: temperature program from 30 to 200 °C (5 min) at 720 °C min^{-1}, with a flow rate of the carrier gas (He) of 50 mL min^{-1}. Thermally desorbed compounds were cryogenically focused by means of a Gerstel CIS-4 PTV injector, which was cooled at −50 °C using liquid CO_2 during the desorption step. Then at the start of the GC run, the PTV injector temperature was raised to 270 °C (3 min) at 12 °C s^{-1}. A liner filled with Tenax was used within the PTV injector. Capillary GC-MS analyses were performed by using a DB-1MS (Agilent Technologies Inc.) column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Chromatographic conditions were as follows: split injection (by selecting the solvent vent mode and and setting the purge flow to split vent at 20 mL min^{-1}); temperature program from 40 °C (10 min) to 190 at 4 °C min^{-1}, and then to 280 °C (5 min) at 30 °C min^{-1} (total run time of 55.50 min); and linear velocity of the He carrier gas was 36 cm s^{-1}. A mass spectrometer with a quadrupole mass filter was used for detection. Mass spectra were generated in the electronic impact ionization mode at 70 eV. Transfer line, source, and quadrupole temperatures were set, respectively, at 300, 230, and 150 °C. Identification of compounds was carried out by comparing mass spectra, obtained by the full scan mode (m/z range 40−400 amu) and Kovats linear retention indices determined on chromatograms of tomato sample isolates with spectra and retention indices obtained from authentic standards. When authentic standards were not commercially available, compounds were tentatively identified based on a comparison with spectra and retention indices reported in the NIST/EPA/NIH Mass Spectra Library 2005 (Table 2). The two nitro compounds were tentatively identified based on their reported presence in tomato volatile fraction,[15] the retention index of structurally related compounds, and on mass spectra characteristics (spectra are reported in Appendix 1 in Supporting Information): 1-nitro-3-methylbutane was identified on the basis of diagnostic signals (m/z 71 and 55) also present in the mass spectra of the structural isomer 2-nitro-pentane. 1-Nitro-2-phenylethane was tentatively identified based on similarity in the fragmentation pattern with 2-nitro-1-phenylethene: in both spectra were present prominent signals at m/z (M-47), 77 and 91. (*E*,*Z*)-2,4-Decadienal was tentatively identified based on its reported presence in tomato volatiles,[26] retention indices, and mass spectra reported on a freely accessible commercial database.[27]

For the semiquantitative determination of volatiles, spectrometric detection in the selected ion monitoring (SIM) mode was used: mass fragments (m/z) selected for each detected compound are reported in Table 2. Concentration levels were expressed as μg equivalents of internal standard per kilogram of fruit fresh weight and are to be considered as relative data because response factors related to the internal standard were not determined.

Organic Acids. About 7 fruits were homogenized, and 5 g of the homogenate were extracted in triplicate with 20 mL of 2% metaphosphoric acid by stirring for 10 min. The obtained mixture was then centrifuged at 15000 rpm for 10 min (at 4 °C), and the supernatant was collected and filtered by a syringe filter. For the chromatographic analysis of the resulting aqueous extract, a Synergi 4u Hydro-RP80A column (5 μm, 4.6 mm × 250 mm), thermostatted to 35 °C, was used. All chromatographic analyses were performed on an Agilent HPLC system with a 1100 Series quaternary pump, a diode array detector, and a refractive index detector. The organic acids were eluted isocratically with aqueous H_3PO_4 (20 mM and pH 2.7) at a flow rate of 0.8 mL min^{-1}, and the eluate was monitored at 214 nm.

Sugars. Five grams of the above-mentioned tomato homogenate were extracted in triplicate with a mixture of acetonitrile/water 1:1 (20 mL) by stirring for 15 min. After centrifugation at 12000 rpm for 10 min (at 10 °C), the supernatant was filtered by a syringe filter. Chromatographic separation was performed by a Supelcosil LC-NH_2 column (5 μm, 4.6 × 250 mm) thermostatted to 35 °C. The mobile phase was acetonitrile/water 80:20, eluted at a flow rate of 1 mL min^{-1}. Column eluent was monitored by the refractive index detector.

Texture Properties. For texture measurements, a destructive deformation test was carried out using a Texture Analyzer TA-XT2i (Stable Micro System, Godalming, Surrey, UK). Ten fruits from each tomato sample were tested. To describe tomato sample texture properties, the parameters of firmness, deformation, and stiffness (or gradient[28]) were measured according to the method described by Batu.[28]

Statistical Analysis. Statistical analyses were performed by using the MATLAB 7.5.0.342 (The MathWorks Inc., Natick, MA) and SPSS 16.0.2 (SPSS Inc., Chicago, IL) software packages. To look for significant effects associated with the postharvest conditions within all samples from the same cultivar, one-way ANOVA analysis was performed on volatiles, acids, sugars, and texture data sets, and means were compared by the Tukey multicomparison test, considering a significance level of $p < 0.05$. Data sets used for principal component analysis (PCA) were obtained by first averaging replicate determinations and then applying autoscaling as a pretreatment. By merging the same data sets used for PCA, a Pearson's correlation matrix was built, choosing a significance level of $p < 0.01$, to highlight possible metabolic relationships across the three cultivars.

■ RESULTS

First Postharvest Experiment. *Cultivar Caramba Tomatoes.* At the end of the postharvest experiment, all of the fruit samples had the firm, turgid appearance of the fresh fruits without signs of decay, except for the sample of tomatoes to be marketed at full ripeness and subjected to recommended commercial storage conditions for an extended time (12 days), which showed surface molds; for this reason, this sample was discarded. PCA was applied to all chemical and physical data determined on all the other samples, and the resulting biplot can be seen in Figure 1. PC1 and PC2 explained 39% and 17% of the variation in the data, respectively.

In the group of tomato samples to be marketed at full ripeness (denoted by RIPE in the figure), the two samples of fruits exposed to short chain conditions (RIPE S 0 or 1) were very similar and well separated from all the other fruit samples subjected to medium and long chain conditions. The overall profile of samples harvested at the Light Red stage and exposed to medium and long chain conditions (RIPE M or L) was not markedly affected by them, undergoing only minor changes through all the evaluated conditions. In the case of tomatoes to be marketed at an intermediate stage of ripeness (denoted by INT in the figure), differentiation between samples exposed to short and medium/long chain conditions was not as clear. In particular, the sample harvested at the Pink stage and exposed for 1 day to short chain conditions (INT S 1) showed a profile that appeared to be somewhat intermediate between the one of the Pink picked sample analyzed at the harvest day (INT S 0) and that of samples harvested at the Red stage (RIPE S 0 or 1). Interestingly, tomatoes harvested at the Breaker stage, exposed to extended long chain conditions and then allowed to achieve full ripeness at room temperature (RIPE L ROOM), did not develop the same profile observed on fruits fully ripened on the vine (RIPE S 0), even though they showed external color corresponding to full ripeness. The overall profile of fruits to be marketed at both ripening stages and exposed to recommended commercial storage conditions (INT REC, RIPE REC) followed a different pattern of variation, mainly described by the sole PC1.

The PCA biplot suggests also the main drivers of differentiation among groups of tomato samples (Figure 1). The profile of Red harvested tomatoes exposed to short chain conditions was characterized by significantly enhanced levels of some volatile compounds, such as the lipid-derived (*E*,*E*)- and (*E*,*Z*)-2,4-decadienal (Figure 2). A significant increase was also found in the level of three volatiles derived from phenylalanine (benzaldehyde, phenylacetaldehyde, and 2-phenylethanol),

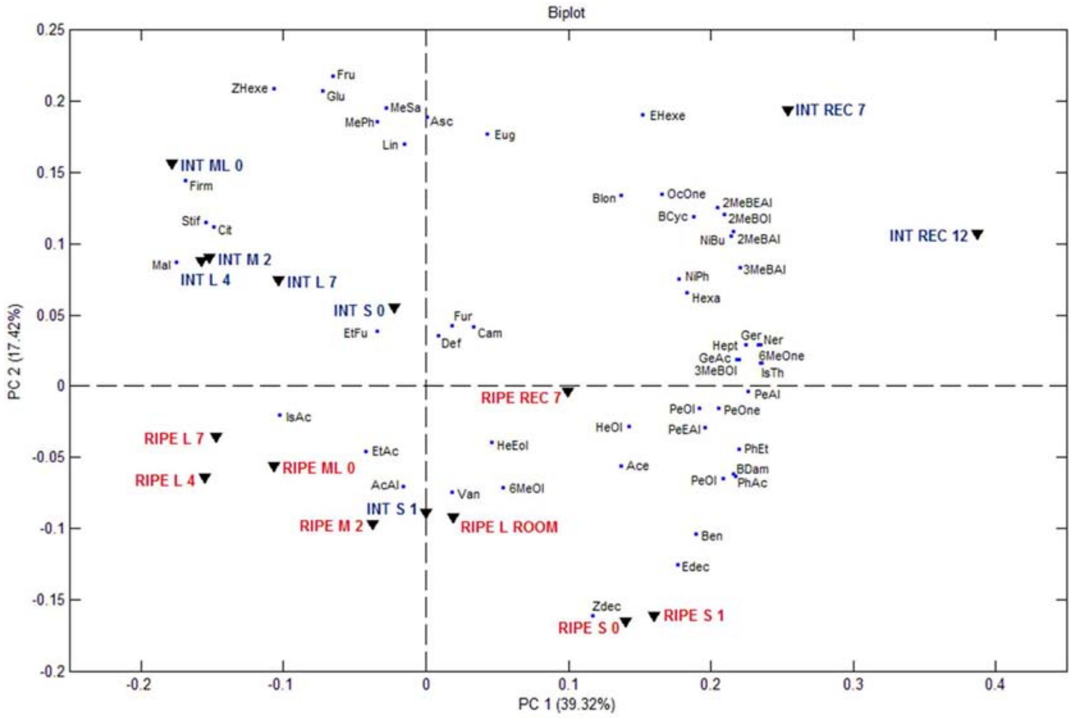

Figure 1. Principal component analysis (PCA) biplot of cv. Caramba tomato samples. Tags for tomato samples indicate fruits marketed at full (RIPE) or intermediate (INT) stage of ripeness. S, M, and L stand for short, medium, and long distribution chain, whereas REC denotes recommended commercial storage. The final number indicates the number of days between harvest and evaluation, whereas L ROOM denotes samples exposed to the long chain and ripened at room temperature afterward.

β-damascenone, and the group of C5 volatiles (1-penten-3-one, 1-penten-3-ol, (*E*)-2-pentenal, 1-pentanol, and 1-pentanal) (the complete data set, including results of statistical analyses, is reported in Appendix 2 in Supporting Information). C6 aldehydes ((*Z*)-3-hexenal, hexanal, and (*E*)-2-hexenal) and the corresponding alcohols ((*Z*)-3-hexenol, hexanol), which are key contributors to the fresh tomato top-note, seemed not to be strongly affected by the distribution chain conditions (Figure 1A, Appendix 3, Supporting Information). A reduced level in the main organic acids, citric and malic, contributed to the differentiation of Red harvested tomatoes exposed to the short chain: in these fruits, their total level was on average 18% lower than in fruits picked at the Light Red stage and subjected to medium or long chains, and 12% lower than in Breaker harvested fruits, exposed to extended long chain conditions and then allowed to achieve full ripeness (Appendix 2, Supporting Information). Fruit samples exposed to recommended commercial storage conditions were associated with increased levels of important tomato volatiles derived from the two aminoacids isoleucine (2-methylbutanal, 2-methylbutanol, and 2-methyl-2-butenal) and leucine (3-methylbutanal and 3-methylbutanol), particularly in the case of fruits marketed at an intermediate stage of ripeness (Figure 2A, Supporting Information). Another aminoacid-derived compound, 2-isobutylthiazole, showed a similar trend (Figure 1A, Supporting Information). A similar increase was also observed on some linear carotenoid-derived volatiles,[29] such as geranylacetone, 6-methyl-5-hepten-2-one, and geranial, whereas changes in sugar contents and texture parameters were not clearly associated with the considered postharvest handling conditions (Appendix 2, Supporting Information).

Cultivar Rebelion Tomatoes. Results of the PCA are reported in Figure 3: the first two PCs explained 51% and 15% of the variation. Also in this case, tomatoes harvested at the Red stage and exposed to short chain (RIPE S) were well separated from all of the other fruits to be marketed at full ripeness and exposed to medium or long chain conditions (RIPE M or L). Also in the group of tomato samples to be marketed at an intermediate stage of ripeness, fruit samples exposed to short chain (INT S) were separated from fruit samples subjected to medium-long chain conditions (INT M or L). In addition, fruits harvested at the Breaker stage, exposed to extended long chain conditions, and then allowed to achieve full ripeness at room temperature (RIPE L ROOM), developed a profile similar to that of Pink harvested fruits exposed to short chain (INT S), but very distant from that observed on fruits picked at full ripeness (RIPE S 0). Similar to what was observed on Caramba tomatoes, fruits exposed to recommended commercial storage conditions (INT REC, RIPE REC) seemed to follow a different pattern of variation when compared to fruits exposed to the more commonly occurring cold storage/transport conditions, i.e., stored within the chilling range (INT M or L, RIPE M or L).

A number of volatiles were strongly associated with the fruits fully ripened on the vine and subjected to short chain conditions, contributing to its marked differentiation from all the other samples. The formation of the phenylalanine-derived compounds 1-nitro-2-phenylethane, phenylacetaldehyde, and 2-phenylethanol was severely inhibited in all samples subjected to medium/long chain conditions (Figures 4 and 3A, Supporting Information). Interestingly, fruits harvested at the Breaker stage and exposed to extended long chain conditions almost completely lose the ability to synthesize these compounds when allowed to ripen at room temperature at the end of the refrigeration time. A similar though less strong inhibitory effect was observed on the formation of the aminoacid-derived 2-isobutylthiazole (Figure 3A, Supporting Information). The formation of the two lipid-derived aroma compounds (*E*,*E*)- and (*E*,*Z*)-2,4-decadienal was

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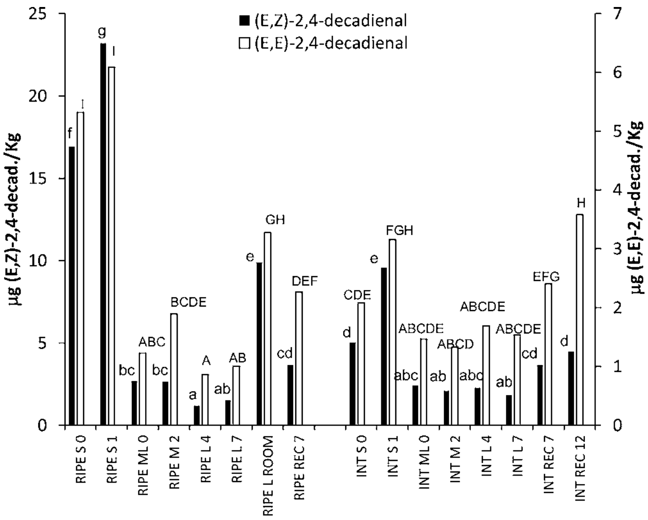

Figure 2. Level (μg equivalents of internal standard per kilogram of fruit fresh weight) of (*E*,*Z*)- and (*E*,*E*)-2,4-decadienal in cv. Caramba tomato samples. Different letters (lower-case for ■ data, upper-case for □ data) indicate significant differences (at $p < 0.05$ level) according to the Tukey test.

affected by medium and long chain conditions in a quite similar way than in Caramba tomatoes (Appendix 2, Supporting Information). Many of the other lipid-derived volatiles, the groups of C5 and C6 volatiles, tended also to accumulate in higher amounts, generally more than double, in fruits exposed to short than to common medium or long chain conditions (Figure 4A, Supporting Information). However, fruits harvested at the Breaker stage and exposed to cold storage up to 7 days partly retained the ability to synthesize these compounds during ripening at room temperature (Appendix 2, Supporting Information). Also in this cultivar, fruits exposed to recommended storage conditions showed enhanced levels of isoleucine and leucine derivatives when compared to fruits cold stored at a lower temperature (Figure 5A, Supporting Information). Similar to what was observed on Caramba tomatoes, organic acids also contributed to the differentiation of tomatoes subjected to short chain when compared to medium/long chain conditions (Appendix 2, Supporting Information). Fruits harvested at both Light Red and Breaker stages and subjected to medium or long chain conditions contained higher amounts (respectively, by 70% and 21%) of citric and malic acids than the short chain counterparts. In addition, fruits harvested at the Breaker stage, exposed to extended long chain and ripened at room temperature afterward, were characterized by a substantially higher level of these acids (+41%) when compared to tomatoes fully ripened on the vine and subjected to short chain conditions. Changes in sugar contents and texture parameters were not clearly linked to the examined postharvest handling conditions (Appendix 2, Supporting Information).

Second Postharvest Experiment. *Cultivar Nerina Tomatoes.* A less clear picture about the influence of the postharvest conditions on the overall profile of tomato fruits resulted from the PCA of experimental data on Nerina fruits (Figure 5). The first two PCs explained 42% and 15% of the variation. Fruits harvested at full ripeness and subjected to short chain (RIPE S) were similar between them, but differentiation with respect to samples harvested at the Green stage, exposed to medium or long chain conditions and then allowed to ripen at room temperature (GREEN M or L), was not as clear as for the other two cultivars. Fruits subjected to medium chain (GREEN M: 2 days refrigeration) were well separated from

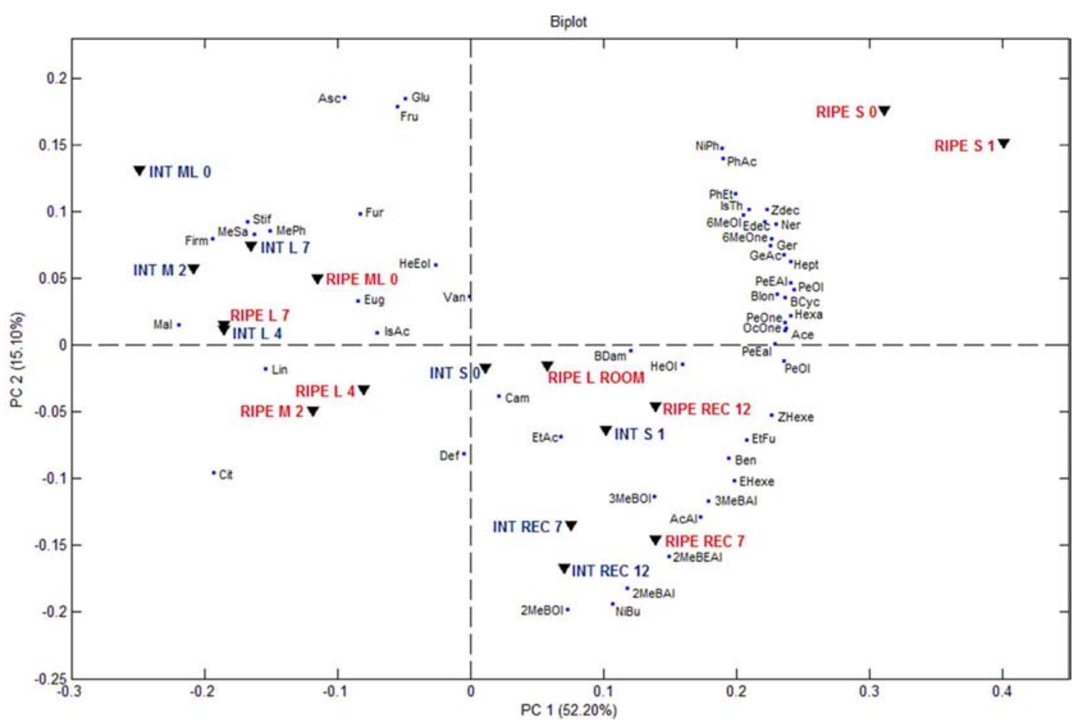

Figure 3. Principal component analysis (PCA) biplot of cv. Rebelion tomato samples. Tags for tomato samples indicate fruits marketed at full (RIPE) or intermediate (INT) stage of ripeness. S, M, and L stand for short, medium, and long distribution chains, whereas REC denotes recommended commercial storage. The final number indicates the number of days between harvest and evaluation, whereas L ROOM denotes samples exposed to the long chain and ripened at room temperature afterward.

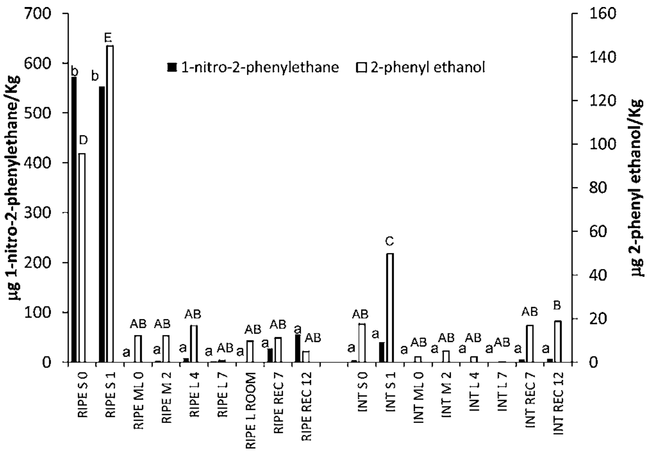

Figure 4. Level (μg equivalents of internal standard per kilogram of fruit fresh weight) of 1-nitro-2-phenylethane and 2-phenyl ethanol in cv. Rebelion tomato samples. Different letters (lower-case for ■ data; upper-case for □ data) indicate significant differences (at $p < 0.05$ level) according to the Tukey test.

short chain fruits, but not fruit samples exposed to longer chain conditions (GREEN L: 6 or 9 days refrigeration). Green harvested fruits subjected to recommended storage conditions for 7 days (GREEN REC 7) were similar to fruits exposed to common long and extended long chain (GREEN L 6 or 9), whereas after 12 days (GREEN REC 12) their profile showed a drift away from these samples and from those fully ripened on the vine. On the whole, the duration of the refrigeration step appeared to have an influence on the profile of fruits exposed to both common cold storage/transport conditions, below the threshold of chilling injury, and recommended storage conditions, above the threshold. Among samples of tomatoes to be marketed at an intermediate stage of ripeness (all INT samples), no clear differentiation between short versus medium/long chain fruit samples was found.

As observed on Rebelion tomato samples, the ability of fruits to synthesize 1-nitro-2-phenylethane and 2-isobutylthiazole seemed to be notably impaired by medium and long chain conditions (Figure 6), when comparing all fruit samples evaluated at the Red

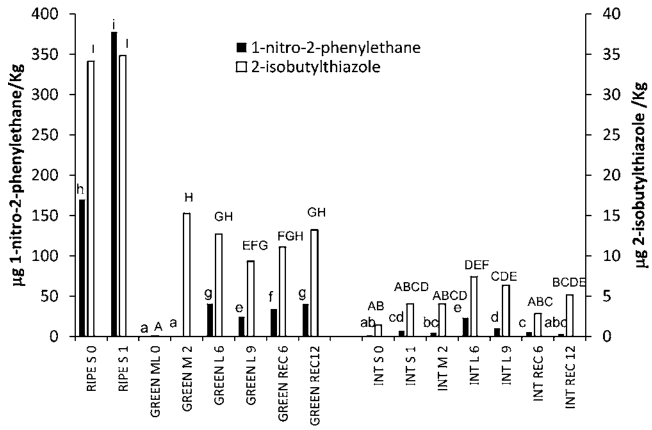

Figure 6. Level (μg equivalents of internal standard per kilogram of fruit fresh weight) of 1-nitro-2-phenylethane and 2-isobutylthiazole in cv. Nerina tomato samples. Different letters (lower-case for ■ data, upper-case for □ data) indicate significant differences (at $p < 0.05$ level) according to the Tukey test.

stage. However, a different trend was observed here for the other two compounds derived from phenylalanine, phenylacetaldehyde, and 2-phenylethanol: in this experiment, the formation of these compounds was markedly enhanced in samples harvested at the Green stage, exposed to medium chain and allowed to

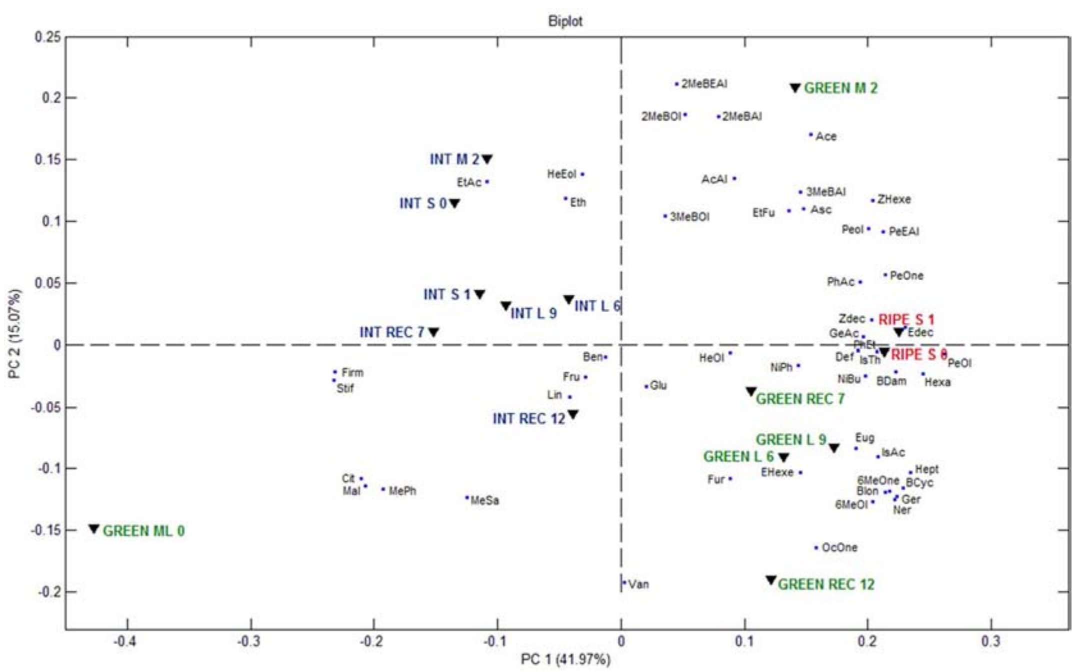

Figure 5. Principal component analysis (PCA) biplot of cv. Nerina tomato samples. Tags for tomato samples indicate fruits harvested at the green (GREEN), turning (INT), or red (RIPE) stage. S, M, and L stand for short, medium, and long distribution chains, whereas REC denotes recommended commercial storage. The final number indicates the number of days between harvest and evaluation for the short chain and the time of the cold storage/transport step in the other cases.

ripen at room temperature, and not significantly altered in the samples exposed to longer chain or to recommended storage conditions (Figure 6A, Supporting Information) when compared to fruits fully ripened on the vine. Enhanced levels of the isoleucine derivatives contributed also to the differentiation of the overall profile of the Green harvested fruits exposed to the medium chain with respect to fruits exposed to longer chain conditions (Figure 7A, Supporting Information). Interestingly, in this cultivar harvesting at the Green stage and refrigeration for an extended time at both 6 and 13 °C did not cause a significant suppression of C6 volatiles in fruits allowed to ripen at room temperature afterward with respect to fruit ripened on the vine (Figure 7A, Supporting Information). Different from what was observed on the other two cultivars, accumulation of isoleucine (Figure 7A, Supporting Information) and leucine derivatives (Appendix 2, Supporting Information) was not enhanced in fruits exposed to recommended storage conditions. Organic acids did not show marked effects associated with the postharvest conditions: among cold stored fruits, only GREEN L6 and GREEN REC 12 samples had enhanced levels with respect to short chain red fruit samples (Appendix 2, Supporting Information). In most cases, no significant effects of the distribution chain conditions were observed on sugar content and firmness parameters.

Correlations between Volatile Compounds. Pearson's correlation coefficients (r) between volatile compounds obtained from the whole data set have been analyzed. Only variables showing correlation coefficients higher than 0.8 and significant at the 0.01 level were considered (Appendix 4 in Supporting Information). Strong linear correlations ($r > 0.9$) were observed between some biochemical related compounds: between the two isoleucine derivatives 2-methylbutanal and 2-methylbutanol, among the open chain carotenoid derived compounds 6-methyl-5-hepten-2-one, neral, and geranial, between 1-pentanol and, separately, 2-heptenal and (*E*,*E*)-2,4-decadienal (lipid derived compounds), and among the phenylpropanoid metabolism related compounds 2-methoxyphenol, methylsalycilate, and eugenol. Less strong linear correlations ($0.9 > r > 0.8$) were observed between other biochemical related compounds: in particular, among 2-methylbutanal, 3-methylbutanal, 1-nitro-3-methylbutane, and 2-methylbutanol (isoleucine and leucine derivatives) and among 1-penten-3-one, 1-penten-3-ol, 1-pentanol, and (*E*)-2-pentanal (C5 lipid derivatives).

■ DISCUSSION

In the present study, the influence of postharvest conditions corresponding to different distribution scenarios and to recommendations for maintaining postharvest quality on some flavor related attributes of fresh tomatoes has been investigated, providing, in particular, detailed information about the effects on the formation of volatile compounds. Previous studies have examined the effects of different standardized postharvest treatments on tomato flavor quality, but contrasting results have been obtained for some aroma compounds.[13−18] Results from these studies are not easily comparable because of different conditions selected for postharvest experiments and different procedures used for the isolation of volatile compounds. In particular, the adoption of different protocols for the deactivation of enzymes during tomato sample preparation, before volatile isolation, is expected to profoundly influence the formation of some important volatile compounds, such as, for instance, the C6 compounds, thus changing the analytical output.[4] With respect to this, in the present study the original method developed by Buttery et al.[23] was followed because most of the tomato volatile published data have been obtained by this method. In addition, a higher number of major tomato volatiles than in previous studies was determined, covering most of the compounds contributing to sensory profile and consumer appreciation[4,30] and giving a more comprehensive picture of postharvest effects on aroma formation.

Moreover, the postharvest experiment was designed in order to reproduce as closely as possible in the laboratory those conditions actually occurring in commercial practice in Italy and corresponding to distribution chains of different length, instead of comparing more simple standardized postharvest procedures.

Significant differences between the three cultivars were observed in the effects of the considered postharvest factors on the overall profile and on many of the evaluated individual quality attributes. This confirmed findings by previous studies highlighting intervarietal differences in fruit response to postharvest handling, with regard to flavor related quality attributes.[10,13,14,18]

In two out of three cultivars, Caramba and Rebelion, the length of the distribution chain significantly affected the overall fruit profile, the effect being more pronounced in tomatoes marketed at full ripeness than in those marketed at an intermediate stage. Fruits exposed to medium or long chain conditions and evaluated just at the end of the refrigeration period showed only limited changes in the overall profile with respect to the same fruit samples at harvest, suggesting that cold storage at 6 °C up to 7 days, slowing down all the main biochemical processes associated to flavor formation, provided at the end of the storage/transport process a fruit quite similar to that at harvest. Consequently, the significant differences in the profile between these fruits subjected to medium or long chain conditions and the counterparts exposed to short chain conditions were due to differences in the ripening stage at harvest. Noticeably, in these two cultivars, at least for fruits picked at the Breaker stage, exposure to cold storage for 7 days could significantly alter the biochemistry of flavor formation during further ripening at room temperature at the end of the refrigeration period. Even though in the case of cv. Nerina conflicting results were obtained on this point, on the whole these observations seemed to confirm that early harvesting combined with cold storage has the potential to affect the biosynthetic pathways of flavor formation when the fruit is brought back to room temperature after exposure to chilling, in line with findings from previous works.[15,16,18,19] These effects could also be put in relation with the changes in flavor perceived on early harvested and cold stored fruits when analyzed at the Red stage and compared to vine ripened tomatoes, as found in one of the few studies reporting sensory data on postharvest effects on fresh tomatoes.[7]

The different pattern of variation in the overall profile of fruits exposed to recommended commercial storage with respect to the simulated medium or long distribution chain conditions suggested that the effects due to cold storage at chilling temperatures, for instance 5−6 °C, could be significantly different from those produced by cold storage above the chilling range, at about 10 °C for red tomatoes and 13° for green tomatoes, and at optimal relative humidity.[22,31] These results could contribute to the explanation of previously reported sensory data showing different effects between chilling and nonchilling storage temperature on the flavor profile of tomato fruits.[7]

Among all volatile compounds, those related to the metabolism of aminoacids seemed to be the most strongly affected by the considered postharvest handling factors. Three compounds derived from phenylalanine, 1-nitro-2-phenylethane, phenylacetaldehyde, and 2-phenylethanol, all of these reported as major contributors of tomato aroma,[4] were markedly affected in the considered cultivars. The formation of 1-nitro-2-phenylethane, which apparently took place in the later stages of vine ripening, was strongly inhibited in Nerina and Rebelion fruits exposed to every evaluated cold storage condition. Similarly, the formation of phenylacetaldehyde and 2-phenylethanol, which share the same immediate precursor with 1-nitro-2-phenylethane, phenylethylamine,[32] was also inhibited in Caramba and Rebelion fruits by postharvest conditions involving refrigeration but not in Nerina fruits, where, on the contrary, enhanced levels were produced in the sample exposed to cold storage for 2 days. These results could suggest a differential effect of the considered postharvest conditions on the conversion of phenylethylamine to, respectively, 1-nitro-2-phenylethane and phenylacetaldehyde/2-phenylethanol in the three considered cultivars.

2-Isobutylthiazole, which has been proposed to be formed from leucine[29] and reported to contribute a pungent−bitter note,[13] was also strongly influenced by the considered postharvest conditions, showing a behavior similar to that of 1-nitro-2-phenylethane in Rebelion and Nerina fruits, and similar to that of leucine and isoleucine derivatives in Caramba fruits.

Formation of isoleucine and leucine derivatives appeared to be highly sensitive to cold storage temperature. It was remarkably promoted by cold storage above the chilling range in Caramba and Rebelion fruits, whereas their content was unaffected or reduced in fruits kept at a chilling temperature. Similarly, increased levels of 2- and 3-methylbutanol were previously found in fruits stored at 10 and 12.5 °C when compared to fruits kept at 5 °C,[13] whereas an enhanced accumulation of 3-methylbutanal has also been observed in tomatoes stored at 10 or 12 °C with respect to storage at higher temperatures (20 or 30 °C).[14,17] An increased level of leucine derivatives might be associated with the previously observed development of off-flavors perceived in fruits exposed to cold storage above the chilling range.[7,12]

Regarding lipid-derived volatile compounds, the most remarkable alterations due to the distribution chain conditions were observed on (*E*,*E*)- and (*E*,*Z*)-2,4-decadienal, recently identified as important odorants in fresh tomatoes[26,30] and associated with sweet and floral notes.[33] According to information obtained by studies using labeled precursors, the regulation of their biosynthesis is distinct from that of the main lipid-derived aroma compounds, such as (*Z*)-3-hexenal and hexanal.[26] In our experiment, their formation was significantly inhibited in Caramba and Rebelion fruits subjected to cold storage. The effect was more pronounced at lower temperature, and the ability to recover from temperature abuse was only partial. The other important lipid-derived volatile compounds, the C5 and C6 groups, on average appeared to be less affected by the considered postharvest conditions than the above compounds. Only in one cultivar were marked reductions observed in medium or long chain fruits when compared to short chain tomatoes, but in this case, fruits were able to partly recover from chilling abuse during ripening at room temperature. Previous studies highlighted different effects of cold storage on C6 compounds depending on cultivar and storage temperature, ranging from reductions or no effect at chilling temperature[13,15,16,18] to increases for some C6 compounds (hexanal, (*E*)-2-hexenal) above the chilling range.[14−17] Our results added other evidence of substantial variability across different cultivars.

Among nonvolatile compounds contributing to tomato flavor, marked changes associated with distribution conditions were observed, as expected, on organic acids, in particular on Caramba and Rebelion fruits. Long distribution chain conditions were associated with higher levels of these compounds, presumably as a result of cold storage, in line with previous findings.[19] These results are in line with the observation of a higher sourness perceived in early harvested fruits, exposed to cold storage and then ripened at room temperature, when compared to vine ripened fruits.[7] Effects on sugars levels and on measured texture properties were not significant or not clearly associated with the considered distribution chain conditions.

Previous studies on fruits harvested at the red ripe stage and belonging to a large number of different genotypes have highlighted the existence of metabolic relationships between many tomato volatile compounds by different approaches.[29,34] These relationships are considered predictive of the commonalities of precursors and limiting steps in the pathways for their synthesis. Correlations observed in the present study confirmed the existence of some of these metabolic relationships also in fruits exposed to a range of postharvest handling conditions, indicating that coordinated biosynthesis of certain groups of volatile compounds takes place not only during ripening on the vine[29,34] but also under the considered postharvest conditions. This was found to be true for the formation of leucine and isoleucine derivatives, for a group of volatiles sharing the same precursor lycopene (6-methyl-5-hepten-2-one, neral, and geranial), and for the group of C5 lipid-derived volatiles. One member of this group, 1-pentanol, was strongly associated with two other lipid-derived volatiles, 2-heptenal, closely resembling previous findings,[34] and (*E*,*E*)-2,4-decadienal, which was not considered in previous studies on metabolic relationships. Our results seemed also to confirm the existence of a correlation between 2-methoxyphenol and the other two phenylpropanoids methylsalycilate and eugenol, while conflicting results have been previously reported on this point.[29,34]

The first detailed studies on the effects of postharvest operations on fresh tomatoes flavor quality[7,9−11] date back to the 1970s, when the constraints of the handling and marketing system were considered as factors which possibly could not be left out of consideration, and consequently, improvements in the management of quality could only be imagined within the context of that system. Nowadays, new consumer demand of locally produced and marketed vegetable products is creating a growing market niche, changing the perspective from which to look at this issue.

Results from the postharvest simulation performed in the present study suggest that remarkable differences may be observed in some flavor related attributes between tomatoes subjected to short, medium, or long distribution chains, or to recommended commercial storage procedures. Among all flavor quality attributes considered in this study, the level of some amino acid derived aroma compounds appear to be particularly sensitive to the practices associated with long distribution chains. The accumulation of organic acids and the biosynthesis of other groups of aroma compounds can also be significantly altered by these conditions. It is worth noting here that in this simulation it was not considered the effect of mechanical injury, which has been shown to influence some of the examined quality attributes.[35] Results of this study may represent the basis for further investigation designed to establish the extent to which these effects can be generalized to other tomato cultivars and to find out whether they can reflect significant sensory differences and influence consumer quality perception.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Mass spectra of two chromatographic peaks tentatively identified as 1-nitro-2-phenylethane and 1-nitro-3-methylbutane (Appendix 1); the complete data set of all analytical determinations and statistical analyses (Appendix 2); figures with concentration level changes of some volatile compounds (Appendix 3); Pearson's correlation coefficients (r) between volatile compounds obtained from the whole data set; only compounds for which at least one coefficient is higher than 0.8 (significant at the 0.01 or 0.05 level) are reported (Appendix 4). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) Martinez, S. et al. *Local Food Systems: Concepts, Impacts, and Issues*, ERR 97, U.S. Department of Agriculture, Economic Research Service: Washington, DC, 2010.

(2) Food Marketing Institute. *U.S. Grocery Shopper Trends*; Food Marketing Institute: Arlington, TX, 2009.

(3) Edward-Jones, G.; et al. Testing the assertion that 'local food is best': the challenges of an evidence-based approache. *Trends Food Sci. Technol.* **2008**, *19*, 265−274.

(4) Baldwin, E. A.; Scott, J. W.; Shewmaker, C. K.; Schuch, W. Flavor trivia and tomato aroma: biochemistry and possible mechanism for control of important aroma components. *HortScience* **2000**, *35*, 1013−1022.

(5) Dorais, M.; Papadopoulos, A. P.; Gosselin, A. Greenhouse tomato fruit quality. *Hortic. Rev.* **2001**, *26*, 239−319.

(6) Saltveit, M. E. Postharvest Biology and Handling. In *Tomatoes*; Heuvelink, E., Ed.; CABI Publishing: Wallingford, UK, 2005; pp 140−170.

(7) Kader, A. A.; Morris, L. L.; Allen Stevens, M.; Albright-Holton, M. Composition and flavor quality of fresh market tomatoes as influenced by some postharvest handling procedures. *J. Am. Soc. Hortic. Sci.* **1978**, *103*, 6−13.

(8) Bai, Y.; Lindhout, P. Domestication and breeding of tomatoes: What have we gained and what can we gain in the future? *Ann. Botany* **2007**, *100*, 1085−1094.

(9) Bisogni, C. A.; Armbruster, G.; Brecht, P. E. Quality comparisons of room ripened and field ripened tomato fruits. *J. Food Sci.* **1976**, *41*, 333−338.

(10) Kader, A. A.; Allen Stevens, M.; Albright-Holton, M.; Morris, L. L.; Algazi, M. Effect of fruit ripeness when picked on flavor and composition in fresh market tomatoes. *J. Am. Soc. Hortic. Sci.* **1977**, *102*, 724−731.

(11) Watada, A. E.; Aulenbach, B. B. Chemical and sensory qualities of fresh market tomatoes. *J. Food Sci.* **1979**, *44*, 1013−1016.

(12) Resurreccion, A. V. A.; Shewfelt, R. L. Relationships between sensory attributes and objective measurements of postharvest quality of tomatoes. *J. Food Sci.* **1985**, *50*, 1242−1245.

(13) Maul, F.; Sargent, S. A.; Sims, C. A.; Baldwin, E. A.; Balaban, M. O.; Huber, D. J. Tomato flavor and aroma quality as affected by storage temperature. *J. Food Sci.* **2000**, *65*, 1228−1237.

(14) Díaz de León-Sánchez, F.; Pelayo-Zaldívar, C.; Rivera-Cabrera, F.; Ponce-Valadez, M.; Ávila-Alejandre, X.; Fernández, F. J.; et al. Effect of refrigerated storage on aroma and alcohol dehydrogenase activity in tomato fruit. *Postharvest Biol. Technol.* **2009**, *54*, 93−100.

(15) Stern, D. J.; Buttery, R. G.; Teranishi, R.; Ling, L.; Scott, K.; Cantwell, M. Effect of storage and ripening on fresh tomato quality, Part I. *Food Chem.* **1994**, *49*, 225−231.

(16) Boukobza, F.; Taylor, A. J. Effect of postharvest treatment on flavour volatiles of tomatoes. *Postharvest Biol. Technol.* **2002**, *25*, 321−331.

(17) Goren, A.; Alkalai-Tuvia, S.; Perzelan, Y.; Aharon, Z.; Ilic', Z.; Fallik, E. Harvested tomato quality and nutritional levels as affected by high temperatures in Mediterranean wholesale markets, and home or refrigerated temperatures. *Adv. Hort. Sci.* **2010**, *24*, 200−206.

(18) Bai, J.; Baldwin, E. A.; Imahori, Y.; Kostenyuk, I.; Burns, J.; Brecht, J. K. Chilling and heating may regulate C6 volatile aroma production by different mechanisms in tomato (*Solanum lycopersicum*) fruit. *Postharvest Biol. Technol.* **2011**, *60*, 111−120.

(19) Thorne, S. N.; Efiuvwevwere, B. J. O. Changes in organic acids in chilled tomato fruit (*Lycopersicon esculentum* Mill). *J. Sci. Food Agric.* **1988**, *44*, 309−319.

(20) Sargent, S. A.; Brecht, J. K.; Olczyk, T. *Handling Florida Vegetables Series: Round and Roma Tomato Types*; (SS-VEC-928) Series of the Horticultural Sciences Department; University of Florida: Gainesville, FL, 2005. http://edis.ifas.ufl.edu/vh079) (accessed Jun 27, 2012).

(21) Auerswald, H.; Peters, P.; Brückner, B.; Krumbein, A.; Kuchenbuch, R. Sensory analysis and instrumental measuremets of short-term stored tomatoes (*Lycopersicon esculentum* Mill). *Postharvest Biol. Technol.* **1999**, *15*, 323−334.

(22) Sargent, S. A.; Moretti, C. L. Tomato. In *The Commercial Storage of Fruits, Vegetables, and Florist and Nursery Stock*, Draft, revised April 2004; Gross, K. C., Wang, C. Y., Saltveit, M., Eds.; U.S. Department of Agriculture: Washington, DC, 2004. http://www.ba.ars.usda.gov/hb66/contents.html) (accessed Jun 27, 2012).

(23) Buttery, R. G.; Teranishi, R.; Ling, L. C.; Flath, R. A.; Stern, D. J. Quantitative studies on origins of fresh tomato aroma volatiles. *J. Agric. Food Chem.* **1988**, *36*, 1247−1250.

(24) Prieto, A.; Basauri, O.; Rodil, R.; Usobiaga, A.; Fernández, L. A.; Etxebarria, N.; Zuloaga, O. Stir-bar sorptive extraction: A view on method optimization, novel applications, limitations and potential solutions. *J. Chromatogr., A.* **2010**, *1217*, 2642−2666.

(25) Raffo, A.; Kelderer, M.; Paoletti, F.; Zanella, A. Impact of innovative controlled atmosphere storage technologies and postharvest treatments on volatile compound production in cv. Pinova apples. *J. Agric. Food Chem.* **2009**, *57*, 915−923.

(26) Mayer, F.; Takeoka, G. R.; Buttery, R. G.; Whitehand, L. C.; Naim, M.; Rabinowitch, H. D. Studies on the aroma of five fresh tomato cultivars and the precursors of *cis*- and *trans*-4,5-epoxy-(*E*)-2-decenals and methional. *J. Agric. Food Chem.* **2008**, *56*, 3749−3757.

(27) The Pherobase database of pheromones and semiochemicals. http://www.pherobase.com (accessed on Sep 15, 2012).

(28) Batu, A. Determination of acceptable firmness and colour values of tomato. *J. Food Eng.* **2004**, *61*, 471−475.

(29) Mathieu, S.; Dal Cin, V.; Fei, Z.; Li, H.; Bliss, P.; Taylor, M. G.; Klee, H. J.; Tieman, D. M. Flavour compounds in tomato fruits: identification of loci and potential pathways affecting volatile composition. *J. Exp. Bot.* **2009**, *60*, 325−337.

(30) Tieman, D.; Bliss, P.; McIntyre, L. M.; Blandon-Ubeda, A.; Bies, D.; Odabasi, A. Z.; et al. The chemical interactions underlying tomato flavor preferences. *Curr. Biol.* **2012**, *22*, 1035−1039.

(31) Suslow, T. W.; Cantwell, M. Tomato. Recommendations for Maintaining Postharvest Quality. http://postharvest.ucdavis.edu/pfvegetable/Tomato/ (accessed on Jun 27, 2012).

(32) Tieman, D.; Taylor, M.; Schauer, N.; Fernie, A. R.; Hanson, A. D.; Klee, H. J. Tomato aromatic amino acid decarboxylases participate

in synthesis of the flavor volatiles 2-phenylethanol and 2-phenylacetaldehyde. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 8287−8292.

(33) Baldwin, E. A.; Goodner, K; Plotto, A.; Pritchett, K.; Einstein, M. Effect of volatiles and their concentration on perception of tomato descriptors. *J. Food Sci.* **2004**, *69*, S310−S318.

(34) Tikunov, Y.; Lommen, A.; Ric de Vos, C. H.; Verhoeven, H. A.; Bino, R. J.; Hall, R. D.; Bovy, A. G. A novel approach for nontargeted data analysis for metabolomics. Large-scale profiling of tomato fruit volatiles. *Plant Physiol.* **2005**, *139*, 1125−1137.

(35) Moretti, C. L.; Sargent, S. A.; Huber, D. J.; Calbo, A. G.; Pushmann, R. Chemical composition and physical properties of pericarp, locule and placental tissues of tomato fruit with internal bruising. *J. Am. Soc. Hortic. Sci.* **1998**, *123*, 656−660.