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Research Article

Influence of Glow Discharge Plasma Treatment on Cashew Apple Juice's Aroma Profile and Volatile Compounds

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Cashew apple juice has a distinctive fruity aroma but contains an undesired balsamic/chemical note caused by the high concentration of styrene and other aromatic hydrocarbons. Cold plasma technology can induce chemical changes to fruit juices' volatile compounds, improving the aroma of fruit juices. This study is aimed at evaluating the chemical effects of cold plasma on the volatile compounds and aroma of cashew apple juice, which is characterized by a complex mixture of compounds. Glow discharge plasma was applied to cashew apple juice, varying the plasma flow rate (10 to 30 mL/min) and processing time (10 to 20 min) at a constant voltage (80 kV). Plasma treatment induced several changes in the juice's volatile compound composition, with a significant decrease in fatty acids and fatty acid esters (92%) and an increase in aldehydes (50%), alcohols (86%), and short-chain esters (21%). The primary reaction observed during plasma treatment was the internal scission of fatty acid and fatty acid esters, which formed short-chain esters and aldehydes. Further hydrogenation of aldehydes produced alcohols. The chemical changes induced by plasma treatment intensified cashew apple juice's aroma by 28% while maintaining its aroma profile.

1. Introduction

Cashew apple (*Anacardium occidentale*) juice is widely consumed in some regions of Brazil, India, and Central Africa. The cashew apple is considered an exotic fruit in most of the world due to its short shelf life, making its distribution difficult to most markets. Cashew apple juice, therefore, is also considered an exotic juice. Its flavor is generally sweet with a combination of tartness and high astringency. Its flavor does not resemble any other commercial fruit.

The aroma of cashew apple juice has been described as fragrant, fruity, and tropical. The aroma profile of the juice can change slightly depending on the cashew variety (yellow, red, and orange), ripeness, and kind of processing method. Its primary aroma descriptor is fruity, correlated with its natural sweetness. Depending on the cultivar (variety), it may have floral, woody, earthy, and citrus notes [1].

From a chemical perspective, the aroma of cashew apple juice is a complex mixture of esters, fatty acids, aldehydes, terpenes, hydrocarbons, and aromatic hydrocarbons [1–3]. The esters contribute to the primary fruity descriptor, while the other chemical compounds are responsible for the secondary notes. Cashew apple contains styrene in its composition, which gives it an aldehydic note that may be unpleasant for some persons [1]. Reducing styrene concentration in cashew apple juice can improve its acceptance.

Cold plasma works through a process that involves ionized gas at relatively low temperatures, typically at or near room temperature. By definition, cold plasma refers to the fourth state of matter, consisting of partially ionized gas composed of free electrons, free radicals, charged ions, and neutral particles. Cold plasma is generated by subjecting a gas to an energy source, such as an electrical discharge, radio frequency, and microwave. This energy input causes the gas to lose electrons, forming positively charged ions and free electrons, which further react creating more complex free radicals. In contact with other compounds, cold plasma induces a series of chemical changes that can modify

surfaces, kill microorganisms, induce enzymatic reactions, and change bioactive compounds [4, 5].

Cold plasma is a technology under development that can be used to sanitize [6–8], remove pesticides and herbicides from food surfaces [9–11], improve nutritional quality [12, 13], mitigate off-flavors [14, 15], and improve sensory quality, such as food aroma [16, 17]. Cold plasma generates reactive oxygen and nitrogen species (ROS and RNS) that can react with many organic compounds in foods. Properly selecting cold plasma technology and operating conditions can improve many food products' nutritional and sensory properties [12, 18–21].

Cold plasma can be utilized through various technological approaches, including glow discharge, dielectric barrier discharge, jet, arc, gliding arc, microwave-driven discharge, and radio frequency-driven discharge plasma [22]. Each of these technologies has its own set of advantages and drawbacks. Compared to other plasma systems, the main advantage of glow discharge plasma is its generation of a gas plasma stream that is subsequently delivered into a spacious chamber for sample treatment. This approach offers the advantage of processing large sample volumes, yet it comes with the drawback of requiring low pressures (<0.5 bar) within the chamber.

The use of cold plasma technology on food property enhancement depends on a deep understanding of the chemical changes induced by plasma. In the past years, many studies have reported the chemical reactions and mechanisms that occur with sugars [23, 24], oligosaccharides [25, 26], furans, pyrazines, and pyridines [17, 27], amino acids [28, 29], esters and thioesters [30], terpenes, and sesquiterpenes [14, 16] when subjected to plasma. However, due to the complexity of functional groups in foods, much work must be done to fully address this technology's capabilities.

Cold plasma processing of fruit juices showed high capability in modulating their aroma and mitigating off-flavors and undesirable aromas. Studies with orange juice showed that the undesired off-flavor caused by 4-terpineol was significantly decreased [14, 15]. Furthermore, 4-terpineol was converted into limonene, orange juice's most characteristic flavor compound. Studies with pineapple juice showed the capacity to change the ester compounds chemically. Such capability reduced the concentration of methyl hexanoate, which has a very pungent sweet flavor, improving the acceptance of the juice [30]. The plasma treatment carried out with camu-camu juice, an exotic Amazonian fruit, showed the ability to modulate the juice's aroma, increasing or decreasing the odor activity value of several descriptors by changing the operating conditions of the treatment [16, 31].

Cashew apple juice is an interesting case study because it has compounds from various classes of organic compounds, enabling us to understand the selectivity of reactive plasma species. This work intended to extend the knowledge on plasma treatment of fruit juices and its effects on aroma. Cashew apple juice was subjected to glow discharge plasma technology at three air flow rates (10 to 30 mL/min) and two processing times (10 and 20 min), and the volatile chemical profile of the juice aroma was identified by gas chromatography coupled to mass spectrometry.

2. Materials and Methods

2.1. Materials. Fruit Ltda (Caucaia, Brazil) provided the cashew apple pulp containing no additives. Cashew apple juice was produced by diluting the pulp with distilled water (1 : 1 *v*/*v*).

2.2. Plasma Processing. Cold plasma treatment was carried out in a glow discharge plasma system (Plasma Etch model PE-50, USA) fully described in [16]. The assays were carried out at three synthetic air flow rates (10, 20, and 30 mL/min) and two processing times (10 and 20 min). These operating conditions were chosen based on prior experience with cold plasma technology applied to fruit juices [13, 14, 16]. The operating conditions were also determined to fit a 2^3 face-centered experimental design with three levels for air flow rate and processing times (0, 10, and 20 min) with 0 min represented by the reference (unprocessed juice). The pressure inside the equipment was maintained at 0.4 bar. Glow discharge plasma should operate under a 0.2 to 0.5 bar pressure for better performance and higher generation of reactive species. The system was operated at 0.4 bar because it is the lowest pressure achieved by the system vacuum pump.

Cashew apple juice (40 mL) was placed inside polypropylene tubes and subjected to plasma treatment. The control group consisted of untreated cashew apple juice. All experiments were done in triplicate.

2.3. Plasma Characterization. The plasma's optical emission spectrum (OES) was attained using a fiber optic spectrometer (Ocean Insight model HR4Pro) associated with a 1 mm diameter optical fiber and a collimating lens. The spectra were measured at a wavelength range from 200 to 900 nm. The spectral resolution of the instrument was 0.06 nm. All analyses were done in triplicate.

2.4. Extraction and Chromatographic Analysis of the Volatile Compounds. The volatile organic compounds of cashew apple juice were extracted using the solid-phase microextraction (SPME) technique. An aliquot of 10 mL of cashew apple juice and 1 g of sodium chloride was placed in a 20 mL vial, equilibrating at 40°C for 20 min. The volatile compounds were extracted for 30 min using a DVB/CAR/PDMS (50/30 μm) fiber placed in the headspace of the vial [32].

Samples were analyzed in a GC-MS (Thermos model ISQ). The samples were desorbed directly in the injector, set at 250°C, working in splitless mode. The volatile was separated in an Equity-1 column (30 m × 0.25 mm ID × 0.25 μm film). The oven programming and chromatograph conditions followed the method described in Porto et al. [30]. The mass spectra were compared with the NIST and Wiley mass spectral library. All analyses were done in triplicate.

2.5. Odor Profile. The volatile compounds were grouped according to their primary odor descriptors in the "The Good Scent Company" database [33]. The odor activity

Table 1: Cashew apple juice volatile compounds with their residence time, Kovats index, odor threshold in water, and aroma descriptors.

Residence time (min)	Kovats index	Volatile compound	Class	Odor threshold in water (mg/L)	Odor descriptor
3.18	699	Ethyl acetate	Ester	25.00	Ethereal
4.20	719	Acetic acid	Acid	25.59	Acidic
5.05	735	3-Amino-2,3-dihydrobenzoic acid	Acid	—	—
5.60	746	3-Methyl-1-butanol	Alcohol	0.410	Fermented
6.45	762	Toluene	Aromatic	0.330	Sweet
7.45	781	Hexanal	Aldehyde	0.005	Green
7.76	787	Ethyl butanoate	Ester	0.020	Fruity
8.16	794	2,3-Butanediol	Alcohol	150.0	Creamy
9.37	818	Ethyl 2-butenoate	Ester	—	—
10.05	831	Ethyl 3-methylbutanoate	Ester	0.003	Fruity
10.95	848	1-Hexanol	Alcohol	2.50	Herbal
11.57	860	Styrene	Aromatic	0.730	Balsamic
13.28	892	Methoxy-phenyl-oxime	Oxime	—	—
14.36	913	Ethyl 2-methyl-2-butenoate	Ester	0.065	Fruity
15.66	938	Ethyl 3-methylpentenoate	Ester	0.001	Fruity
16.55	955	Vanillic acid	Acid	—	—
17.88	980	Octanal	Aldehyde	0.007	Aldehydic
17.97	982	Ethyl hexanoate	Ester	0.001	Fruity
18.53	993	2-Methypropyl 3-methylbutanoate	Ester	—	—
18.91	1000	Decane	Alkane	10.0	—
19.96	1020	Unknown	—	—	—
20.32	1027	Ethyl 2-hexenoate	Ester	0.00014	Fruity
20.55	1031	Limonene	Terpene	1.040	Citrus
20.72	1035	Acetophenone	Ketone	0.800	Floral
21.12	1042	1-Octanol	Alcohol	0.875	Waxy
21.30	1046	Ethyl 2-hydroxyhexanoate	Ester	51.4	Floral
23.39	1086	Nonanal	Aldehyde	0.001	Aldehydic
23.76	1093	3-Methylbutyl 3-methylbutanoate	Ester	0.020	Fruity
24.14	1100	Undecane	Alkane	—	—
24.52	1110	Methyl octanoate	Ester	0.200	Fruity
24.73	1116	p-Dimethylstyrene	Aromatic	0.530	Phenolic
24.81	1118	Butyl 2-methyl-2-butenoate	Ester	—	—
24.94	1121	Alloocimene	Hydrocarbon	0.140	Floral
25.06	1124	2,5-Dihydroxybenzoic acid	Acid	—	—
25.40	1134	Pentyl 3-methylbutanoate	Ester	—	—
25.67	1141	2-Methylpropyl hexanoate	Ester	0.020	Fruity
25.93	1148	Ethyl benzoate	Ester	0.150	Minty
26.47	1162	Nonanol	Alcohol	1.000	Floral
27.11	1179	3-Methylbutyl 2-methyl-2-butenoate	Ester	—	—
27.29	1184	Ethyl octanoate	Ester	0.005	Waxy
27.41	1187	Decanal	Aldehyde	0.030	Aldehydic
27.90	1200	Dodecane	Alkane	2.140	Alkane
28.20	1213	Ethyl phenylacetate	Ester	0.650	Floral
28.30	1217	Vanillic acid	Acid	—	—
28.53	1227	Ethyl 2-octenoate	Ester	—	—
28.75	1236	3-Methylbutyl hexanoate	Ester	0.032	Fruity
28.86	1241	2-Decenal	Aldehyde	0.0004	Fatty
28.94	1244	g-Octalactone	Lactone	0.007	Coconut

Table 1: Continued.

Residence time (min)	Kovats index	Volatile compound	Class	Odor threshold in water (mg/L)	Odor descriptor
29.19	1255	Ethyl 6-methyl-2,4-heptadienoate	Ester	—	—
29.25	1257	Nonanoic acid	Acid	3.00	Waxy
29.82	1282	Ethyl nonanoate	Ester	12.0	Waxy
30.25	1300	Tridecane	Alkane		
30.65	1322	Hydrocinnamic acid	Acid	5.00	Floral
30.89	1336	d-Elemene	Sesquiterpene	—	—
31.20	1353	Unknown	—	—	—
31.53	1371	Hexyl hexanoate	Ester	1.890	Fruity
31.65	1378	Copaene	Sesquiterpene	0.006	Woody
31.70	1381	Ethyl decanoate	Ester	0.122	Waxy
31.88	1391	b-Elemene	Sesquiterpene	—	—
32.05	1400	Tetradecane	Alkane	1.00	Waxy
32.19	1409	Unidentified aromatic	—	—	—
32.27	1414	Coumarin	Aromatic	0.034	Tonka
32.37	1421	Caryophyllene	Sesquiterpene	0.064	Spicy
32.55	1433	Geranylacetone	Ketone	6.40	Floral
32.60	1436	Ethyl cinnamate	Ester	0.001	Balsamic
32.71	1443	a-Bergamotene	Sesquiterpene	—	—
32.77	1447	e-Muurolene	Sesquiterpene	—	—
32.94	1459	a-Humulene	Sesquiterpene	0.120	Woody
33.20	1476	g-Muurolene	Sesquiterpene	—	—
33.29	1482	Germacrene D	Sesquiterpene	0.0012	Woody
33.45	1492	2,4-Di-tert-butyl phenol	Phenol	0.500	Phenolic
33.53	1497	9,11-Eremophiladiene	Sesquiterpene	—	—
33.57	1500	Pentadecane	Alkane	13000	Waxy
33.74	1513	g-Cadinene	Sesquiterpene	0.002	Woody
33.82	1519	b-Cadinene	Sesquiterpene	—	—
33.99	1532	d-Cadinene	Sesquiterpene	0.002	Herbal
34.05	1536	d-Caracolene	Sesquiterpene	—	—
34.46	1567	5-Dodecenoic acid	Acid	—	—
34.61	1578	Ethyl dodecanoate	Ester	3.50	Waxy
34.82	1594	Unknown	—	—	—
34.90	1600	Hexadecane	Alkane	13000	Chemical
35.17	1618	Methyl jasmonate	Ester	0.070	Floral
35.45	1642	g-Dodecalactone	Ketone	0.007	Fruity
35.60	1655	Dioctyl ether	Ether	—	—
36.34	1718	Methyl myristate	Ester	—	—
36.60	1741	Myristic acid	Acid	10.0	Waxy
36.67	1747	Ethyl myristate	Ester	0.180	Waxy
37.18	1791	2-Ethylhexyl salicylate	Ester	—	—
37.25	1797	Hexadecanal	Aldehyde	0.075	Cardboard
37.38	1809	Methyl pentadecanoate	Ester	—	—
37.45	1816	Unknown	—	—	—
37.56	1826	3-Methylbutyl dodecanoate	Ester	—	—
37.68	1838	Pentadecanoic acid	Acid	10.0	Waxy
38.10	1879	Homomenthyl salicylate	Ester	—	—
38.40	1908	Methyl palmitate	Ester	2.0	Waxy
38.52	1919	Palmitelaidic acid	Acid	—	—

Table 1: Continued.

Residence time (min)	Kovats index	Volatile compound	Class	Odor threshold in water (mg/L)	Odor descriptor
38.76	1943	Palmitic acid	Acid	10.0	Waxy
39.08	1974	Ethyl palmitate	Ester	2.0	Waxy
39.59	2023	Unknown	—	—	—
40.44	2106	Methyl stearate	Ester	—	—
40.69	2130	Stearic acid	Acid	20.0	Waxy
40.77	2138	Ethyl oleate	Ester	—	—
40.88	2149	Unknown	—	—	—

value (OAV) was determined based on the odor thresholds in water obtained in the literature [34–46]. The six primary odor descriptors were presented in radar plots: fruity, aldehydic, balsamic, fatty, waxy, and woody.

2.6. Statistical Analysis. Statistical analysis was done using Statistica v.13 (TIBCO Software).

3. Results and Discussion

3.1. Volatile Compounds in Cashew Apple Juice. One hundred and five compounds were identified in cashew apple juice, accounting for 98 ± 1% of the total weight. Five compounds (2 ± 1% of the total weight) were not identified. Table 1 presents the volatile compounds identified in cashew apple juice and information regarding their odor thresholds and aroma descriptors.

Cashew apple juice has a complex mixture of volatile compounds that includes acids, alcohols, aldehydes, aromatic hydrocarbons, esters, ethers, fatty esters, ketones, linear hydrocarbons, phenols, terpene, and sesquiterpenes. The main volatile components are styrene (32.5% *w*/*w*), ethyl 3-methylbutanoate (11.6%), ethyl 2-butenoate (5.0%), palmitic acid (4.6%), and 3-methyl-1-butanol (3.9%). The compounds that most contribute to the cashew apple juice aroma, based on their odor activity values, are ethyl 3-methylbutanoate, ethyl 2-hexenoate, ethyl hexanoate, ethyl 3-methylpentanoate, and nonanal. Styrene, toluene, and p-dimethylstyrene are considered off-flavors of cashew apple juice.

The main volatile compounds observed in the cashew apple juice analyzed in this work are similar to those previously reported in the literature [1–3]. Variations in the concentration of the compounds were due to differences in cultivar, year of collection, and maturity stage, which are part of the natural variation that occurs in the fruit composition profile.

3.2. Changes in Volatile Composition Profile Induced by Plasma Treatment. Glow discharge plasma treatment has induced several chemical changes in the volatile composition profile of cashew apple juice. Table 2 presents the mass fraction of each compound before (control) and after plasma treatment at the tested operating conditions. Figure 1 shows a heat map indicating the changes in composition in a visual format. Blue indicates an increase in the compound concentration, and red indicates a decrease. Light colors indicate changes up to 50%, and bold colors indicate more than 50%.

The most significant net changes in mass fraction were observed for styrene, 3-methyl-1-butanol, 2,3-butadienol, ethyl 2-butenoate, ethyl 3-methylbutanoate, ethyl acetate, homomenthyl salicylate, methoxy-phenyl-oxime, methyl stearate, palmitelaidic acid, and palmitic acid. These were the compounds that most gained or lost mass during plasma treatment.

Several minor compounds presented a high percentual change in mass, such as acetic acid (-100%), octanal (+106%), 2-methylpropyl 3-methylbutanoate (+235%), vanillic acid (+131%), 2-decenal (+173%), γ-octalactone (+426%), myristic acid (-100%), 3-methylbutyl dodecanoate (-100%), pentadecanoic acid (-91%), methyl palmitate (-93%), palmitic acid (-100%), stearic acid (-100%), and ethyl oleate (-87%). This changes evidence that plasma treatment affects the volatile compounds of cashew apple juice. This result corroborates with studies on pineapple [30], orange [14], and camu-camu juice [16] that also showed a significant influence of plasma treatment on the volatile profile of fruit juices.

Among the chemical groups, plasma treatment increased the concentration of aldehyde (50%), esters (21%), linear hydrocarbons (37%), and sesquiterpenes (44%) and significantly decreased the concentration of fatty acids and fatty acid esters (92%). The changes in concentration of phenolic acids, alcohols, aromatic hydrocarbons, terpenes, and lactones depended on the operating conditions applied. Such behavior is explained by the different types and concentrations of reactive plasma species formed in each operating condition [16, 30].

Mass balance analysis allowed us to identify chemical changes occurring during plasma treatment. The most significant differences were observed with fatty acids and fatty acid esters, which were reduced by 92% after plasma treatment. The changes affected all fatty acids and fatty acid esters, but the most significant reduction was observed for palmitic acid, palmitelaidic acid, myristic acid, methyl stearate, and stearic acid.

Fatty acids and fatty acid esters can undergo internal scission reactions, which can be induced by free radicals or enzymes [47]. These reactions give rise to "green leaf volatiles," primarily small chain aldehydes, alcohols, and organic acids. The increase of all aldehydes and some alcohols accompanied the reduction in the fatty acids and fatty acid

Table 2: Mass fraction of volatile compounds in cashew apple juice subjected to plasma treatment.

Residence time (min)	Volatile compound	Control	GP 10 mL/min 10 min	GP 10 mL/min 20 min	GP 20 mL/min 10 min	GP 20 mL/min 20 min	GP 30 mL/min 10 min	GP 30 mL/min 20 min
3.18	Ethyl acetate	3.23	4.08	5.66	5.34	4.27	5.29	4.98
4.20	Acetic acid	1.43	1.24	0.00	0.72	0.92	0.00	1.20
5.05	3-Amino-2.3-dihydrobenzoic acid	3.91	2.50	5.11	7.47	1.42	3.04	6.63
5.60	3-Methyl-1-butanol	3.88	9.17	3.07	4.46	9.75	3.81	4.26
6.45	Toluene	0.19	0.07	0.21	0.24	0.23	0.18	0.36
7.45	Hexanal	0.15	0.09	0.23	0.17	0.15	0.18	0.28
7.76	Ethyl butanoate	1.15	0.82	1.33	1.31	1.61	1.18	1.23
8.16	2.3-Butanediol	0.24	1.81	0.34	0.81	0.51	0.30	0.29
9.37	Ethyl 2-butenoate	5.04	5.61	5.52	6.45	6.12	6.18	6.35
10.05	Ethyl 3-methylbutanoate	11.67	11.42	13.66	12.82	13.37	14.88	13.45
10.95	1-Hexanol	1.18	1.30	1.30	1.61	1.57	1.55	1.61
11.57	Styrene	32.50	29.28	35.40	28.76	32.58	36.66	29.15
13.28	Methoxy-phenyl-oxime	0.95	4.68	0.71	2.16	2.71	0.46	1.21
14.36	Ethyl 2-methyl-2-butenoate	3.31	3.75	4.27	4.17	4.18	4.51	4.12
15.66	Ethyl 3-methylpentenoate	0.86	0.86	1.08	0.91	1.07	1.13	1.01
16.55	Vanillic acid	0.68	0.69	0.59	0.99	0.80	0.55	0.94
17.88	Octanal	0.09	0.12	0.13	0.15	0.18	0.15	0.19
17.97	Ethyl hexanoate	2.66	2.72	3.40	2.91	3.10	3.25	2.85
18.53	2-Methypropyl 3-methylbutanoate	0.04	0.07	0.08	0.12	0.13	0.08	0.11
18.91	Decane	0.16	0.20	0.24	0.23	0.21	0.19	0.24
19.96	Unknown	0.42	0.34	0.58	0.47	0.41	0.47	0.58
20.32	Ethyl 2-hexenoate	0.38	0.37	0.59	0.45	0.41	0.49	0.59
20.55	Limonene	0.04	0.04	0.06	0.04	0.06	0.07	0.09
20.72	Acetophenone	0.30	0.38	0.49	0.50	0.48	0.56	0.90
21.12	1-Octanol	1.43	1.39	1.34	2.63	1.31	1.56	2.42
21.30	Ethyl 2-hydroxyhexanoate	0.11	0.16	0.14	0.14	0.13	0.15	0.16
23.39	Nonanal	0.80	0.89	1.00	0.92	0.92	0.98	1.04
23.76	3-Methylbutyl 3-methylbutanoate	0.23	0.24	0.27	0.23	0.25	0.30	0.28
24.14	Undecane	0.09	0.10	0.14	0.14	0.11	0.14	0.16
24.52	Methyl octanoate	0.03	0.04	0.05	0.05	0.05	0.04	0.04
24.73	p-Dimethylstyrene	0.05	0.08	0.05	0.08	0.08	0.03	0.04
24.81	Butyl 2-methyl-2-butenoate	0.05	0.06	0.07	0.07	0.07	0.06	0.05
24.94	Alloocimene	0.01	0.01	0.01	0.01	0.02	0.01	0.01
25.06	2.5-Dihydroxybenzoic acid	0.21	0.25	0.18	0.26	0.24	0.15	0.21
25.40	Pentyl 3-methylbutanoate	0.03	0.03	0.04	0.04	0.03	0.04	0.03
25.67	2-Methylpropyl hexanoate	0.06	0.14	0.08	0.09	0.09	0.08	0.09
25.93	Ethyl benzoate	0.08	0.14	0.10	0.11	0.13	0.12	0.10
26.47	Nonanol	1.86	2.39	2.15	2.39	2.07	2.17	2.30
27.11	3-Methylbutyl 2-methyl-2-butenoate	0.22	0.20	0.21	0.21	0.21	0.24	0.24
27.29	Ethyl octanoate	1.11	1.14	1.31	1.18	1.19	1.31	1.37
27.41	Decanal	0.11	0.12	0.13	0.14	0.11	0.14	0.19
27.90	Dodecane	0.05	0.08	0.07	0.08	0.09	0.07	0.09
28.20	Ethyl phenylacetate	0.07	0.20	0.10	0.11	0.10	0.11	0.11
28.30	Vanillic acid	0.02	0.09	0.05	0.06	0.05	0.05	0.06

Table 2: Continued.

Residence time (min)	Volatile compound	Control	GP 10 mL/min 10 min	GP 10 mL/min 20 min	GP 20 mL/min 10 min	GP 20 mL/min 20 min	GP 30 mL/min 10 min	GP 30 mL/min 20 min
28.53	Ethyl 2-octenoate	0.08	0.05	0.10	0.09	0.09	0.11	0.10
28.75	3-Methylbutyl hexanoate	0.16	0.18	0.21	0.18	0.19	0.21	0.24
28.86	2-Decenal	0.04	0.10	0.11	0.11	0.10	0.11	0.12
28.94	γ-Octalactone	0.02	0.06	0.06	0.08	0.05	0.06	0.09
29.19	Ethyl 6-methyl-2.4-heptadienoate	0.02	0.03	0.05	0.06	0.04	0.05	0.04
29.25	Nonanoic acid	0.02	0.02	0.02	0.02	0.02	0.02	0.01
29.82	Ethyl nonanoate	0.12	0.14	0.16	0.14	0.14	0.15	0.17
30.25	Tridecane	0.04	0.04	0.04	0.06	0.04	0.05	0.09
30.65	Hydrocinnamic acid	0.03	0.07	0.04	0.05	0.04	0.05	0.04
30.89	δ-Elemene	0.03	0.03	0.07	0.03	0.04	0.05	0.06
31.20	Unknown	0.17	0.21	0.22	0.19	0.19	0.20	0.24
31.53	Hexyl hexanoate	0.04	0.04	0.04	0.04	0.03	0.04	0.04
31.65	Copaene	0.08	0.08	0.11	0.08	0.10	0.10	0.14
31.70	Ethyl decanoate	0.26	0.29	0.37	0.39	0.30	0.32	0.43
31.88	β-Elemene	0.09	0.13	0.13	0.12	0.12	0.12	0.18
32.05	Tetradecane	0.09	0.12	0.09	0.09	0.08	0.08	0.09
32.19	Unidentified aromatic	0.15	0.21	0.19	0.19	0.17	0.14	0.17
32.27	Coumarin	0.06	0.10	0.07	0.07	0.08	0.03	0.08
32.37	Caryophyllene	0.11	0.14	0.18	0.12	0.15	0.16	0.23
32.55	Geranylacetone	0.17	0.21	0.23	0.15	0.15	0.16	0.28
32.60	Ethyl cinnamate	1.08	1.20	1.20	1.31	1.11	1.24	1.31
32.71	α-Bergamotene	0.02	0.03	0.03	0.02	0.03	0.03	0.03
32.77	ε-Muurolene	0.01	0.02	0.02	0.02	0.02	0.01	0.02
32.94	α-Humulene	0.06	0.05	0.06	0.06	0.06	0.06	0.06
33.20	γ-Muurolene	0.04	0.04	0.07	0.05	0.06	0.06	0.08
33.29	Germacrene D	0.27	0.19	0.23	0.17	0.18	0.18	0.24
33.45	2.4-Di-tert-butyl phenol	0.11	0.11	0.09	0.10	0.07	0.10	0.09
33.53	9.11-Eremophiladiene	0.06	0.23	0.16	0.10	0.12	0.12	0.16
33.57	Pentadecane	0.07	0.00	0.06	0.06	0.06	0.06	0.05
33.74	γ-Cadinene	0.02	0.03	0.03	0.03	0.03	0.03	0.04
33.82	β-Cadinene	0.40	0.48	0.41	0.42	0.36	0.38	0.48
33.99	δ-Cadinene	0.02	0.03	0.02	0.02	0.03	0.02	0.04
34.05	δ-Caracolene	0.02	0.03	0.04	0.03	0.03	0.03	0.04
34.46	5-Dodecenoic acid	0.11	0.18	0.16	0.15	0.12	0.12	0.15
34.61	Ethyl dodecanoate	0.12	0.13	0.30	0.17	0.15	0.26	0.30
34.82	Unknown	0.34	0.23	0.30	0.24	0.14	0.20	0.18
34.90	Hexadecane	0.19	0.23	0.17	0.30	0.20	0.23	0.19
35.17	Methyl jasmonate	0.03	0.04	0.08	0.05	0.05	0.06	0.02
35.45	γ-Dodecalactone	1.35	1.13	1.48	1.21	0.93	1.00	1.17
35.60	Dioctyl ether	0.05	0.07	0.09	0.05	0.04	0.04	0.14
36.34	Methyl myristate	0.10	0.15	0.06	0.08	0.06	0.08	0.07
36.60	Myristic acid	0.47	0.14	0.03	0.00	0.00	0.00	0.00
36.67	Ethyl myristate	0.24	0.22	0.22	0.19	0.12	0.15	0.21
37.18	2-Ethylhexyl salicylate	0.69	0.05	0.05	0.03	0.02	0.04	0.03
37.25	Hexadecanal	0.06	0.08	0.07	0.09	0.06	0.08	0.06
37.38	Methyl pentadecanoate	0.08	0.06	0.02	0.05	0.02	0.04	0.03

Table 2: Continued.

Residence time (min)	Volatile compound	Control	GP 10 mL/min 10 min	GP 10 mL/min 20 min	GP 20 mL/min 10 min	GP 20 mL/min 20 min	GP 30 mL/min 10 min	GP 30 mL/min 20 min
37.45	Unknown	0.10	0.08	0.04	0.17	0.04	0.03	0.05
37.56	3-Methylbutyl dodecanoate	0.39	0.00	0.00	0.00	0.00	0.00	0.00
37.68	Pentadecanoic acid	0.29	0.15	0.07	0.06	0.03	0.06	0.06
38.10	Homomenthyl salicylate	1.57	0.08	0.08	0.06	0.06	0.06	0.06
38.40	Methyl palmitate	0.28	0.05	0.03	0.04	0.02	0.04	0.04
38.52	Palmitelaidic acid	2.05	0.35	0.04	0.00	0.00	0.00	0.00
38.76	Palmitic acid	4.60	1.78	0.11	0.11	0.07	0.00	0.06
39.08	Ethyl palmitate	0.07	0.06	0.04	0.04	0.02	0.04	0.03
39.59	Unknown	0.16	0.00	0.00	0.00	0.00	0.00	0.00
40.44	Methyl stearate	1.19	0.53	0.04	0.06	0.03	0.02	0.01
40.69	Stearic acid	0.24	0.11	0.01	0.00	0.00	0.00	0.00
40.77	Ethyl oleate	0.13	0.05	0.04	0.03	0.02	0.02	0.03
40.88	Unknown	0.02	0.00	0.00	0.00	0.00	0.00	0.00

GP: glow discharge plasma.

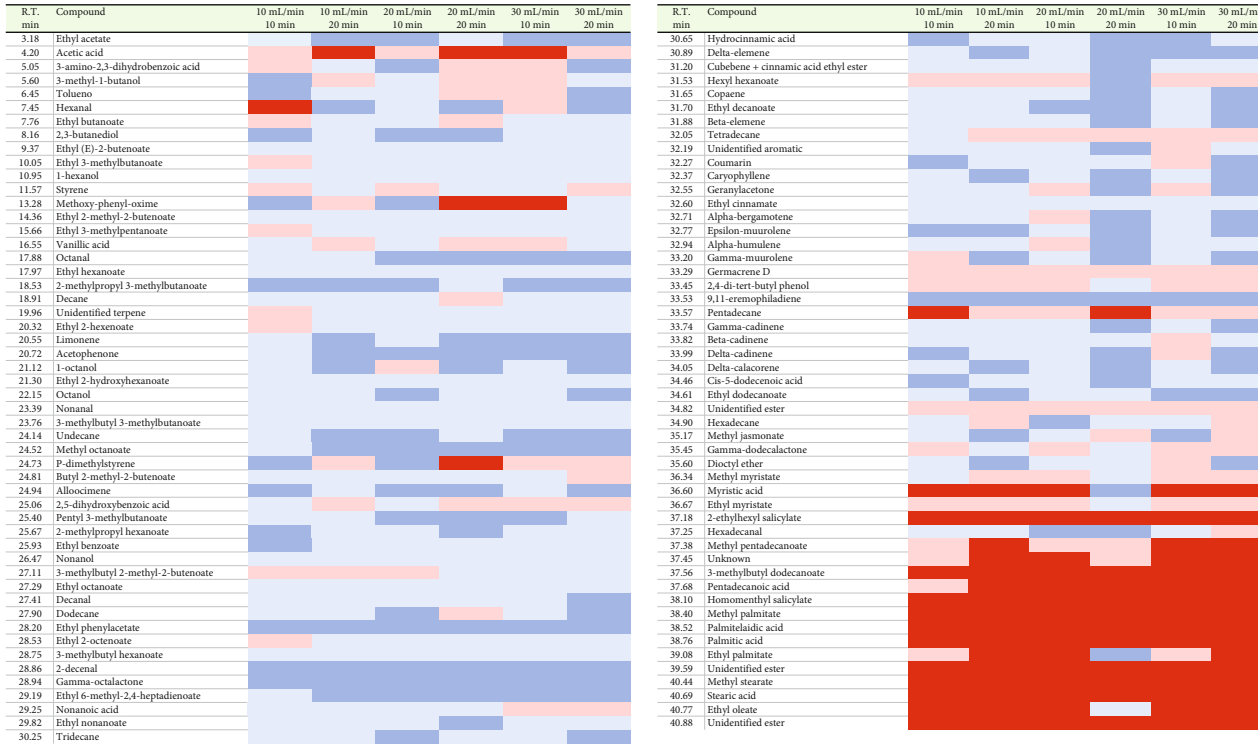

Figure 1: Heat map presenting the modifications in the volatile components mass fractions with untreated juice as a comparison basis.

esters. Palmitic acid, methyl palmitate, and ethyl palmitate could be the source of the increase in hexadecanal through dehydration of the acid group and methyl group abstraction of the methyl and ethyl groups of the fatty acid esters. Palmitelaidic acid could also be the source of hexadecanal through dehydration of the acid group followed by the hydrogenation of the carbon double bond. Such reactions depend on the concentration of hydrogen radicals present in high amounts in air glow plasma (Figure 2). The optical emission spectra attained from the plasma chamber indicated the presence of N_2^+ (427 nm), H_α (486 nm), H_β (656 nm), and atomic oxygen (777 and 845 nm) as the primary plasma reactive species.

The increase observed in 2-decenal and nonanal can be derived from the scission of ethyl oleate. Nonanal and octanal could be formed from the scission of stearic acid, methyl

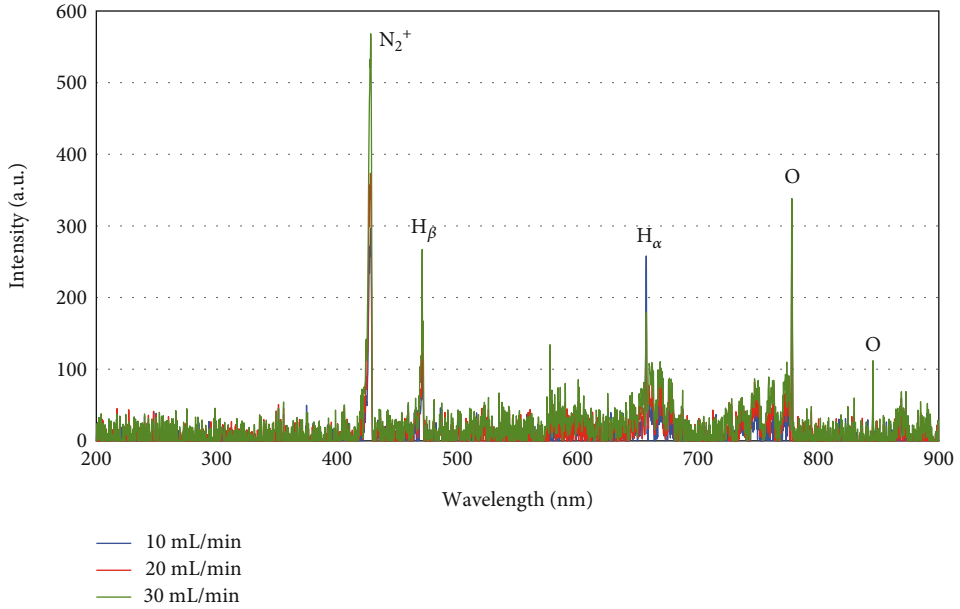

Figure 2: Optical emission spectra of air plasma produced inside the chamber of the glow discharge plasma.

stearate, and palmitelaidic acid. At the same time, the increase in hexanal concentration may be linked to the internal scission of myristic acid, ethyl myristate, methyl myristate, and cis-5-dodecenoic acid. Zhou et al. [48], working with fresh-cut cantaloupes, also observed an increase in hexanal, nonanal, and other aldehydes after plasma application. However, they have not discussed the causes for the observed increase in concentration.

The increase in hexanol, octanol, and nonanol can be attributed to the hydrogenation of hexanal, octanal, and nonanal produced by the scission of the fatty acids and fatty acid esters. Zhou et al. [48] observed an increase in several alcohols, such as heptanol, octanol, and nonanol, plasma application on fresh-cut cantaloupe, but have not discussed the causes for these chemical changes.

When ethyl and methyl esters undergo plasma-induced scission, they generate an aldehyde and a short-chain ester. This reaction generally occurs at the carbon double bond of unsaturated esters, but saturated esters may break near the central carbon when subjected to plasma. This reaction usually involves an oxygen free radical forming an epoxy group at the carbon double bond, further decomposing, forming an aldehyde and a short-chain ester [30]. Such a reaction explains the increase in short-chain esters such as ethyl hexanoate, ethyl octanoate, ethyl nonanoate, ethyl decanoate, and methyl octanoate.

The changes among the short-chain esters were also relevant. Extended treatment times in plasma (20 min) tended to produce shorter esters. Such phenomenon is explained by methyl group abstraction of the farthermost methyl group of the ester chain or a branched methyl group. These reactions have been detailed in pineapple juice subjected to plasma treatment [30]. As observed previously with pineapple juice, ethyl esters showed to be more stable during plasma application than methyl esters and fatty acids.

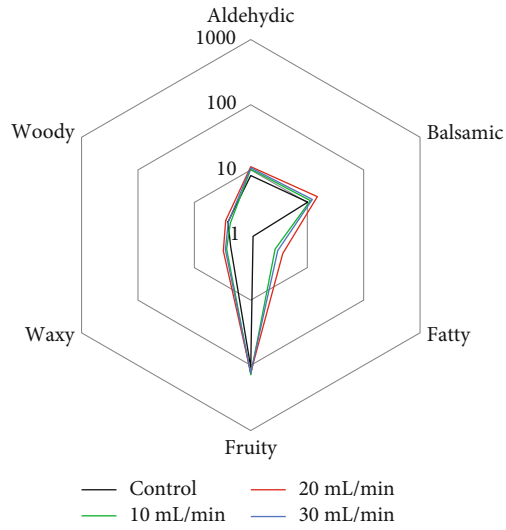

Figure 3: Aroma profile of the untreated and plasma-treated cashew apple juice. Plasma treatment was carried out in glow discharge plasma for 20 min at plasma air flow rates of 10, 20, and 30 mL/min.

The concentration of styrene in the plasma-treated juice fluctuated around the concentration of the control. Still, it was impossible to identify any major reaction that occurred or might have affected styrene.

3.3. Changes in the Aroma Profile. Figure 3 presents an aroma radar with the six primary aroma descriptors of the untreated and plasma-treated cashew apple juice. Cashew apple juice is marked by its distinctive fruity aroma, which comprises 81.1% of its odor activity value. The aroma profile is also characterized by its balsamic (7.8%), aldehydic (6.2%), woody (1.9%), and waxy (1.7%) aromas, which are

Table 3: Odor activity values (OAV) of the primary aroma descriptors of the untreated and plasma-treated cashew apple juice. Plasma treatment was carried out in glow discharge plasma for 20 min at plasma air flow rates of 10, 20, and 30 mL/min.

Aroma	Control	10 mL/min	20 mL/min	30 mL/min
Fruity	105.0 ± 3.1^{c}	137.0 ± 4.1^{a}	126.5 ± 3.8^{b}	129.3 ± 3.9^{b}
Balsamic	10.2 ± 0.3^{c}	11.4 ± 0.3^{b}	15.1 ± 0.5^{a}	12.3 ± 0.4^{b}
Aldehydic	8.2 ± 0.2^{c}	10.2 ± 0.3^{b}	11.2 ± 0.3^{a}	10.8 ± 0.3^{ab}
Woody	2.5 ± 0.1^{ab}	2.3 ± 0.1^{b}	2.8 ± 0.1^{a}	2.5 ± 0.1^{ab}
Waxy	2.3 ± 0.1^{b}	2.7 ± 0.1^{a}	3.1 ± 0.1^{a}	2.8 ± 0.1^{a}
Fatty	1.1 ± 0.0^{c}	2.7 ± 0.1^{b}	3.7 ± 0.1^{a}	3.0 ± 0.1^{b}
Other notes	0.5 ± 0.0^{b}	0.9 ± 0.1^{a}	0.9 ± 0.1^{a}	1.2 ± 0.1^{a}
Total	129.8 ± 3.9^{b}	167.2 ± 5.0^{a}	163.2 ± 4.9^{a}	161.9 ± 4.8^{a}

Different superscripts indicate significant statistical differences within each aroma descriptor (rows).

Table 4: Normalized odor activity values (OAV) of the primary aroma descriptors of the untreated and plasma-treated cashew apple juice. Plasma treatment was carried out in glow discharge plasma for 20 min at plasma air flow rates of 10, 20, and 30 mL/min.

Aroma	Control	10 mL/min	20 mL/min	30 mL/min
Fruity	81.1 ± 2.4^{a}	82.1 ± 2.5^{a}	77.8 ± 2.3^{a}	80.1 ± 2.4^{a}
Balsamic	7.8 ± 0.4^{b}	6.7 ± 0.3^{c}	9.1 ± 0.5^{a}	7.5 ± 0.4^{bc}
Aldehydic	6.2 ± 0.3^{a}	6.0 ± 0.3^{a}	6.7 ± 0.3^{a}	6.6 ± 0.3^{a}
Woody	1.9 ± 0.1^{a}	1.4 ± 0.1^{b}	1.7 ± 0.1^{ab}	1.5 ± 0.1^{ab}
Waxy	1.7 ± 0.1^{ab}	1.6 ± 0.1^{b}	1.9 ± 0.1^{a}	1.7 ± 0.1^{ab}
Fatty	0.8 ± 0.0^{c}	1.6 ± 0.1^{b}	2.2 ± 0.1^{a}	1.8 ± 0.1^{ab}

Different superscripts indicate significant statistical differences within each aroma descriptor (rows).

Table 5: Mass fraction of the main chemical groups of the untreated and plasma-treated cashew apple juice. Plasma treatment was carried out in glow discharge plasma for 20 min at plasma air flow rates of 10, 20, and 30 mL/min.

Aroma	Control	10 mL/min	20 mL/min	30 mL/min
Esters	88.7 ± 2.7^{a}	88.9 ± 2.7^{a}	86.9 ± 2.6^{a}	88.0 ± 2.6^{a}
Aldehydes	7.3 ± 0.2^{c}	8.0 ± 0.2^{b}	9.2 ± 0.3^{a}	8.8 ± 0.3^{a}
Sesquiterpenes	2.0 ± 0.1^{a}	1.5 ± 0.1^{b}	1.9 ± 0.1^{ab}	1.7 ± 0.1^{ab}
Lactones	1.5 ± 0.1^{ab}	1.3 ± 0.1^{bc}	1.7 ± 0.1^{a}	1.1 ± 0.1^{c}
Aromatics	0.4 ± 0.0^{a}	0.3 ± 0.0^{a}	0.3 ± 0.0^{a}	0.3 ± 0.0^{a}

Different superscripts indicate significant statistical differences within each chemical group (rows).

complemented by fatty (0.8%), green (0.3%), herbal (0.1%), and floral (0.1%) notes. The fruity aroma comes from the high concentration of short-chain esters, such as ethyl 3-methylbutanoate, ethyl 2-methyl-2-butenoate, ethyl 3-methylpentanoate, ethyl butanoate, ethyl hexanoate, ethyl 2-hexenoate, and 2-methylpropyl 3-methylbutanoate. The balsamic aroma is mainly due to aromatic hydrocarbons, such as styrene, cinnamic acid, and ethyl cinnamate. The aldehydic aroma comes primarily from the aldehydes, such as octanal, nonanal, and decanal. The woody and waxy aromas are caused by sesquiterpenes and fatty acid esters.

Plasma treatment increased the OAV of most aroma descriptors in the cashew apple juice, intensifying its aroma (Table 3). The intensification of the natural aroma of cashew apple juice was between 24% (30 mL/min) and 28% (10 mL/min). The intensification of aroma was higher at lower air plasma flow rates than at high flow rates. At higher flow rates, the higher concentration of reactive plasma species caused more chemical reactions that have affected compounds with low odor threshold, such as ethyl 3-methylbutanoate, ethyl 3-methylpentanoate, ethyl hexanoate, ethyl 2-hexenoate, and γ-dodecalactone, all of them having fruity aroma.

Despite the significant changes regarding the OAVs of each aroma descriptor between the untreated and plasma-treated, the aroma profile (Figure 2) did not present a significant shift regarding the contribution of each descriptor to the cashew apple juice aroma, except for the fatty descriptor that increased by 173%. Since the fatty descriptor is a minor descriptor of the cashew apple juice aroma, this increase does not compromise the aroma of the juice. Table 4 presents the normalized aroma profile of cashew apple juice. No significant changes were observed in the contribution of the fruity and aldehydic descriptors toward the juice aroma profile. The most important difference in the aroma profile was the considerable increase in the fatty notes, which became the fourth most noticeable aroma note in the plasma-treated juice.

Although several chemical changes were observed in the juice's volatile compounds, there were no significant changes in the chemical groups (Table 5). Esters and lactones, the main group that gives the fruity aroma, did not change significantly after plasma treatment, explaining why the fruity aroma continued to be predominant in cashew apple juice. The increase in the aldehyde mass fraction contributed to the increase of the OAVs of the aldehydic and fatty descriptors, which was mainly caused by the scission of fatty acids and fatty acid esters into 2-decenal (fatty), decanal (aldehydic), and nonanal (aldehydic). The OAV of the woody descriptor followed the changes in the mass fraction of the sesquiterpene group.

Styrene is the main contributor to the balsamic descriptor, which some consumers consider an undesired flavor or off-flavor of cashew apple juice. Glow discharge plasma could not reduce the contribution of this descriptor in the cashew apple juice's aroma profile. Plasma treatment could only slightly reduce the contents of styrene and dimethyl styrene in the juice, but not enough to significantly change the aroma profile.

Compared to other fruit juices, the total OAV in plasma-treated cashew apple juice increased as in orange juice subjected to the same treatment [14]. The increase in short-chain esters favored the increase in OAV in cashew apple juice. In pineapple juice, the total OAV diminished due to decreased concentration of short-chain esters [30]. The most significant difference between these two juices is that cashew apple juice has more long-chain esters than pineapple juice, which goes through scission, forming its characteristic fruity aroma derived from its short-chain esters.

Lower plasma flow rates increased the concentration of esters, especially short-chain esters with low odor thresholds, due to the chemical changes discussed in Section 3.2. As the plasma flow rate increased, the concentration of short-chain esters with low odor thresholds slightly decreased due to methyl abstraction and isomerization, resulting in esters with higher odor thresholds. Furthermore, lipid scission reactions were more intense at higher plasma flow rates, increasing the concentration of aldehydes, which are less desired compounds.

4. Conclusions

This study evaluated the effects of glow discharge plasma on cashew apple juice, which contains a complex mixture of volatile compounds. Plasma treatment induced various changes in the composition of the juice's volatile compounds. The primary reaction observed during plasma treatment was the internal scission of fatty acids and fatty acid esters. Such a reaction decreased by 92% the content of fatty acid and fatty acid esters. The internal scission of fatty acids and fatty acid esters has formed several short-chain esters and aldehydes with low odor thresholds, contributing to the intensification of the odor activity value of cashew apple juice. The aldehyde and short-chain esters increased by 50% and 21%, respectively, increasing OAV by 28%. Hydrogenation of aldehydes resulted in the formation of alcohols, which increased by 86%. Plasma treatment has not significantly changed the concentration of styrene, toluene, and p-dimethylstyrene and could not reduce the concentration of these off-flavors. Glow discharge plasma increased the odor activity value of cashew apple juice, with the lowest flow rate (10 mL/min) resulting in the highest OAV. The lowest flow rate has also resulted in the highest fruity aroma and lowest balsamic and aldehydic notes, thus increasing desired notes and decreasing undesired ones. The increase in plasma flow rate induced undesired chemical changes, leading to a lower aroma quality.

Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflict of interest.

Authors' Contributions

D. L. H. Maia was responsible for the investigation and formal analysis. S. Rodrigues was responsible for the resources and writing—review and editing. F. A. N. Fernandes was responsible for the conceptualization, formal analysis, and writing—review and editing.

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