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Volatile profile and potential predictors of astringency loss in fresh, whole 'Rama Forte' persimmon fruit

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ABSTRACT

Volatile profile of fresh, whole 'Rama Forte' persimmons treated with CO_2 or ethanol (EtOH) vapor for astringency removal, and the relationship of the main volatile organic compounds (VOCs) with the loss of astringency were investigated. Persimmons were harvested at the commercial maturity stage and treated with 70 % CO_2 , 18 h, or 1.70 mL kg⁻¹ EtOH, 6 h. Headspace solid-phase microextraction coupled to gas chromatography-mass spectrometry allowed the tentative identification of 34 VOCs, 15 of them are reported for the first time on persimmons. Ethanol was the relevant compound common to CO_2 and EtOH-treated samples in the first days after treatment, while acetoin, hexanal, and trans-2-hexenal ((*E*)-hex-2-enal) were the relevant VOCs had their relative intensity increased. Pentadecanal, ethyl acetate, acetoin, and ethanol may be potential predictors of astringency loss in fresh, whole 'Rama Forte' persimmons.

1. Introduction

Persimmons are a fruit belonging to the *Ebenaceae* family (Yesiloglu et al., 2018). The concentration of water-soluble tannins at harvest defines if persimmons are astringent or non-astringent, although fruit from all the cultivars become edible when they reach maturity (Yonemori et al., 2000). Sugiura (1984, 2005) suggested splitting the persimmon cultivars into two groups: a volatile-independent group, with pollination constant non-astringent (PCNA) type, and a volatile-dependent group, with pollination constant astringent (PCA), pollination variant astringent (PVA) and pollination variant non-astringent (PVNA) types. The astringency can be removed by the solubilization of soluble tannins, which provide the astringent taste (Amorim et al., 2023). Those tannins are polymerized by acetaldehyde that accumulate in the flesh during exposure to either ethanol (EtOH) vapor or high levels of CO₂ (Taira, 1996).

'Rama Forte' is the most important persimmon variety grown in Brazil, a PVA-type cultivar. Harvesting takes place from March to June, with April being the most productive month (Amorim et al., 2020). Those fruit are usually consumed in Brazil when the flesh becomes red and juicy, after being treated with ethylene or EtOH for astringency removal (Prohort, 2016). Alternatively, high CO₂ concentrations can be used to obtain crisp and non-astringent 'Rama Forte' persimmons (Muñoz, 2002).

The volatile organic compounds (VOCs) are diverse in fruits, consisting of hundreds of chemical compounds (Abbas et al., 2023), which is partly responsible for the specific flavor found in different fruit species (Abbas et al., 2023; Jiang & Song, 2010). The VOCs are affected by several factors such as genetics, environmental conditions, production practices, and maturity degree, besides postharvest handling, and storage settings, which can drive modifications in the pathways involved in the volatile biosynthesis (Gonçalves et al., 2018).

The VOCs responsible for fruit aroma can be classified as primary, when found in whole fruit, or secondary compounds when resulting from tissue disruption (Drawert et al., 1969; Kays & Wang, 2000; Valero & Serrano, 2010). Whole and squeezed flesh samples of 'Rojo Brillante' persimmons (PVA type) showed an identical qualitative volatile profile after commercial astringency removal by CO₂, but quantitative

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differences among samples were found (Taiti et al., 2018). On the other hand, apple natural aroma can be highly modified by enzymatic processes during the cellular disruption caused by fruit processing (Drawert et al., 1969).

The VOCs can be used as indicators of fruit ripening (Drawert et al., 1969), and some of them have been identified as potential candidates for involvement in specific metabolic processes, such as astringency removal. (Amorim et al., 2020; Besada et al., 2013). A study carried out on 'Rama Forte' persimmon fruit treated with EtOH and CO2 for deastringency allowed the tentative identification of 33 volatile compounds in frozen, ground flesh samples. Two of them, 2,4-di-tert-butylphenol and pentadecanal, were found on persimmon fruit treated with both CO2 and EtOH after five days. Those compounds were identified as potential markers for astringency removal (Amorim et al., 2020). The use of solidphase microextraction (SPME) fiber-based headspace sampling followed by gas chromatography-mass spectrometry (GC-MS) allows for the qualitative and quantitative analysis of VOCs present in horticultural crops. In addition to GC-MS, in situ identification can be achieved with sensor-based technology, which enables the sampling and analysis of volatile compounds at the site of emission (Tiwari et al., 2020).

The purpose of our study was to present the volatile profile of fresh, whole 'Rama Forte' persimmons during astringency removal by CO_2 and EtOH treatments, and to examine the relationship between the VOCs and loss of astringency. Furthermore, our objective was to ascertain the existence of the potential volatile markers that had previously been identified in frozen, ground flesh of 'Rama Forte' persimmons, in the fresh, whole persimmon fruit. The identification of the volatile markers for the loss of astringency in those fresh, whole persimmons offers a promising avenue for advancing the study of intelligent packaging for 'Rama Forte' persimmons.

2. Materials and methods

2.1. Fruit material

Yellow-orange skin color 'Rama Forte' fruit were harvested from a persimmon orchard based in the Rio Grande do Sul State, Southern Brazil ($28^{\circ} 51' S, 51^{\circ} 16' W, 658 m$).

Fruit were transported to the lab into harvest crates $(36.0 \times 55.0 \times 30.5 \text{ cm})$, which were internally protected with bubble wrap to protect the fruit against mechanical injuries, like impact and abrasion. The persimmons were selected for the absence of pests, diseases, and mechanical injury. Fruit with 6 to 8 cm in size (largest diameter) and yellow-orange skin color, as described in the Classification of Persimmon Fruit from the Brazilian Program for the Modernization of Horticulture (Programa Brasileiro para a Modernização da Horticultura, 2009), were carefully selected.

2.2. Astringency removal treatments

The selected fruit were left overnight in the lab at 18.0 \pm 1.0 °C and then they were split into two groups of 225 persimmons each, which were exposed to CO₂ or EtOH vapor for astringency removal. Treatments were performed according to Amorim et al. (2020). For the CO₂ and EtOH treatments, the fruit were exposed to 70 % CO₂ for 18 h and to 1.70 mL kg⁻¹ EtOH for 6 h, respectively, inside a hermetic plastic container (0.61 \times 0.97 \times 0.60 m) with an internal ventilation system. Both treatments were performed at 20.0 \pm 1.0 °C. The hermetic containers were opened and ventilated immediately after finishing the treatments. Fruit were kept at 18.0 \pm 1.0 °C and assessed for up to eight days.

2.3. Sample preparation and volatile organic compounds analysis by headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography-mass spectrometry (GC-MS)

2.3.1. Sample preparation

Fresh persimmons (three replicates) were sampled for the volatile profile from day 3 to day 7 after CO_2 treatment, and from day 5 to day 8 after EtOH treatment since the compounds that should potentially indicate loss of astringency increase along the time after the treatment (Amorim et al., 2020).

Our previous study also indicated that non-treated 'Rama Forte' persimmon fruit persisted astringent and immature by the day 8 after harvest and did not show the compounds which were identified as potential markers for astringency removal caused by CO_2 and EtOH treatments (Amorim et al., 2020). Therefore, the non-treated persimmons were not included in this study.

One fresh, whole persimmon at a time was added to a 0.5 L glass flask (11.38 \times 11.38 \times 7.45 cm) with an airtight lid (Marinex 6448). A rubber septum was fitted to the lid to allow sampling. Glass flasks were kept in a 40 °C water bath for 60 min with no agitation. In order to capture the volatile compounds, a manual SPME holder (Supelco, Bellefonte, PA, USA) together with a 1 cm length Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber (50/30 μ m) (Supelco, Bellefonte, PA, to the glass flask headspace.

2.3.2. Instrumental analysis

Volatile organic compounds were determined by GC–MS (GC-7890B/MSD-5977 A, Agilent, Santa Clara, CA, USA). The injector with a SPME liner (Agilent Ultra Inert liner) operated in splitless mode at 250 °C. Desorption and fiber reconditioning were performed on the GC liner at 250 °C for 3 min. Chromatographic separations were made on a 5 % phenyl-methyl column (HP5-MS – 30 m × 0.25 mm ID × 0.25 µm film) with helium as carrier gas at 1.0 mL min⁻¹. Oven temperature conditions were 35 °C for 5 min, 5 °C min⁻¹ ramp until 180 °C, held at 180 °C for 10 min, and then, 10 °C min⁻¹ ramp until 250 °C. The final temperature (250 °C) was held for 5 min. Mass spectrometer (single quadrupole) was operated in the Electron Ionization (EI), positive mode, at 70 eV with ion source and interface temperatures at 230 °C and 280 °C, respectively. The scan mass range was adjusted for 35 to 400 *m/z* (adapted from Martineli et al. (2013)).

Individual VOC were identified by collating their linear retention indexes (LRI) with a C_8 - C_{30} *n*-alkanes series (Van den Dool & Kratz, 1963). The mass spectra were contrasted with the NIST Chemistry WebBook (2018) and with those available in the literature (Adams, 2017; Franco & Janzantti, 2005).

2.4. Astringency index in persimmon fruit samples

The astringency index was visually estimated by assessing color development during the reaction between soluble tannins and ferric chloride (FeCl₃). Twenty CO_2 and EtOH-treated persimmons were daily sampled for eight days after treatment. Fruit was cut in the equatorial region, and the freshly cut surface from the top half was immediately printed on a filter paper previously treated with a 5 % FeCl₃ solution as Gazit and Levy (1963). The printed paper was visually scored on a scale from 1 (not astringent) to 5 (extremely astringent) (Gazit & Levy, 1963).

2.5. Statistical analyses of the GC-MS dataset

An unsupervised chemometric approach by principal component analysis (PCA) was developed to explore the influence of deastringency treatments by CO_2 and EtOH on VOCs. The CO_2 treatment was evaluated in 5 experimental times: T3, T4, T5, T6, and T7 (i.e., three, four, five, six, and seven days after treatment, respectively); and EtOH treatment was evaluated in 4 experimental times: T5, T6, T7, and T8 (i.e., five, six, seven, and eight days after treatment, respectively). Afterwards, a numerical matrix was constructed for each treatment and exported to the PLS-ToolboxTM software (version 8.6.2, Eigenvector Research Incorporated, Manson, WA USA). The singular value decomposition (SVD) algorithm was applied to decompose the auto-scaled matrices.

The supervised chemometric approach by partial least squares discriminant analysis (PLS-DA) was applied on the same GC-MS datasets (CO₂ and EtOH) to evaluate the robustness of the samples clustering, as well as to highlight the most relevant compounds for the fruit discrimination based on deastringency treatments. The SIMPLS algorithm was applied for modeling according to the previously persimmon fruit clustering verified in PCA scores at a confidence level of 95 %. The SIMPLS algorithm developed partial least squares regression calculating the PLS factors directly as linear combinations of the original variables. The number of latent variables (LV) was selected based on the statistical parameters: modeling errors (RMSEC - root mean square error of calibration, RMSECV - root mean square error of cross validation); correlation coefficients on calibration (r_{cal}^2) and cross-validation (r_{val}^2) ; bias and coefficient of variation (CV) bias. The venetian blinds method (5 splits and 1 sample per split) was applied for cross validation (Alves Filho et al., 2019).

Univariate statistical analysis was developed by analysis of variance (ANOVA single factor, OriginTM 9.4 software) to statistically certify the differences between the persimmon fruit according to the period of the deastringency treatment. The means comparison of the samples was developed using the Tukey test (*p*-value <0.05), and the variance homogeneity into each sample group was verified by the Levene test (Sucupira et al., 2017). Astringency index data were shown as the mean

 \pm standard error of the mean (mean \pm SEM).

3. Results

3.1. Identification of the volatile organic compounds on fresh, whole persimmons

Thirty-four VOCs were tentatively identified in the persimmons, including 17 terpenes, 4 aldehydes, 3 alcohols, 3 ketones, 2 esters, 1 ether, 2 phenols, 1 hydrocarbon, and 1 phenylpropene. The thirteen following compounds were found only on the CO₂-treated samples: isopentyl alcohol (3-methylbutan-1-ol) (5), 1-hexanol (hexan-1-ol) (8), α -thujene (9), 1-butoxy-2-propanol (11), sabinene (12), β -pinene (13), ethyl hexanoate (17), 2,6-dimethylnonane (20), allo-ocimene (29), neoallo-ocimene (30), estragole (31), 4,6-di-tert-butyl-m-cresol (2,4ditert-butyl-5-methylphenol) (32), and pentadecanal (34). Three VOCs were exclusive from EtOH-treated samples: δ -3-carene (16), linalool (27), and butylated hydroxytoluene (2.6-ditert-butyl-4-methylphenol) (33). The eighteen other compounds: ethanol (1), ethyl acetate (2), 2pentanone (pentan-2-one) (3), acetoin (4), hexanal (6), trans-2-hexenal ((E)-hex-2-enal) (7), α -pinene (10), 6-methyl-5-heptene-2-one (6methylhept-5-en-2-one) (14), β -myrcene (15), α -phellandrene (18), α -terpinene (19), p-cymene (21), limonene (22), eucalyptol (23), cis- β -ocimene (24), trans- β -ocimene (25), γ -terpinene (26), and nonanal (28) were found in both CO_2 and EtOH-treated samples (Table 1).

Table 1

Tentatively	y identified com	pounds in fresh,	whole	'Rama Forte'	persimmons after astr	ingend	cy removal	performed b	y CO	2 and EtOH treat	nents.
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Peak	RT (min)	RI*	RI _{lit} **	Compound	Match (%)	CO ₂	Ethanol
1	1.529	<800	448	ethanol	87	+	+
2	2.372	<800	607	ethyl acetate	90	+	+
3	3.349	<800	686	2-pentanone (pentan-2-one)	86	+	+
4	3.833	<800	720	acetoin	88	+	+
5	4.732	<800	734	isopentyl alcohol (3-methylbutan-1-ol)	81	+	_
6	6.689	801	800	hexanal	94	+	+
7	8.783	854	854	trans-2-hexenal ((E)-hex-2-enal)	96	+	+
8	9.412	873	869	1-hexanol (hexan-1-ol)	89	+	_
9	11.493	927	924	α-thujene	88	+	-
10	11.695	932	932	α-pinene	94	+	+
11	12.136	945	947	1-butoxy-2-propanol (1-butoxypropan-2-ol)	86	+	-
12	13.185	973	969	sabinene	90	+	-
13	13.253	974	974	β -pinene	90	+	-
14	13.776	989	980	6-methyl-5-heptene-2-one (6-methylhept-5-en-2-one)	91	+	+
15	13.891	992	988	β -myrcene	76	+	+
16	14.114	998	1101	δ -3-carene	88	_	+
17	14.242	1002	996	ethyl hexanoate	86	+	-
18	14.272	1002	1002	α-phellandrene	92	+	+
19	14.713	1015	1014	α-terpinene	83	+	+
20	14.996	1024	1022	2,6-dimethylnonane	89	+	_
21	15.009	1024	1020	<i>p</i> -cymene	91	+	+
22	15.141	1028	1024	limonene	92	+	+
23	15.202	1030	1026	eucalyptol	92	+	+
24	15.510	1039	1032	<i>cis-β</i> -ocimene	91	+	+
25	15.848	1050	1044	trans-\u03c3-ocimene	92	+	+
26	16.156	1059	1059	γ-terpinene	91	+	+
27	17.522	1100	1095	linalool	83	_	+
28	17.668	1106	1108	nonanal	92	+	+
29	18.443	1130	1128	allo-ocimene	91	+	-
30	18.820	1142	1140	neoallo-ocimene	91	+	-
31	20.541	1199	1195	estragole	91	+	-
32	28.934	1516	_	4,6-di-tert-butyl-m-cresol (2,4-ditert-butyl-5-methylphenol)	86	+	-
33	28.955	1517	1517	butylated hydroxytoluene (2,6-ditert-butyl-4-methylphenol)	87	-	+
34	33.704	1718	1715	pentadecanal	78	+	_

RT: retention time (min).

RI*: Retention index: retention time using alkanes series (C_8 - C_{30}) converted in independent constant; chromatographic column 5 % phenyl-methyl column (HP5-MS – 30 m × 0.25 mm ID × 0.25 µm film).

RI_{lit**}: Retention index from literature (Adams, 2017; NIST Chemistry WebBook 2018).

(+) present; (-) absent.

3.2. Exploratory multivariate analysis on GC-MS dataset

An unsupervised multivariate analysis by PCA was developed for exploratory evaluation of the VOCs variability from the fresh persimmon fruit treated for astringency removal. Figs. 1 and 2 illustrate the PC1 \times PC2 scores (A), samples influence achieved by Hotelling T² versus modeling errors from Q residuals (B), and respective loadings (C) of the persimmons treated by CO₂ and EtOH, respectively.

The scores result from the deastringency performed by CO_2 (Fig. 1) and EtOH (Fig. 2) treatments showed tendency of separation of samples on the first two PC, with 82.72 % and 80.68 % of the total variance, respectively. Both PCA results showed fruit separation within scores based on days after treatment, with PC1 as the main responsible axis for that separation. Figs. 1B and 2B illustrated the absence of outliers on modeling (no values of Hotelling T² and Q residuals higher than the threshold lines at 1). Furthermore, despite some samples presented relative high Q residual values, they did not negatively influence both modeling (CO₂ and EtOH) by their low influence (low Hotelling T² values) (Ballabio & Consonni, 2013).

The CO₂-treated samples, which were analyzed at three, four, and five days after treatment (T3, T4, and T5) clustered at negative scores of PC1 and PC2. Samples analyzed on day six after treatment (T6) clustered at positive scores of PC1 and those analyzed on day seven (T7) located at negative scores of PC1 and positive scores of PC2 (Fig. 1A). Persimmons from days three to five after treatment showed higher amounts of ethanol (1), ethyl acetate (2) and 2,6-dimethylnonane (20), which decreased over time. T6 fruit samples had increased amounts of α -thujene (9), α -pinene (10), 1-butoxy-2-propanol (1-butoxypropan-2-ol) (11), sabinene (12), β -pinene (13), 6-methyl-5-heptene-2-one (6-methylhept-5-en-2-one) (14), β -myrcene (15), α -phellandrene (18), α -terpinene (19), *p*-cymene (21), limonene (22), eucalyptol (23), *cis*- β -ocimene (24), *trans-\beta*-ocimene (25), γ -terpinene (26), nonanal (28), allo-ocimene (29), neoallo-ocimene (30), estragole (31), 4,6-di-tert-butyl-m-cresol (2,4-ditert-butyl-5-methylphenol) (32), and pentadecanal (34). Persimmons from the last day after treatment (T7) showed higher amounts of 2pentanone (pentan-2-one) (3), acetoin (4), isopentyl alcohol (3-methylbutan-1-ol) (5), hexanal (6), trans-2-hexenal ((E)-hex-2-enal) (7), 1hexanol (hexan-1-ol) (8), and ethyl hexanoate (17) (Fig. 1C).

EtOH-treated samples, which were analyzed at five and six days (T5 and T6) after treatment clustered at negative scores of PC1 and PC2. Samples from day seven (T7) after treatment clustered at positive scores of PC1 and those from day eight (T8) located at negative scores of PC1 and positive scores of PC2 (Fig. 2A). Persimmon samples from days 5 and 6 (T5 and T6) showed increased amounts of ethanol (1) and δ -3carene (16), which diminished over time. T7 fruit samples presented higher amounts of α -pinene (10), 6-methyl-5-heptene-2-one (6-methylhept-5-en-2-one) (14), β -myrcene (15), α -phellandrene (18), α -terpinene (19), *p*-cymene (21), limonene (22), eucalyptol (23), *cis-β*-ocimene (24), trans- β -ocimene (25), γ -terpinene (26), linalool (27), nonanal (28) and butylated hydroxytoluene (2,6-ditert-butyl-4-methylphenol) (33)(Fig. 2C). Persimmon fruit from the last day after treatment (T8) had higher amounts of ethyl acetate (2), 2-pentanone (pentan-2-one) (3), acetoin (4), hexanal (6) and trans-2-hexenal ((E)-hex-2-enal) (7).

Overall, both treatments diminished the contents of hydrocarbons, but increased aldehydes, ketones, esters, and terpenes. In particular, fruit from the penultimate experimental day (T6 from CO_2 treatment, and T7 from EtOH treatment) showed greater amounts of terpenes, which decreased to the last experimental day. Furthermore, EtOH treatment showed slower and weaker effects on the fruit ripening than the CO_2 treatment based on, respectively, the chemical variability (hydrocarbons, aldehydes, ketones, esters, and terpenes) and the scores values observed on its samples.

After the overview on the persimmon fruit variability according to both deastringency treatments, a PLS-DA method was developed. For CO₂ treatment: T3, T4 and T5 samples at negative scores of PC1 and PC2 belonged to the first group; T6 at positive scores of PC1 was classified as the second group, while T7 at negative scores of PC1 and positive of PC2 was the third group. Likewise, for EtOH treatment: T5 and T6 samples at negative scores of PC1 corresponded to the second group; and T8 at negative scores of PC1 corresponded to the second group; and T8 at negative scores of PC1 and positive of PC2 was referred as the third group. Thus, the PLS-DA results corroborated the robustness of samples clustering detected by PCA for both treatments (low errors and bias values, and high correlation coefficients), as well as highlighted the most relevant compounds for the samples discrimination in their respective scores plots. Those relevancies were revealed by the VIP (variable importance



Fig. 1. (A) Scores coordinate system (PC1 \times PC2) of VOCs from fresh, whole 'Rama Forte' persimmon fruit analyzed by GC–MS after three (T3), four (T4), five (T5), six (T6) and seven (T7) days of the CO₂ treatment; (B) influence plot by Hotelling's T² \times Q residuals; and (C) PC1 \times PC2 loadings with the numbers referring to the described compounds in Table 1, with colors related to the scores clustering.



Fig. 2. (A) Scores coordinate system (PC1 \times PC2) of VOCs from fresh, whole 'Rama Forte' persimmon fruit analyzed by GC–MS after five (T5), six (T6), seven (T7) and eight (T8) days of the EtOH treatment; (B) influence plot by Hotelling's T² \times Q residuals; and (C) PC1 \times PC2 loadings with the numbers referring to the described compounds in Table 1, with colors related to the scores clustering.

in projection) scores results, which are illustrated in Fig. 3A and B for CO_2 and EtOH treatments, respectively. The statistical parameters from both PLS-DA modeling (CO₂ and EtOH treatments) are described in Table 2.

According to Fig. 3a and b, ethanol (1), acetoin (4), hexanal (6) and *trans*-2-hexenal ((*E*)-hex-2-enal) (7) were highlighted by VIP analysis (colored bars with intensity above the threshold at 1) as the most relevant compounds for persimmons discrimination for both CO₂ and EtOH treatments. Additionally, 1-hexanol (hexan-1-ol) (8), β -pinene (13), ethyl hexanoate (17), 2,6-dimethyl-nonane (2,6-dimethylnonane) (20), and nonanal (28) were found to be relevant compounds only for the

CO₂-treated fruit; while ethyl acetate (2) and 2-pentanone (pentan-2one) (3) were relevant compounds only for the EtOH-treatment. The compounds bar colors are referred to the samples clustering at the PCA analysis: Figs. 1a for CO₂ treatment; and Fig. 2a for EtOH treatment. The low errors values on calibration (RMSEC) and CV (RMSECV) modeling, the proximity between RMSEC and RMSECV values, as well as the low calibration and CV bias, and high correlation coefficients on calibration (r_{cal}^2) and CV (r_{CV}^2) reveled the satisfactory classification capacity of both models (CO₂ and EtOH treatments).

In order to investigate the statistical significance of the VOCs for the persimmon fruit discrimination according to the deastringency



Fig. 3. Relevant compounds highlighted by the VIP analysis for fresh, whole 'Rama Forte' persimmon fruit based on deastringency treatment: A) CO₂; B) EtOH. The bars colors are referred to the PCA plots, and the compound numbering follows the retention time described in Table 1.

Table 2

Statistical parameters from the PLS-DA modeling for CO_2 and EtOH deastringency treatments.

Model	CO_2	EtOH
LV number	2	2
Captured variance (%)	82.67	80.31
RMSEC	0.14	0.11
r_{cal}^2	0.92	0.95
RMSECV	0.22	0.23
r_{CV}^2	0.82	0.86
bias	0.00	0.00
CV bias	-0.05	-0.11

treatments, an analysis of variance (ANOVA) was developed. In this regard, those VOCs with significant changes according to the PLS-DA modeling were semi-quantified and expressed as the relative change. Figs. 4 and 5 present the variations of the compounds in persimmon fruit with the standard deviation of the treatment's replicates. The peak intensity of the compounds (relative intensity as y axis) could not be compared among them, since the ionization capacity in a MS analysis depends on the intrinsic structural characteristics of each compound (Watson & Sparktam, 2007).

The results provided by the multivariate statistical analyses (PCA and PLS-DA) were corroborated by ANOVA for each compound into the deastringency treatments by CO₂ and EtOH (Fig. 4 and 5). The decrease of ethanol (A) was observed mainly in the last two days for both CO₂ and EtOH treatments (Fig. 4 and 5). Moreover, increases of acetoin (B), hexanal (C), *trans*-2-hexenal ((*E*)-hex-2-enal) (D), 1-hexanol (hexan-1-ol) (E), β -pinene (F), and ethyl hexanoate (G) were statistically certified over time after CO₂ treatment. The higher intensity of the compound 2,6-dimethylnonane (H) was noticed on day four after treatment. Persimmon samples from days three and seven showed the same intensity of nonanal (I) (Fig. 4). The increase of ethyl acetate (B), 2-pentanone (pentan-2-one) (C), acetoin (D), hexanal (E) and trans-2-hexenal ((E)-hex-2-enal) (F) was noticed over time after EtOH treatment.

3.3. Astringency index (AI) in persimmon fruit

 CO_2 -treated persimmons showed AI of 2.00 immediately after the treatment, which characterize them as slightly astringent fruit (Gazit & Levy, 1963). Astringency below 1.5 was found on day one after treatment and it was completely removed on day three, when the AI reached 1.0, hence the persimmons were considered as non-astringent. Persimmon fruit evaluated immediately after the EtOH treatment were as astringent as non-treated freshly-picked persimmons (AI = 5.0), but they became moderately astringent (AI = 3.0) on day three after treatment. Slightly astringent fruit were noticed on day five after treatment (AI = 1.9). Astringency below 1.5 was noticed only at the end of the period (day eight) when the AI reached level 1.3 (Table 3).

4. Discussion

Little is known about the VOCs in persimmon fruit, even so, all the studies were carried out with frozen, ground samples from both nontreated and treated fruit for astringency removal (Amorim et al., 2020; Besada et al., 2013; Horvat et al., 1991; Martineli et al., 2013; Taira et al., 1996; Wang et al., 2011). The analysis of fresh, whole 'Rama Forte' persimmons treated for astringency removal allowed the tentative identification of 34 VOCs, distributed as follows: 17 terpenes, 4 aldehydes, 3 alcohols, 3 ketones, 2 esters, 2 phenols, 1 ether, 1 hydrocarbon, and 1 phenylpropene. Eight terpenes (α -pinene, β -pinene, β -myrcene, α -phellandrene, *p*-cymene, limonene, eucalyptol, and γ -terpinene) out of seventeen terpenes found in our study were also identified in the ground flesh of 'Rama Forte' persimmon fruit treated with EtOH vapor or high concentration of CO₂ for astringency removal (Amorim et al., 2020). In addition, seven of them (β -pinene, β -myrcene, α -terpinene, *p*-cymene, limonene, γ -terpinene, and δ -3-carene) were found in the ground flesh of 'Mikado' persimmons after the astringency removal by EtOH (Martineli et al., 2013). Terpenes were found in higher number in fresh, whole persimmons than in ground persimmon samples. Our study describes the presence of the monoterpenes α -thujene, sabinene, *cis-\beta*-ocimene, trans-



Fig. 4. Volatile organic compounds variations in fresh, whole 'Rama Forte' persimmon fruit after three (T3), four (T4), five (T5), six (T6) and seven (T7) days of the CO_2 treatment. Means comparison developed by Tukey test (*p*-value <0.05), and variance homogeneity verified by the Levene test.



Fig. 5. Volatile organic compounds variations in fresh, whole 'Rama Forte' persimmon fruit after five (T5), six (T6), seven (T7) and eight (T8) days of the EtOH treatment. Means comparison developed by Tukey test (p-value <0.05), and variance homogeneity verified by the Levene test.

Table 3

Astringency index in 'Rama Forte' persimmon fruit from the end of CO₂ and ethanol treatments and on the subsequent eight days at room temperature.

Deastringency	Days after treatment									
treatment	End of treatment	1	2	3	4	5	6	7	8	
CO ₂ * Ethanol*	$\begin{array}{c} 2.0 \pm 0.00 \\ 5.0 \pm 0.00 \end{array}$	$\begin{array}{c} 1.20 \pm 0.09 \\ 4.75 \pm 0.12 \end{array}$	$\begin{array}{c} 1.40\pm0.11\\ 3.60\pm0.13\end{array}$	$\begin{array}{c} 1.00\pm0.00\\ 3.00\pm0.00\end{array}$	$\begin{array}{c} 1.00\pm0.00\\ 2.30\pm0.16\end{array}$	$\begin{array}{c} 1.00\pm0.00\\ 1.90\pm0.07\end{array}$	$\begin{array}{c} 1.00\pm0.00\\ 1.60\pm0.11\end{array}$	$\begin{array}{c} 1.00 \pm 0.00 \\ 1.55 \pm 0.11 \end{array}$	$\begin{array}{c} 1.05\pm0.05\\ 1.30\pm0.11\end{array}$	

Mean \pm SEM of 20 fruit.

β-ocimene, allo-ocimene, and neoallo-ocimene for the first time in persimmons. Terpenes are a significant group of aromatic compounds. Many of them exhibit bioactive properties and often contribute to the flavor of fruits (Kupska et al., 2016).

The aldehydes identified on fresh, whole 'Rama Forte' persimmons (hexanal, nonanal, trans-2-hexenal ((*E*)-hex-2-enal), and pentadecanal) were also found in the ground 'Rama Forte' persimmon samples (Amorim et al., 2020). The aldehydes hexanal, nonanal, and trans-2hexenal ((E)-hex-2-enal) were reported on the flesh of 'Triumph' persimmons as well (Wang et al., 2011). Hexanal was also identified in several cultivars from PCNA and non-PCNA groups at harvest, as well as in non-PCNA cultivars after CO₂ treatment (Besada et al., 2013). The VOC trans-2-hexenal ((E)-hex-2-enal) was identified as one of the two major components in both astringent (Giombo, Aizumi Shiraza, and Sheng) and non-astringent (Fuyu, Hanafuyu, and Shogatsu) persimmon cultivars studied by Horvat et al. (1991). According to Horvat et al. (1991), the volatiles bornyl acetate and *trans*-2-hexenal ((E)-hex-2-enal) are likely the primary contributors to persimmon aroma.

Alcohol volatile compounds are important in most fruits and vegetables, but tend to play a minor role in aroma and flavor (Espinoza et al., 2019). Our study identified ethanol, isopentyl alcohol (3-methylbutan-1-ol), and 1-hexanol (hexan-1-ol) on fresh, whole persimmons. Previous studies have also reported 1-hexanol (hexan-1-ol) on persimmons (Besada et al., 2013; Taira et al., 1996; Wang et al., 2011). Ethanol was found on non-PCNA persimmon cultivars after CO2 treatment (Besada

et al., 2013).

Acetoin and 6-methyl-5-heptene-2-one (6-methylhept-5-en-2-one), which belong to the ketones group, have been previously reported on persimmons (Taira et al., 1996; Wang et al., 2011).

In addition to the six terpenes mentioned above, other compounds have been identified in persimmons for the first time, including ethyl acetate, 2-pentanone (pentan-2-one), isopentyl alcohol (3-methylbutan-1-ol), 1-butoxy-2-propanol (1-butoxypropan-2-ol), ethyl hexanoate, 2,6dimethylnonane, estragole, 4,6-di-tert-butyl-m-cresol (2,4-ditert-butyl-5-methylphenol), and butylated hydroxytoluene (2,6-ditert-butyl-4methylphenol).

The VOCs responsible for the fruit aroma can be classified as primary if they are present in whole fruit or secondary if they are produced as a result of tissue disruption (Valero & Serrano, 2010). Thirty-three VOCs, including 10 terpenes, 10 esters, 5 aldehydes, 3 ketones, 2 carboxylic acid, 1 phenol, and two fatty acids were found on the ground flesh of 'Rama Forte' persimmons (Amorim et al., 2020). Our results for the fresh, whole fruit mainly showed a higher number of terpenes and a smaller number of esters. Moreover, we did not detect the presence of fatty acids (free or esterified derivatives) that were identified in the frozen, ground persimmon samples (Amorim et al., 2020). Differences in volatile aroma profiles were also observed between whole and ground 'Castlebrite' apricots during storage (Defilippi et al., 2009).

The expected clear distinction between samples from the first and the last days after treatment was observed, but samples from penultimate day after treatment drifted away from both clusters of samples. Ethanol was the relevant compound common to CO2 and EtOH-treated samples at the beginning of the post-treatment period, whereas 2,6-dimethylnonane was relevant only to CO2-treated samples, and ethyl acetate was relevant only to EtOH-treated persimmons. Most astringent persimmon cultivars show an increase in the levels of ethanol and acetaldehyde when exposed to oxygen depletion conditions induced by high concentrations of CO₂ (Besada et al., 2013; Matsuo & Ito, 1977; Pesis & Ben-Arie, 1984). Likewise, the deastringency performed by EtOH vapor provides the immediate accumulation of ethanol in the persimmon flesh. In addition, the enzyme alcohol dehydrogenase, which catalyzes the oxidation of ethanol to acetaldehyde, favors the formation of ethanol due to the extremely small equilibrium constant and relatively small Km value for acetaldehyde (Matsuo & Ito, 1977). On the other hand, the common relevant VOCs found in the last post-treatment days were acetoin, hexanal, and trans-2-hexenal. The compounds 1-hexanol (hexan-1-ol) and ethyl hexanoate were only relevant for CO2, while 2pentanone (pentan-2-one) was only relevant for the EtOH treatment. Acetoin has a pleasant creamy yogurt odor (Xiao & Lu, 2014). Such volatile compound is naturally present in fruits (Xiao & Lu, 2014), and its concentration changes as the ripening progresses (Shiota, 1991). Acetoin was not detected on unripe pawpaw, but its concentration was as high as 227 and 3123 μ g kg⁻¹ on ripe and overripe pawpaw fruit, respectively (Shiota, 1991). Hexanal is generated via the enzymatic action of lipoxygenase and can be detected in whole fruits at advanced stages of ripening (Defilippi et al., 2009). The aldehyde trans-2-hexenal ((E)-hex-2-enal), mentioned by Horvat et al. (1991) as one of the main contributors to persimmon aroma, was found to be the major wound volatile component in strawberry fruit upon wounding (Myung et al., 2006). All three relevant VOCs common to both CO₂ and EtOH-treated samples in the last days after treatment are mainly related to wounding or overripening, when the cellular membranes of the fruits become more permeable, allowing lipoxygenase to interact with its substrates (Wang et al., 2020).

On days three and four, when the CO₂-treated persimmons became completely non-astringent, the nonanal, ethanol, and 2,6-dimethylnonane were the major compounds detected. In addition, acetoin, hexanal, trans-2-hexenal ((E)-hex-2-enal), 1-hexanol (hexan-1-ol), β -pinene, and ethyl hexanoate increased over time after treatment. EtOH-treated fruit showed an increase in ethyl acetate, 2-pentanone (pentan-2-one), acetoin, hexanal, and *trans*-2-hexenal ((E)-hex-2-enal) over time after treatment, which was accompanied by a decrease in astringency to the lowest levels. Nevertheless, the volatile compounds hexanal, *trans*-2hexenal ((E)-hex-2-enal), and nonanal were identified in non-treated 'Rama Forte' persimmons that remained astringent for 8 days after harvest (Amorim et al., 2020), suggesting that those compounds are not related to the astringency loss process.

Two volatile compounds, 2,4-di-*tert*-butylphenol (2,4-ditert-butylphenol) and pentadecanal, were previously identified as potential markers for astringency removal by CO_2 and EtOH treatments in 'Rama Forte' ground flesh (Amorim et al., 2020). The aldehyde pentadecanal was also identified in this study on fresh, whole 'Rama Forte' fruit. The former one was not found on whole persimmon fruit, but its isomer, the phenol 4,6-di-*tert*-butyl-m-cresol (2,4-ditert-butyl-5-methylphenol) was identified. This VOC was found throughout the whole post-treatment period, except on day five. Both compounds 4,6-di-*tert*-butyl-m-cresol (2,4-ditert-butyl-5-methylphenol) and pentadecanal were observed only on CO_2 -treated persimmons, but were not pointed as relevant compounds by the VIP analysis.

Although several mechanisms may be involved in the loss of astringency of PVA, PVNA, PCA, and PCNA persimmon fruit (Tessmer et al., 2016; Novillo et al., 2013; Yonemori & Matsushima (1987, Yonemori and Matsushima, 1985); Sugiura & Tomana, 1983; Sugiura et al., 1979), some compounds seem to be common to natural and artificial astringency removal, since the phenol 2,4-ditert-butylphenol was found as one of the major volatile compounds on the ground flesh of the nonastringent 'Fuyu' persimmon fruit (PCNA-type) (Matos, 2020). Besada et al. (2013) also suggested some volatiles as candidates to be involved in the natural and artificial process of astringency loss in several varieties of sweet and astringent persimmons.

Our study on fresh whole persimmons revealed at least one of the compounds previously proposed as potential markers of astringency removal in ground 'Rama Forte' persimmons, and highlighted other VOCs observed when astringency is lost. Since astringency loss and flesh softening occur simultaneously in EtOH-treated persimmons, esters such as ethyl acetate, and ketones such as acetoin may be associated with both processes and could be used as predictors of the loss of astringency in those fruit. Regarding CO_2 -treated persimmons, which lose astringency quickly and maintain their flesh's crispness, ethanol appears to be a potential predictor of astringency loss. Ethanol is produced by the oxygen depletion conditions induced by the treatment and is continuously converted into acetaldehyde, which is involved in the polymerization of soluble tannins and the subsequent loss of astringency.

The identification of these VOCs provides a basis for further research into the development of intelligent packaging that can detect the loss of astringency in persimmons and communicate this information to the consumer, indicating that the persimmon is ready to eat.

5. Conclusion

Analysis of fresh, whole 'Rama Forte' persimmon fruit treated with CO_2 and EtOH for astringency removal allowed the tentative identification of 34 volatile compounds, and 15 out of them are reported for the first time on persimmons. When astringency reached its lowest levels, some of the major VOCs had their relative intensity increased. The aldehyde pentadecanal, previously suggested as a potential marker compound for astringency removal in ground flesh, was also found on fresh, whole 'Rama Forte' persimmons. Other volatile compounds, such as ethyl acetate, acetoin, and ethanol may also be potential predictors of astringency loss.

CRediT authorship contribution statement

Lucimara Rogéria Antoniolli: Writing – original draft, Visualization, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. Elenilson Godoy Alves Filho: Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis. Tigressa Helena Soares Rodrigues: Writing – review & editing, Methodology, Funding acquisition, Formal analysis. Deborah Santos Garruti: Writing – review & editing, Methodology. Kirley Marques Canuto: Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

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