

Characterization and Semiquantitative Analysis of Volatiles in Seedless Watermelon Varieties Using Solid-Phase Microextraction

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Seedless triploid watermelons have increased in popularity since the early 1990s, and the demand for seedless fruit is on the rise. Sweetness and sugars are crucial breeding focuses for fruit quality. Volatiles also play an important role; yet, we found no literature for seedless varieties and no reports using solid-phase microextraction (SPME) in watermelon. The objective of this experiment was to identify volatile and semivolatile compounds in five seedless watermelon varieties using carboxen divinylbenzene polydimethylsiloxane solid-phase microextraction (SPME) with gas chromatography–mass spectrometry (GC-MS). Fully ripe watermelon was squeezed through miracloth to produce rapid juice extracts for immediate headspace SPME GC-MS. Aldehydes, alcohols, ketones, and one furan (2-pentyl furan, a lipid oxidation product) were recovered. On the basis of total ion count peak area, the most abundant compounds in five varieties were 3-nonen-1-ol/(*E,Z*)-2,6-nonadienal (16.5–28.2%), (*E*)-2-nonenal (10.6–22.5%), and (*Z*)-6-nonenal (2.0–11.3%). Hexanal was most abundant (37.7%) in one variety (Pure Heart). The most abundant ketone was 6-methyl-5-hepten-2-one (2.7–7.7%). Some sensory attributes reported for these compounds are melon, citrus, cucumber, orange, rose, floral, guava, violet, vegetable, green, grassy, herbaceous, pungent, fatty, sweet, and waxy. Identifying and relating these compounds to sensory attributes will allow for future monitoring of the critical flavor compounds in seedless watermelon after processing and throughout fresh-cut storage.

KEYWORDS: Aroma compounds; flavor; gas chromatography; mass spectrometry; melon; solid-phase microextraction; watermelon [*Citrullus lanatus* (Thunb.)]

INTRODUCTION

Per capita watermelon [*Citrullus lanatus* (Thunb.)] consumption in the United States has been somewhat stable since 1990 at roughly 14.3 ± 1.1 lbs/year, and seedless watermelon shipments constitute three-fourths of the movement of all domestically grown watermelons (1). The portion dedicated to fresh cuts has been increasing and now constitutes roughly 25% of the total fresh-cut fruit market (2). Consumers desire seedless watermelons, especially when conveniently packaged as fresh cuts. As a result, new “firmer” seedless varieties have recently been developed and are becoming available. Seed companies breed such releases for sugar content, size, flesh firmness, appearance, and yield. However, there have been very limited reports regarding volatile flavor compounds in watermelon (see Table 1).

In a comprehensive review of volatile compounds in watermelon, 71 compounds were reported (3). Most compounds were aldehydes, alcohols, ketones, and furans. Only roughly 15 compounds typically associated with fruity and fruit flavors,

such as esters and acids, were reported. Of those 71 compounds, 52 were reported for the first time, while using gas chromatography (GC). This was a significant increase from the previous 26 volatile compounds established in watermelons (4). The last comprehensive review of volatile compounds in watermelons tabulated only 75 compounds (5). Again, the majority were aldehydes and alcohols with 23 alcohols, 21 aldehydes, eight ketones, seven hydrocarbons, one acid, two lactones, 12 furans, and one oxide. The main volatile components reported in watermelon were C₉ aldehydes, alcohols, and their esters (3–8). Nonetheless, we have been unable to procure any reports regarding volatiles in seedless watermelon varieties.

Most typical sample preparation for compound isolation involves steps that are time and labor intensive, are prone to volatile loss, and often use solvents that are toxic or potential carcinogens. Furthermore, solvent extractions are generally accomplished at high temperatures or under reduced pressure, conditions that can destroy or alter some volatile flavor compounds and/or produce artifacts. Our long-term objective is to rapidly analyze flavor and aroma compounds in fresh-cut fruits and ultimately correlate chemical analyses with those findings obtained by trained sensory panelists. Therefore, we

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Table 1. Volatile and Semivolatile Flavor Compounds Recovered in Seedless Watermelon Juice Via Spme GC-MS^a

no. ^b	compounds ^c	RI ^d	refs	ID ^e	source ^f
1	acetaldehyde		4, 16	T	
2	(E)-2-butenal			T	
3	1-penten-3-ol		3, 15	S	F
4	1-pentene-3-one			S	A
5	2,3-pentanedione			T	
6	pentanal	700	3, 15	S, V	U
7	2-ethyl furan	703		T, V	
8	(E)-2-pentenal	753	3, 15	S, V	A
9	1-pentanol	765	3, 4, 15	S, V	P
10	(Z)-penten-1-ol	769	3	T, V	
11	(Z)-3-hexenal	799		T, V	
12	hexanal	803	3, 6, 15, 16	S, V	U
13	unk (98, 83, 69)	845			
14	(E)-2-hexenal	853	3, 6, 15	S, V	A
15	(Z)-3-hexen-1-ol	855	3, 4, 15, 16	S, V	B
16	1-hexanol	867	3, 4, 15	S, V	P
17	(Z)-4-heptenal	901		T, V	
18	heptanal	903	3	S, V	U
19	2,4-hexadienal	911		T, V	
20	(E)-2-heptenal	958	3, 6, 15	S, V	A
21	benzaldehyde	966	3	T, V	
22	1-heptanol	969		S, V	P
23	1-octen-3-one	978	3	S, V	A
24	1-octen-3-ol	980	3	S, V	A
25	6-methyl-5-hepten-2-one	985	3, 15, 33	S, V	A
26	2-pentyl furan	992	3, 15	S, V	A
27	6-methyl-hept-5-en-2-ol	993		S	A
28	(E,E)-2,4-heptadienal	998	3, 15	T, V	
29	octanal	1005	3, 15	S, V	U
30	(E,E)-2,4-heptadienal	1015	3, 15	T, V	
31	2-ethyl-1-hexanol	1031		S, V	A
32	unk (140, 96, 83, 69)	1034			
33	unk (124, 109, 95, 67)	1038			
34	benzyl alcohol	1040	3, 4	T, V	
35	unk (126, 111, 97, 69)	1042			
36	unk (83, 70, 55)	1051			
37	(E)-2-octenal	1063	3, 6, 15	S, V	A
38	(E)-2-octen-1-ol	1069	3, 15	T, V	
39	1-octanol	1073	3	S, V	P
40	4-nonenal	1096		T	
41	unk (138, 122, 84, 69)	1098			
42	(Z)-6-nonenal	1104	6, 15, 28	S	A
43	nonanal	1107	3, 6, 15, 28	T, V	
44	unk (138, 123, 109, 95, 81, 70)	1145			
45	unk (96, 83, 70)	1150			
46	(Z)-3-nonen-1-ol	1158	3, 6, 15, 16, 28	S, V	B
47	(E,Z)-2,6-nonadienal	1159	3, 6, 15, 16, 28	S, V	B
48	(Z,Z)-3,6-nonadien-1-ol	1161	3, 6, 15, 16, 28	S	B
49	(E)-2-nonenal	1167	6, 15, 16, 28	S, V	A
50	(Z)-6-nonen-1-ol	1171	3, 6, 15, 28	T	
51	1-nonanol	1172	3, 6, 15, 16, 28	S, V	A
52	(E,E)-2,4-Nonadienal	1216		T, V	
53	unk (152, 137, 123, 109)	1229			
54	(Z)-citral	1242	3, 33	S, V	A
55	3-octanone	1247		T, V	
56	unk (136, 121, 110, 98, 83)	1265			
57	(E)-citral	1272	3, 33	S, V	A
58	5-pentyl-2(5H)-furanone	1345		T	
59	(E)-geranylacetone	1450	3, 15, 16, 33	S, V	A

^aReferences indicate previous reports of the compound in watermelon.

^bCompound no. corresponds with identifications used in Figure 1. ^cunk, unknown; major ion fragmentation patterns are listed parenthetically. ^dRI calculated according to the M&M. ^eID, identifications based according to abbreviations where: S, confirmed with standards; T, tentatively identified; and V, verified RI match for a DB-5 column published in Flavorworks (version 2.0, Flavometrics, Anaheim Hills, CA) and/or the Flavornet website (<http://www.flavornet.org/flavornet.html>). ^fStandards acquired from: A, Aldrich; B, Bedoukian; F, Fluka; P, Poly Science; and U, Ultra Scientific.

analyzed for aroma and volatile flavor compounds at approximately the temperature of the human palate, where mastication

occurs. Flavor and off-flavor aromas have been assessed in numerous fruits and juices by solid-phase microextraction (SPME) (9–14). SPME was chosen because it is rapid, less laborious, relatively inexpensive, and does not require solvents, purge and trap, preconcentration, or vigorous extraction and heating (which may alter endogenous compounds), and the absorptive nature of the fibers permits assays at nondestructive temperatures.

We subsequently initiated a study to investigate the flavor profile of several seedless watermelon varieties. Our objective was to recover and characterize volatile compounds in seedless watermelon via gas chromatography–mass spectrometry (GC-MS) using a simple, rapid, automated analysis and ultimately gain the ability to track flavor changes in stored fresh-cut products. This information will serve as a basic background to future works geared toward studying volatile changes and sensory attributes in stored fresh-cut seedless watermelons.

MATERIALS AND METHODS

Plant Material. Several varieties of seedless watermelon [*C. lanatus* (Thunb.)] were grown in Woodland, CA, on raised beds with drip irrigation on 80 in. (203 cm) centers with 5 week old transplants spaced every 4 feet (122 cm) down the row. This included standard fertilization (N–P–K), as based on soil test analysis, and water applied through a drip system every 3–5 days, as based on weather conditions. With the exception of Petite Perfection Pure Heart ($n = 3$), analyses were repeated with each variety (Palomar, Tri-X 313, RWT8129, and RWT8154) from two separate triplicates ($n = 6$), and representative volatile profiles were presented. Fruits were harvested commercially, based on fruit size, “thumping”, and the desiccation of the subtending tendril. Fruits were chilled (~15 °C) until being packed with Styrofoam beads and shipped overnight to the Southern Regional Research Center (SRRC, New Orleans, LA) for immediate analysis the following morning.

Sample Preparation. Whole fruits were sanitized in 100 μ L L⁻¹ NaClO (pH ~ 6.7), rinsed in deionized water, and peeled. All sanitized melons, subsequent cutting procedures, and fresh-cut tissues were prepared and handled with latex gloves. “Individual-sized” or “refrigerator” fruits (8154 and Pure Heart) were peeled on a Muro CP-44 melon peeler (Tokyo, Japan), and larger fruits (Palomar, Tri-X 313, and 8129) were hand-peeled with sharp knives. The stem and blossom portions were cut off on a cutting board, and then, melons were moved to a clean cutting board where all white and light pink exocarp was trimmed off. Fruits were cut equatorially into roughly 5 cm segments and then cut into bars (2.5 cm × 2.5 cm × 5.0 cm) with a Silver King KutLett SKK2 (Minneapolis, MN) head lettuce slicer. Volatile samples were prepared (six reps for all varieties except Pure Heart, $n = 3$) by squeezing three randomized bars through Miracloth, and 3 mL of juice was immediately pipetted into 10 mL glass vials containing 1.1 g of NaCl. Benzoanthiophene was added as an internal standard (IS) at 100 g kg⁻¹ (ppb, final concentration). Vials were sealed tightly with screw caps fitted with a Teflon/silicon septum and placed on a Combi-Pal autosampler (Leap Technologies, Carrboro, NC) cooling rack at 4 °C.

SPME Analysis. Automated 1-cm 50/30 carboxen divinylbenzene polydimethylsiloxane (carboxen/DVB/PDMS) 100 μ m SPME fibers (Supelco, Inc., Bellefonte, PA) were used. Previously, cantaloupe, strawberry, and orange juice were sampled by SPME using 100 μ m PDMS fibers (10, 12, 14); yet, low molecular weight alcohols were not effectively captured (10). Because watermelons have few esters, numerous low molecular weight alcohols, ketones, and aldehydes, and furan compounds, we chose a balanced fiber capable of adsorbing a wide range of polarities and molecular weight compounds, according to Sigma Aldrich (Supelco) (http://www.sigmaldrich.com/Brands/Supelco_Home/Datanodes.html?cat_path=970367&supelco_name=SPME&id=970367). Sample vials were removed from the 4 °C holding tray of the autosampler and equilibrated for 10 min via oscillation in a 40 °C chamber, followed immediately by a 12.5 min

Table 2. Relative Percentage of the Most Abundant 11 Compounds Recovered in Seedless Watermelon Juices Via Spme GC-MS

compounds	RML8129		RML8154			Palomar			Tri-X-313			Pure Heart		
	avg ^a	SD (n = 6)	SD (n = 3)	avg	SD (n = 6)	SD (n = 3)	avg	SD (n = 6)	SD (n = 3)	avg	SD (n = 6)	SD (n = 3)	avg	SD (n = 3)
hexanal	7.1	3.2	1.9	15.7	2.2	1.9	9.8	2.5	0.5	16.9	4.2	1.4	37.6	1.8
6-methyl-5-hepten-2-one	2.7	0.5	0.3	7.7	2.3	0.8	3.9	1.4	0.3	4.2	0.5	0.3	3.2	0.3
(E)-2-octenal	0.8	0.2	0.3	1.9	0.5	0.6	2.2	0.2	0.1	2.1	0.3	0.2	1.1	0.0
4-nonenal	1.5	0.5	0.4	0.9	0.1	0.1	1.9	1.3	0.6	0.9	0.3	0.1	2.4	0.2
(Z)-6-nonenal	11.3	4.8	1.4	6.4	2.8	2.0	2.0	0.7	0.5	5.6	1.8	1.3	5.2	1.9
Nonanal	6.5	2.7	0.4	7.7	1.8	0.6	4.8	1.8	1.1	7.6	1.8	1.9	NR ^b	
(Z)-3-Nonen-1-ol and (E,Z)-2,6-nonadienal	28.2	5.8	2.1	17.2	1.9	0.6	24.9	3.7	1.3	20.6	3.6	0.8	16.5	1.2
(Z,Z)-3,6-nonadien-1-ol	8.9	2.8	2.6	4.9	1.1	0.5	5.1	1.6	2.1	6.0	0.8	0.9	3.1	0.5
(E)-2-nonenal	14.0	2.1	2.5	14.7	2.9	0.9	22.5	6.7	1.9	12.6	4.3	1.6	10.6	0.7
1-nonanol	0.7	0.2	0.2	0.7	0.2	0.1	0.7	0.1	0.1	0.9	0.1	0.1	NR	
sum	81.6			77.8			77.9			77.3			79.8	

^a Avg, averaged peak area, according to the M&M. Standard deviations (SD) listed for the overall averages where $n = 6$ and for an individual triplicate. ^b NR, not recovered.

SPME exposure to the headspace above the slurry at 40 °C, as previously reported (10). Vials were continuously swirled during SPME exposure with an agitation speed of 100 rpm.

GC-MS Parameters and Analysis. SPME fibers were desorbed at 250 °C for 1 min in the injection port of an HP6890/5973 GC-MS (Agilent Technologies Wilmington, DE; formerly Hewlett-Packard, Palo Alto, CA) with a 5% phenyl polysiloxane ZB-5 (Zebron Phenomenex, Torrance, CA) 30 m, 0.25 mm i.d., 1 μm film thickness, or DB-5 column (J & W Scientific, Folsom, CA), 30 m, 0.25 mm i.d., 0.5 μm film thickness. Fibers remained in the heated injection port for 5 min as a bake-out step. The GC was equipped with a Micro Cryo-trap (Scientific Instrument Services, Ringoes, N.J.), and compounds were cryofocused at -60 °C using carbon dioxide during the 1 min desorption. The injection port was operated in splitless mode and subjected to a pressure of 173 kPa (25 psi) of ultrahigh-purity He (99.9995%) for the first minute, then set at a constant velocity of 40 cm s⁻¹ for the remainder of the GC run. The initial oven temperature was 50 °C, held for 1 min, ramped at 5 °C min⁻¹ to 100 °C, then ramped at 10 °C min⁻¹ to 190 °C, and ramped at 30 °C min⁻¹ to 250 °C and held for 1 min. The HP5973 quadrupole mass spectrometer was operated in the electron ionization mode at 70 eV, a source temperature of 150 °C, quadrupole at 106 °C, with a scan from m/z 33 to 300. Data were collected with HP ChemStation software (D.01.02.16) and searched against the NIST (v. 1.5) and Wiley (v. 7.0 NIST98) libraries (Palisade Corp., Newfield, NY). Compounds were preliminarily identified by library search, and then, the identities of most were confirmed by comparison of their GC retention time (RTs) with authentic compounds, MS ion spectra, or an in-house retention index (RI). The RTs from a series of straight-chain alkanes (C₇-C₂₀) produced on the aforementioned columns under identical conditions were used to calculate RIs for all identified compounds. As this is mainly a qualitative appraisal of volatile compounds, we performed estimates of the relative percentage of given compounds based on integrated ion areas divided by the total chromatograms ion area, minus known impurities. Spectra were integrated based on qualifying and progeny ions to discriminate and identify compounds as compared against standards and an in-house RI data library. Standards were acquired from Aldrich (Milwaukee, WI), Bedoukian (Danbury, CT), Fluka (Switzerland), Poly Science (Niles, IL), and Ultra Scientific (North Kingstown, RI), according to **Table 2**.

RESULTS AND DISCUSSION

Using SPME with five varieties of rapidly juiced seedless watermelon samples, we recovered 59 volatile compounds via GC-MS (**Table 1**). Of these compounds, 12 were not previously reported, and the majority were confirmed with standards (**Table 1**). To date, 10 compounds remain unidentified. Previous reports for watermelon have tabulated many more compounds. However, because of extraction methods (vacuum and/or steam distillation) and possible oxidation or chemical alteration, less

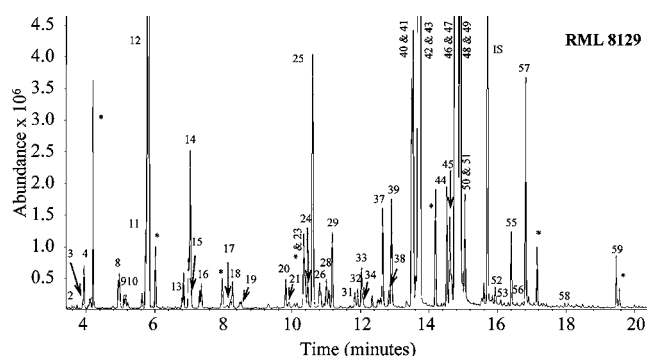


Figure 1. Total ion spectra from commercially ripe seedless RML8129 watermelon fruit. One representative run of the six replicates is presented. Peak numbering corresponds with **Table 1**. For clarity and because many compounds were confidently recovered at quantifiable levels with low relative abundance, not all are labeled. An asterisk (*) indicates peaks associated with column and/or SPME fiber impurities; IS, internal standard.

volatile compounds and/or possible artifacts are in those lists. We recovered five of the 25 compounds reported via vacuum distillation and GC (4), 12 of 18 reported using vacuum steam distillation (6), 32 of 71 compounds recovered by distilling juice under reduced pressure followed by Freon-11 extraction (3), 25 of 37 compounds reported by ref 15, and nine of 36 reported via steam distillation, Liken-Nickerson extraction (16). Our results obviously indicate fewer overall compounds recovered. However, this SPME method recovers mainly low- to midmolecular weight semivolatile and volatile compounds. There is also the possibility that seedless varieties do not have the same general volatile profile as compared to their seeded counterparts.

A total ion trace illustrates the relatively complex semivolatile and volatile compound flavor profiles for selected seedless watermelons (**Figure 1**). An unreleased seedless variety being developed for exceedingly firm flesh and fresh cutting, RML8129, is presented in the chromatogram. This variety had predominately C₉ aldehyde and alcohol compounds, clustered between peaks 40 and 51. RML8129 had the highest relative percentage of (Z)-6-nonenal (no. 42), and the lowest percentage of hexanal (no. 12) as compared with the other four varieties (**Table 2**). On the other hand, Tri-X-313 and Pure Heart had the highest levels of hexanal. With the exception of Pure Heart, the combined peak comprised by (Z)-3-nonen-1-ol (no. 46) and (E,Z)-2,6-nonadienal (no. 47) dominated the profiles in these

seedless watermelon varieties. The relative percentages for the dominant compounds recovered and integrated are presented in **Table 2**.

The majority of compounds recovered in seedless watermelon with this SPME GC-MS method were C₆ and C₉ alcohols and aldehydes. On the basis of relative percentages, just 11 predominant volatiles accounted for approximately 77.3–81.6% the total volatile profile in five varieties (**Table 2**). A similar recovery pattern was also reported in seeded watermelon fruits (3, 6, 15), with (Z)-3-nonen-1-ol and (Z,Z)-(3,6-nonadien-1-ol) predominating. As previously reported in seeded watermelons, (Z)-3-nonen-1-ol, and (Z,Z)-3,6-nonadien-1-ol were highly abundant compounds, along with hexanal, (E,Z)-2,6-nonadienal, and (E)-2-nonenal, in these seedless varieties (**Table 2**). The relative percentage estimates for (E,Z)-2,6-nonadienal and (Z)-3-nonen-1-ol are grouped, even though we can resolve these via unique GC RTs when performing specific selected ion searches on the MS. Because four of the five varieties were repeated ($n = 3$) in two separate triplicates, the standard deviations appear excessively high for the major compounds recovered (**Table 2**). Marked differences between $n = 3$ vs $n = 6$ deviations are likely due to marked maturity differences of individual fruits as received from the same “uniform field and harvest”. The first triplicates were carefully selected based on fruit appearance, desiccation of the harvest stem, and resonant sound upon thumping. The remaining triplicates were fruits run the following day, which were less uniform. Seasonal variation in volatile recovery in numerous melons has also been observed (17). Subsequently, we presented the $n = 6$ combined deviation and also displayed the lower (generally) deviations associated with apparently more uniform fruit, illustrated in the $n = 3$ vs $n = 6$ standard deviation columns (**Table 2**).

Although C₆ and C₉ compounds in fruits are often considered oxidation products (18–24), they have been considered to impart important typical melon, watermelon, and fruit flavor–aroma attributes (18, 22, 23, 25–27) and have also been reported as such in flavor compound software (e.g., FlavorWorks 2.0, Flavometrics, Anaheim Hills, CA). Many of these C₉ compounds have been attributed to characteristic aroma attributes (parenthetically listed below) in watermelons, melons, and cucurbits. For example, (Z)-3-nonen-1-ol (fresh melon-like odor), (Z,Z)-3,6-nonadien-1-ol (sweet and watermelon-like, watermelon rind, and boiled leaflike), (E,Z)-2,6-nonadienal (cucumber, violet, green, and waxy), and (E)-2-nonenal (fatty, penetrating, and waxy) have been reported as characteristic flavor components in seeded watermelon (3, 15, 28). The alcohol (Z,Z)-3,6-nonadien-1-ol was considered to be the most powerful contributor to the characteristic aroma of watermelon (3). The aldehyde (Z)-6-nonenal (melon or green melon and citrus) was considered flavor important and more abundant in watermelon as compared with muskmelon (28). Both (Z)-3-nonenal (green and watermelon-like) and (Z,Z)-3,6-nonadienal (green and watermelon-like) have been considered flavor important (3). We believe these two compounds might be listed in **Table 1**, classified as unidentified, but standards are not available, and we have found no MS ion reports for these. This is due to the fact that three out of four compounds that eluted with close proximity to the RT and RI of the identified C₉ compounds have similar ion fragmentation patterns (likely isomers) as compared with the identified alcohols and aldehydes. Although not a “major” compound, we recovered (Z)-6-nonen-1-ol (no. 50, cucumber, green, melon, powerful, sweet, and pumpkin) in all varieties, and this compound was also suspected to contribute to watermelon flavor (15).

The most abundant ketone recovered (2.7–7.7%) was 6-methyl-5-hepten-2-one (herbaceous, green, oily, and pungent) (**Table 2**). This compound has been recovered in diverse crops such as apple, paprika, tomato, and watermelon and reported to be an oxidative byproduct or degradation product derived from lycopene, α -farnesene, citral, or conjugated trienols (29–33). We previously reported this oxidative product along with citral (neral and geranial) in cantaloupe (10), and subsequently, recovery herein is not unexpected due to the large lycopene concentrations found in watermelon (34).

Acids and esters have been reported in watermelons (4, 15, 16); yet, we found none with this SPME GC-MS method, similar to refs 3 and 6. We have used this method, and extremely similar methods, with various SPME fibers in thousands of other melon (cantaloupe, Charentais, Galia, honeydew, and Juan Canary) and fruit samples, recovering several esters (9, 10, 17, 25, 35). Subsequently, esters do not appear to be present in these seedless watermelon varieties, as previously indicated by others in certain seeded varieties (3, 5, 6). Subtle volatile differences might occur in seeded vs seedless fruit since ethylene synthesis in seedless fruits is minimal and ethylene production in other melons is required to initiate a cascade of enzymatic activities associated with ester volatile production (36–39).

Considering the above, the relatively simple yet subtle flavors in seedless watermelons associated with alcohols and aldehydes appear to be highly similar to seeded varieties and likely dependent upon tissue disruption (oxidation). However, there is an apparent lack of acids and esters previously reported in seeded fruit. Accordingly, we surmise that the aforementioned C₉ aldehyde and alcohol compounds are most important regarding the flavor and aroma of seedless watermelons.

ABBREVIATIONS USED

Carboxen/DVB/PDMS, carboxen divinylbenzene polydimethylsiloxane; GC, gas chromatograph; MS, mass spectrometry; RI, retention index; RT, retention time; SPME, solid-phase microextraction.

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