Aroma Composition Changes in Early Season Grapefruit Juice Produced from Thermal Concentration

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Differences in aroma components and total volatiles between a single unpasteurized Marsh grapefruit juice and its 65 °Brix concentrate reconstituted to 10 °Brix were examined using GC−olfactometry (GC−O) and GC−FID. Total volatiles (FID) in the reconstituted concentrate were reduced to less than 5% of initial values, but 57% of total aroma (GC−O) remained. Forty-one aroma-active compounds were observed in unpasteurized single strength juice, whereas 27 components were found in the unflavored reconstituted concentrate. Aroma-active compounds were classified into grapefruit/sulfury, sweet/fruity, fresh/citrusy, green/fatty/metallic, and cooked/meaty groups. Five of six components in the sweet/fruity and 14 of 18 green/fatty/metallic components survived thermal concentration. However, only 4-mercapto-4-methyl-2-pentanone in the grapefruit/sulfury group, and linalool and nootkatone from the fresh/citrusy group, were found in the reconstituted concentrate. Methional was the only aroma compound in the cooked/meaty category found in both juice types. β-Damascenone and 1-*p*-menthen-8-thiol were found only in the reconstituted concentrate. 4-Mercapto-4-methyl-2-pentanol was found for the first time in grapefruit juice.

KEYWORDS: GC−O; time−intensity measurement; flavor; aroma-impact compounds; aroma changes; grapefruit-smelling compounds; unsaturated fatty aldehydes; 1,10-dihydronootkatone; 4-mercapto-4-methyl-2-pentanone; β-damascenone; 1-*p*-menthen-8-thiol

INTRODUCTION

Citrus juices were originally concentrated and later frozen to provide a convenient year-round source for these juices which were previously seasonal products. The diminished volume and weight of concentrated juices reduced costs associated with packaging materials, storage space, transportation, and refrigeration compared to those of single strength juices (*1*). Freeze concentration (*2*) and reverse osmosis (*3*), among other technologies, have been considered as alternatives to thermal evaporation for the preparation of citrus juice concentrates. However, because of favorable economics, thermal evaporation is still the most widely used concentration process in the citrus industry. Freshly squeezed juice is pumped into an evaporator where most of the water is removed through vacuum-assisted heating. Commercial evaporators typically have several stages that sequentially heat the juice to ever higher temperatures and then rapidly cool it (*4,5*). The volatiles lost during concentration are recovered (for the most part) in the condensate of the first evaporation stage (essence) and subsequently added back to the

concentrate along with peel oil to restore the original volatile profile.

The quality of citrus juices from concentrate has improved as manufacturers have become more skilled in restoring volatiles lost during concentration. However, not-from-concentrate juices are still generally considered to have better flavor, suggesting that additional improvements in flavor restoration are still necessary. The inferior flavor of juices reconstituted from concentrate is primarily due to inadequate restoration of aroma volatiles in the proper proportions and part the result of new aroma compounds that are formed which also alter the flavor profile. Because both the juice concentrate and condensed volatiles used to restore flavor have experienced elevated temperatures, it is necessary to evaluate the concentrate separately from the flavor restoration mixture to determine where flavor changes have occurred. It has also been shown (*6−8*) that many of aroma active compounds in citrus juices exist as low-level compounds that are not usually detected by normal FID or MS detectors. A bioassay such as GC−O must be used to detect these aroma-active compounds. The purpose of this study was to examine the changes in aroma-active compounds formed or lost during the process of making concentrated grapefruit juice using thermal evaporation by employing a combination of GC−FID and GC−O so that it

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would be possible to restore only those compounds which needed restoration and to be aware of newly formed aroma compounds which may need to be masked.

MATERIALS AND METHODS

Grapefruit Juice. Early season (Nov. 2000) white grapefruit was purchased from a local packing house and processed in the University of Florida−Lake Alfred pilot plant. Fruits were washed, dried, and sized before extraction. Extraction was accomplished using commercial FMC model 391-B and 491 extractors with standard juice settings. An FMC model 35 juice finisher was used with a moderate squeeze setting. The finished juice had a Brix value of 11.6°, an acid content of 1.53%, and a Brix/acid ratio of 7.6. Oil level was 0.0012%. This juice was concentrated to 65 °Brix using a thermally accelerated short-time evaporator, TASTE, built by Cook Machinery, Dunedin, Florida. The concentrate was then reconstituted to 10.2 °Brix by diluting with water, but without restoring any volatiles. Oil level in the reconstituted juice was 0.0004%. Juice samples were packaged in 32-oz glass bottles and stored at −8 °C until analyzed.

Chemicals. Standard aroma compounds were obtained in the following ways. Ethyl 2-methylpropanoate, methional, 2-methyl-3-furanthiol, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, vanillin, *γ*-deca-lactone, 1-octen-3-one, (*E*)-2-hexenal, (*E*)-2-nonenal, (*E*)-2-decenal, (*E*)-2-undecenal, (*E,Z*)-2,6-nonadienal, (*E,E*)-2,4-nonadienal, and (*E,E*)-2,4-decadienal were purchased from Aldrich (Milwaukee, WI). 3-Mercapto-hexyl acetate and 3-mercaptohexan-1-ol were bought from Interchim (Montlucon, France). Limonene, octanal, nonanal, (*Z*)-3-hexenal, noot-katone, 1,10-dihydro nootkatone, linalool, and terpinen-4-ol were obtained as gifts from SunPure (Lakeland, FL). 1-*p*-Menthen-8-thiol and *γ*-damascenone were obtained from Givaudan (Lakeland, FL). 4-Mercapto-4-methyl-2-pentanone and 4-mercapto-4-methyl-2-penta-nool were synthesized in our laboratory. (*Z*)-2-Nonenal was found in purchased (*E*)-2-nonenal at 5−10% level and (*Z*)-2-decenal was found in purchased (*E*)-2-decenal at a similar level. (*E,Z*)-2,4-Nonadienal and (*E,Z*)-2,4-decadienal were respectively present in the purchased (*E,E*)-2,4-nonadienal and (*E,E*)-2,4-decadienal, whereas *trans*-4,5-epoxy-(*E*)-2-decenal was found in an oxidized sample of (*E,E*)-2,4-decadienal. Their identities were confirmed by retention indices and odor qualities.

Aroma Extraction. Grapefruit juice volatiles were extracted with a 1:1 mixture of pentane and diethyl ether (2 × 10 mL). 2-Heptade-canone (5 *μ*L of 4000 ppm), was added to 10 mL of juice as an internal standard, and the juices were extracted using a Mixxor-like apparatus consisting of two 50-mL syringes joined with a three-way leur-tipped directional valve. The extracts were concentrated to 50 *μ*L by using a stream of high purity nitrogen prior to chromatographic analysis. Details can be found in ref *6*.

Gas Chromatography (GC−FID). Volatile components in juice extracts were separated using a HP-5890 GC (Palo Alto, CA) using a flame ionization detector (FID) with either a DB-Wax column (30 m × 0.32 mm i.d. × 0.5 *μ*m) or DB-5 column (30 m × 0.32 mm i.d. × 0.25 *μ*m) both from J&W Scientific (Folsom, CA). Initial oven temperature was 40 °C for the DB-Wax column then increased to 240 °C at 7 °C/min, and finally held at 240 °C for 5 min. Initial oven temperature for the DB-5 column was 40 °C, then increased to 290 °C at 7 °C/min. Helium was used as carrier gas at a flow rate of 1.55 mL/min. Injector and detector temperatures were 225 °C and 290 °C, respectively. A 0.5-*μ*L aliquot of sample was injected in the splitless mode with a purge time of 0.5 min. Chromatograms were recorded and integrated using Chromperfect (Justice Innovations, Inc., Mountain View, CA) using a data acquisition rate of 10 points/s.

GC−Olfactometry (GC−O). Volatile components were separated using an HP-5890 GC (Palo Alto, CA) equipped with a sniffing port (DATU, Geneva, NY) and a FID. A GC splitter (Gerstel, Baltimore, MD) split the column effluent between the FID and olfactometer in a 1:2 ratio, respectively [See ref *6* for details]. Panelists were asked to describe each odor detected in the GC effluent. Aroma descriptors, along with the respective retention times, were recorded manually and later transcribed into the chromatographic software for inclusion with the olfactometry time−intensity data.

Time−Intensity Olfactometry Data Acquisition and Analysis. Assessors were asked to indicate aroma intensity continuously during the chromatographic run using a linear potentiometer. The device has a pointer that can be moved across a 10-cm span to indicate aroma intensity. The 0−1.0 V output was interfaced to a Chromperfect A/D board and associated software that digitally recorded both time and intensity. Chromatographic software was used to create aromagrams and to calculate olfactory peak area, peak height peak duration, and linear retention index values for each component. Two trained assessors were employed to evaluate each sample in duplicate. Four individual time-intensity aromagrams were obtained for each juice for both polar and nonpolar columns. Thus, in total, eight measurements were obtained for each juice type. Mean aroma intensities of each odorant were calculated by averaging the peak height among the four runs, consider-ing the nondetected peak area as zero. Aroma-active components were defined as only those compounds producing an intensity response at the same retention time and similar descriptor from at least half of the panel responses.

RESULTS AND DISCUSSION

Preliminary Juice Aroma Characterization. Five assessors, all experienced in aroma description, were asked to describe the aroma characteristics of the unpasteurized, single strength, early season grapefruit juice and the unflavored reconstituted juice. The aroma of the single strength juice was described as grapefruity, fruity, and citrusy. Initial expectations were that the unflavored reconstituted juice would have little aroma because all of the volatile materials (primarily limonene) had been removed. Limonene had previously been reported as an essential component to reflavorize orange juice concentrate (*9*). Although diminished, there was a surprising amount of aroma activity in the reconstituted juice concentrate. However, its aroma profile was profoundly different from that of the initial juice. The overall aroma from the unflavored reconstituted juice was described as cooked/sweet, green/geranium/metallic/paint, and earthy/muddy. The reasons for these profoundly different aroma profiles can be seen from the selective loss of aroma components described in the following sections.

Comparison of Major Volatile Components. Volatile components in each juice extract were measured using GC−FID. FID chromatograms of extracts of the initial juice and the diluted concentrate are compared in **Figure 1**. Forty-four of the largest peaks are numbered (Roman numerals) and listed in **Table 1**. Tentative identifications were based on their retention index values on a DB-5 column. As shown in **Figure 1** and **Table 1**, 99% of limonene (x), 96% (*E*)-caryophyllene (xxvii), and 84% nootkatone (xxxix), the three dominant volatiles in unpasteurized juice, were lost during the thermal concentration process. Thirty other components, including α-pinene (vii), γ-terpinene (xii), δ-elemene (xxiv), α-humulene (xxviii), and γ-cadinene (xxxii), were completely lost. These losses are probably due to the combination of thermal instability and physical evaporation during the concentration process. Some components (xxi, xxxxiii, and xxxxiv) lost only 20−40% of their initial values. In sharp contrast, other components such as iii (ethyl butyrate), v (2*E*-hexenal), xi (*E*-β-ocimene), xiii (cis-linalool oxide), xiv (*trans*-linalool oxide), and xxxxii, were essentially unchanged during the concentration process. Interest-ingly, (*S*)-ethyl 2-methylbutanoate (iv) increased 34% during the thermal concentration, suggesting that it had been thermally generated. Although, on average, 95% of total volatile compo-nents were lost during thermal concentration, specific losses ranged from 100% to a net gain of in the case of (*S*)-ethyl 2-methylbutanoate. Even though 95% of total volatile peak area was lost during the concentration process, the aroma activity of the reconstituted concentrate was not proportionally reduced.
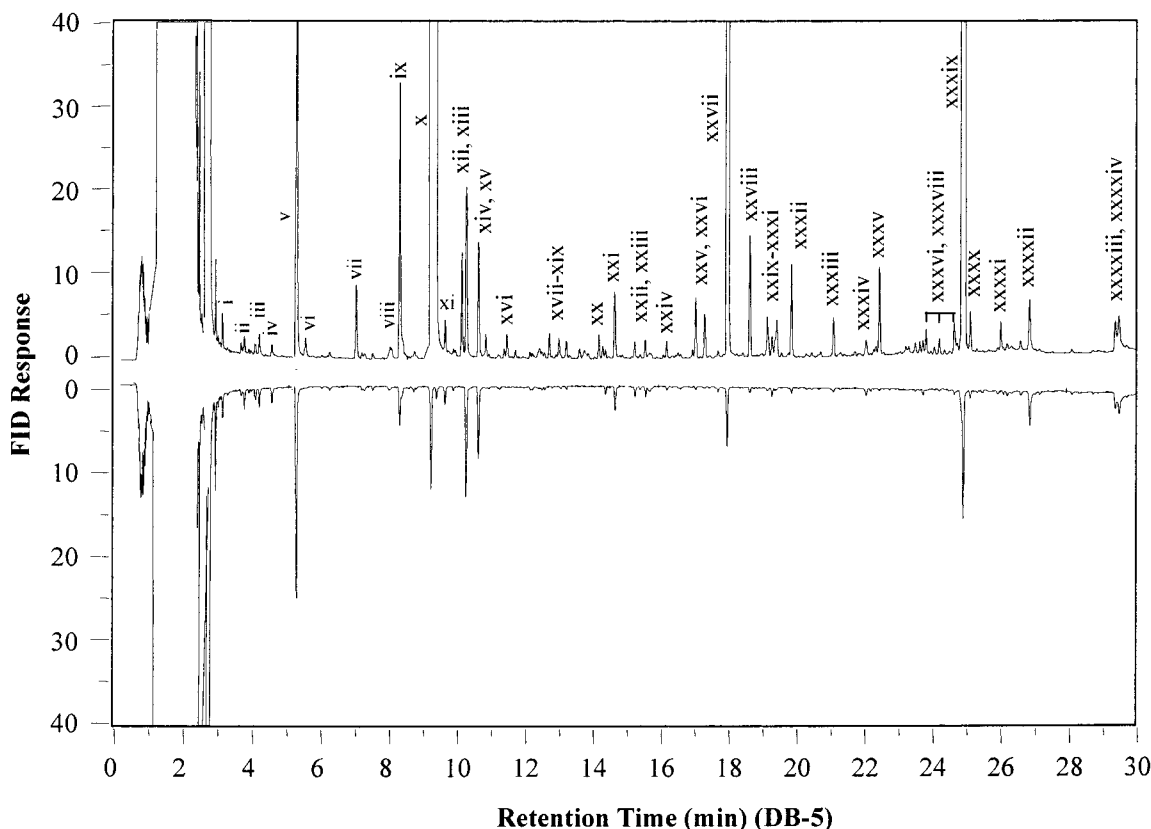
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Figure 1. Comparison of FID chromatograms of the single strength juice (top) and the unflavored, reconstituted concentrate (bottom).

Detection and Identification of Aroma-Active Compounds. Between both juices, 43 aroma active compounds were observed. The descriptors and the linear retention index values on two dissimilar chromatographic supports (DB-5 and a DB-Wax) are listed in **Table 2**. Thirty-seven of the 43 aroma active compounds were identified based on the combination of aroma descriptors and retention indices. Identifications were confirmed using GC−O data from standard compounds except for compounds **1**, **3**, **9**, **14**, and **36**.

Seven GC−O peaks could be classified as possessing sulfury/grapefruit aroma characteristics. These odorants include: 4-mercapto-4-methyl-2-pentanone (**7**), 4-mercapto-4-methyl-2-pentanol (**12**), 3-mercapto hexan-1-ol (**18**), 3-mercapto hexyl acetate (**25**), 1-*p*-menthen-8-thiol (**28**), 1, 10-dihydro nootkatone (**40**), and nootkatone (**41**). The combination of these odorants is responsible for the unique aroma of grapefruit juice compared to that of other citrus juices. The structures of these odorants are illustrated in **Figure 2**. Three of them; namely 4-mercapto-4-methyl-2-pentanone (*7*), 1-*p*-menthen-8-thiol (*10*), and nootkatone (*11*) had been proposed as character impact odorants of grapefruit. We previously reported 3-mercapto hexan-1-ol and 3-mercapto hexyl acetate in not-from-concentrate grapefruit juice (*12*). The aromas of these two compounds had been described as grapefruit, passion fruit, and box tree, and their perception thresholds in alcohol solution were reported to be 4 and 60 ng/L, respectively (*13*). They have been identified in both Sauvignon Blanc wines (*13*) and passion fruit (*14*). However, this work represents the first report of 4-mercapto-4-methyl-2-pentanol in grapefruit juice. It had previously been identified in Sauvignon Blanc wines. The aroma of 4-mercapto-4-methyl-2-pentanol has been described as citrus zest with a perception threshold of 55 ng/L alcohol (*13*). This study contains the first evidence of direct aroma activity for 1,10-dihydronootkatone in grapefruit juice. The odor character and threshold value of

this compound have been studied with respect to nootkatone (*15*). The authors synthesized this compound from nootkatone and reported that it had a desirable grapefruit aroma and that the threshold value was 50 ppb which was even lower than that of nootkatone (175 ppb). Demole and Enggist (*16*) reported finding this compound in a grapefruit juice fraction containing primarily nootkatone, but did not indicate aroma activity.

Nine odorants had sweet/fruity aroma characteristics. They were identified as two esters (**1, 3**), two furanones (**13, 14**), β-damascenone (**33**), vanillin (**34**), γ-decalactone (**35**), and two remaining unknowns (**38, 42**).

Seventeen carbonyl compounds, including many aldehydes and ketones from fatty acid degradations, were found. The aroma characteristics of these odorants are green, citrus, geranium, metallic, and fatty. They were identified as two saturated fatty aldehydes (**10, 17**), seven mono-unsaturated fatty aldehydes (**2, 4, 19, 21, 26, 27, 31**), five double-unsaturated fatty aldehydes (**20, 23, 24, 29, 30**), two vinyl ketones (**8, 9**), and an epoxy unsaturated aldehyde (**32**).

Other odorants identified include terpenes, terpene alcohols, and a terpene ketone (**9, 11, 16, 22**), and three sulfur compounds (**5, 6** and **36**) from the degradation of amino acids such as methionine or cysteine. Odorants **1, 2, 3, 6, 7, 10, 11, 13, 16, 17, 19, 21, 28, 34,** and **41** had been previously reported in freshly hand-squeezed grapefruit juice (*7*).

Comparison of the Aroma Profiles. Composite aromagrams of the original early season grapefruit juice (top) and reconstituted concentrate (bottom) juices are shown in **Figure 3**. Odorants with similar aroma notes were grouped into five aroma categories: (a) grapefruit/sulfury, (b) sweet/fruity, (c) fresh/citrusy, (d) green/fatty/metallic, and (e) cooked/meaty.

The green/fatty/metallic aroma category had the most aroma compounds (eighteen) and the aroma components with the greatest intensity. There were eight odorants with sweet/fruity

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Table 1. Tentative Identification of Major Volatiles in the Grapefruit Juices Based on Linear Retention Index on DB-5 Column and Their Percentage Loss during the Thermal Concentration Process[a]

peak no.	name	LRI (DB-5)	% loss
i	ethyl 2-methylproanoate (**1**)	742	> 99
ii	unknown	775	> 99
iii	ethyl butyrate	797	42
iv	ethyl 2-methylbutanoate (**3**)	816	−34
v	(*E*)-2-hexenal (**4**)	852	43
vi	hexanol	864	> 99
vii	α-pinene	933	> 99
viii	β-pinene	978	> 99
ix	myrcene	990	84
x	limonene (**11**)	1038	99
xi	(E)-β-ocimene	1049	42
xii	γ-terpinene	1070	> 99
xiii	*cis*-linalool oxide	1076	35
xiv	*trans*-linalool oxide	1092	34
xv	nonanal (**16**) + linalool (**17**)	1101	> 99
xvi	allo-ocimene	1129	> 99
xvii	terpinen-4-ol	1184	> 99
xviii	(*E,Z*)-2,4-nonadienal (**23**)	1196	> 99
xix	α-terpineol	1206	> 99
xx	(*Z*)-2-decenal (**26**)	1249	> 99
u	unknown	1271	62
xxii	(*E,Z*)-2,4-decadienal (**29**)	1298	> 99
xxiii	undecanal	1313	> 99
xxiv	δ-elemene	1343	> 99
xxv	neryl acetate	1385	> 99
xxvi	geranyl acetate	1398	> 99
xxvii	(*E*)-caryophyllene	1433	96
xxviii	α-humulene	1466	> 99
xxix	β-selinene	1493	> 99
xxx	valencene	1500	> 99
xxxi	β-bisabolene	1508	> 99
xxxii	γ-cadinene	1531	> 99
xxxiii	caryophyllene oxide	1600	> 99
xxxiv	unknown	1655	> 99
xxxv	unknown	1678	> 99
xxxvi	1,10-dihydronootkatone (**40**)	1761	> 99
xxxvii	α-sinensal	1786	> 99
xxxviii	unknown	1814	> 99
xxxix	nootkatone (**41**)	1834	84
xxxx	unknown	1844	> 99
xxxxi	unknown	1902	> 99
xxxxii	unknown	1960	30
xxxxiii	unknown	2135	69
xxxxiv	unknown	2144	79
total			95

[a] Arabic numbers (in parentheses) after a compound name indicates that the compound has aroma activity and its aroma properties are listed in **Table 2**.

notes. The components in this category contributed moderately to the overall aroma of the original juice. Only six compounds were classified into the grapefruit/sulfury category, but these compounds collectively impart the unique grapefruit aroma characteristics to the juice. Another six components contribute to the fresh/citrusy note to the juice. Finally, two meaty odorants as well as one cooked-potato-smelling odorant comprised the cooked/meaty category. These aroma notes in the observed specific balance provided the grapefruity, fruity, citrusy aroma impression of the original juice.

However, as shown in **Figure 3**, the aroma balance in the unflavored reconstituted juice is considerably different from that of the original juice. It is surprising to find so much aroma activity in the reconstituted juice since 95% of the total volatile material had been removed. However, total aroma activity, as determined by average GC−O panel responses, was only reduced 43%. The source of these persistent aroma compounds is uncertain at this time. However, as it has been previously shown that citrus juice pulp and cloud (insoluble solids) can retain considerable volatiles (*17, 18*), many of the volatiles observed in the reconstituted juice may have been trapped in the pulp during thermal concentration. The aroma compounds in the green/fatty/metallic and sweet/fruity categories were least affected by thermal concentration. Even though the relative intensities of the aroma components in the reconstituted juice were appreciably different from those of the original juice, most of the components in these two groups survived the thermal concentration process. In contrast, the grapefruit/sulfury and fresh/citrusy aroma groups were severely impacted. Only two of the six original odorants in the grapefruit/sulfury category and only one of the six original odorants in the fresh/citrusy survived the thermal concentration process. Because most of the grapefruit/sulfury and fresh/citrusy aromas were missing, the aroma impression of reconstituted concentrate was described as cooked-sweet, green-geranium-metallic-paint, and earthy-muddy.

Aroma Impact Compounds: Chemical/Physical Changes. Comparing the two aromagrams, 41 aroma-impact compounds were detected in the original juice, whereas only 27 were found in the reconstituted concentrate. Sixteen aroma impact compounds were lost physically and/or chemically and two were generated during the process of thermal concentration. Twenty-five odorants survived the thermal concentration process because of one or both of the following reasons. The compounds are high-boiling and thermally stable, thus they survived the thermal concentration process. Other compounds might be physically
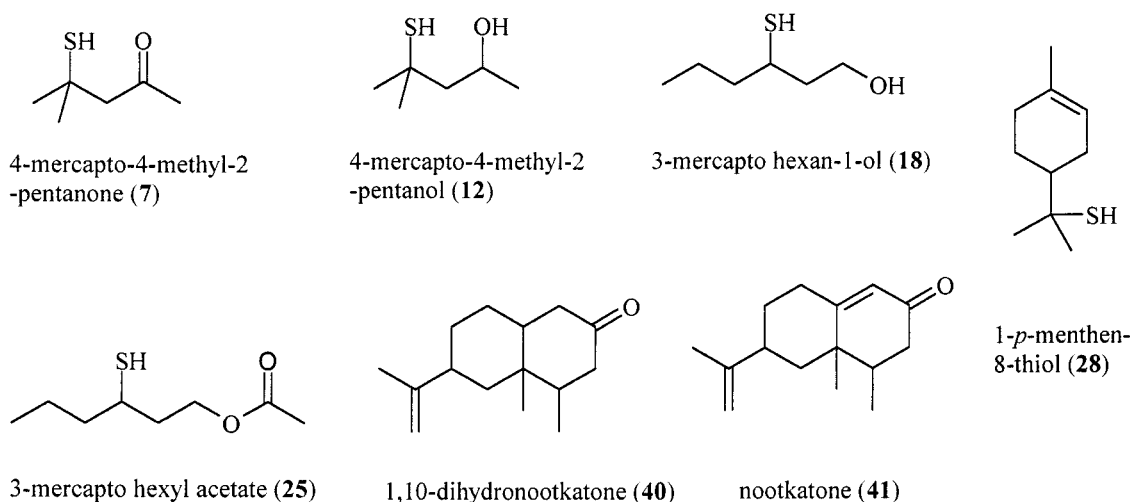
Figure 2. Chemical structures of odorants with grapefruit-sulfury notes identified in early season white grapefruit juices.

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Table 2. Identification of Aroma Active Compounds in the White Early Season Grapefruit Juices

no.	identification	descriptor	KI (DB-5)	KI (DB-Wax)
1	ethyl 2-methylpropanoate[a]	sweet, fruity	744	965
2	(Z)-3-hexenal[a]	green	797	1147
3	(S)-ethyl 2-methylbutanoate[b]	fishy, fruity	819	1051
4	(E)-2-hexenal[a]	green	852	1232
5	2-methyl-3-furanthiol[a]	meaty	865	1274
6	methional[a]	potato	904	1468
7	4-mercapto-4-methyl-2-pentanone[a]	sulfury	942	1380
8	1-octen-3-one[a]	mushroom	976	1309
9	(Z)-1,5-octadien-3-one[b]	geranium	983	1383
10	octanal[a]	fresh, minty	1004	1300
11	limonene[a]	terpeney	1033	1210
12	4-mercapto-4-methyl-2-pentanol[a]	grapefruit	1042	1534
13	4-hydroxy-2,5-dimethyl-3(2H)-furanone (Furaneol)[a]	caramel	1059	2049
14	2(or 5)-ethyl-4-hydroxy-5(or 2)-methyl-3(2H)-furanone (Homofuraneol)[b]	caramel	1078	2070
15	unknown	dish water	1087	nd
16	linalool[a]	fresh	1097	1555
17	nonanal[a]	citrusy	1102	1395
18	3-mercapto hexan-1-ol[a]	grapefruit	1126	1835
19	(Z)-2-nonenal[a]	geranium,	1149	1518
20	(E,Z)-2,6-nonadienal[a]	cucumber	1157	1601
21	(E)-2-nonenal[a]	soapy	1164	1549
22	terpinen-4-ol[c]	apple	1177	nd
23	(E,Z)-2,4-nonadienal[a]	geranium	1196	1670
24	(E,E)-2,4-nonadienal[a]	fatty, fried	1217	1716
25	3-mercapto hexyl acetate[a]	grapefruit	1244	1725
26	(Z)-2-decenal[a]	soapy	1251	1625
27	(E)-2-decenal[a]	geranium,	1266	1655
28	1-p-menthen-8-thiol [a]	grapefruit	1291	1615
29	(E,Z)-2,4-decadienal[a]	geranium3	1295	1779
30	(E,E)-2,4-decadienal[a]	fatty, fried	1319	1829
31	(E)-2-undecenal[a]	geranium	1352	1769
32	trans-4,5-epoxy-(E)-2-decenal[b]	green, metallic	1379	2025
33	β-damascenone[a]	sweet, honey	1390	1845
34	vanillin[a]	vanilla	1406	2602
35	γ-decalactone[a]	coconut	1467	2152
36	bis-(2-methyl-3-furyl)disulfide[c]	meaty	1542	nd
37	unknown	peppery	1672	2203
38	unknown	dried fruit	1696	nd
39	unknown	peppery	1726	2313
40	1,10-dihydro nootkatone[a]	grapefruit	1766	2384
41	nootkatone[a]	grapefruit	1835	2586
42	unknown	sweet	1862	nd
43	unknown	woody, pungent	2026	nd

[a] Odorants were identified ibased on comparison of odor description and RIs on DB-5 and DB-Wax columns with standard compounds. [b] Odorants were identified on the basis of comparison of odor description and RIs on DB-5 and DB-Wax columns with reported data because standards were not available. [c] Odorants were tentatively identified based on comparison of RI on a DB-5 column and odor descriptor with standard compounds.

or chemically unstable, but losses were compensated for by the generation of additional material from their precursors in the juice.

Sulfury/Grapefruit Compounds. Several thiols have been suggested as key aroma impact compounds in grapefruit juice. Two of the most potent are 1-*p*-menthene-8-thiol (**28**) and 4-mercapto-4-methyl-2-pentanone (**7**). However, in this study, 1-*p*-menthene-8-thiol was found only in the concentrated juice and not in the original juice. Hydrogen sulfide has been reported in freshly extracted grapefruit juice (*19*). Limonene (the major volatile component in grapefruit juice) or α-pinene can react with hydrogen sulfide to produce 1-*p*-menthene-8-thiol (*20*). Thus, 1-*p*-menthene-8-thiol (**28**) may be a reaction product, which would be observed only in juices that had experienced significant heating. It is also worth noting that this compound was originally identified in canned grapefruit juice (*10*), which is typically a thermally abused product. Most of the other sulfur-containing compounds, such as 4-mercapto-4-methyl-2-pentanol (**12**) and 3-mercapto hexyl acetate (**25**), were not observed in the concentrated juice suggesting they might be thermally unstable.

Sweet/Fruity Compounds. β-Damascenone (**33**) is a potent, sweet smelling compound found only in the concentrated juice.

Although originally reported in tobacco and rose oil (*21, 22*), it has since been reported as being an aroma-impact compound in a wide range of fruits. Free β-damascenone is formed from the acid hydrolysis of its glycosylated precursor (*23−25*). As heating should increase the rate of hydrolysis, it is not surprising to find this compound primarily in the heated juice.

Two odorants, ethyl-2-methylpropanoate (**1**) and γ-decalactone (**35**), were severely impacted from thermal processing. Ethyl-2-methylpropanoate (**1**) was completely absent in the concentrate. This is not surprising given its high volatility. γ-Decalactone (**35**) is a relatively high-boiling compound, thus extensive evaporation losses would not be expected. Since its aroma intensity decreased during concentration, it may also be thermally unstable.

Fresh/Citrusy. Linalool was the only compound of the original group of six that was found in the concentrated sample, suggesting the other five were lost as a result of evaporation or thermal instability. Most of these compounds are relatively low-boiling substances. Thus, octanal (**10**), limonene (**11**), linalool (**16**), and nonanal (**17**) are lost primarily through evaporation. However, linalool can undergo an acid-catalyzed hydration to form α-terpineol (*26*), which did increase in the concentrated juice.
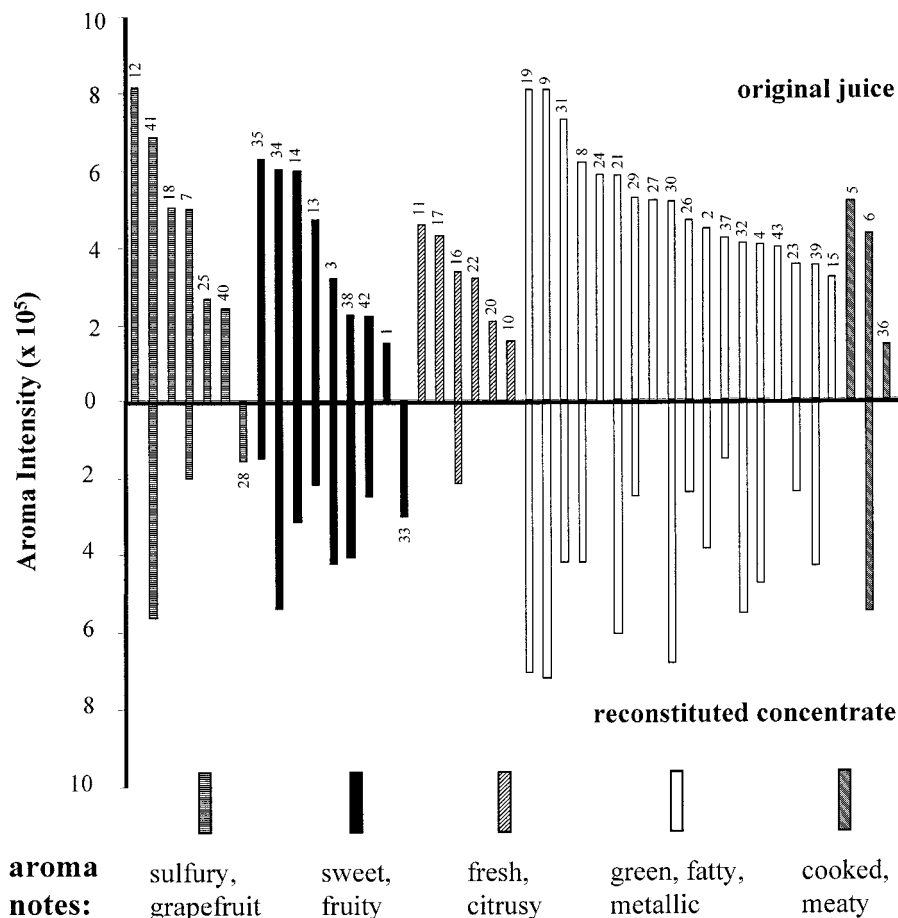
Figure 3. Composite aromagrams of single strength (upper) and unflavored reconstituted (lower) early season white grapefruit juices. Aroma impact compounds are grouped into five aroma catagories: (a) sulfury/grapefruit; (b) sweet/fruity; (c) fresh/citrusy; (d) green/fatty/metallic; and (e) cooked/meaty.

Green/Fatty/Metallic Compounds. The 18 green/fatty/metallic notes observed in **Figure 3** are primarily aldehydes, although four compounds are unidentified. Seven of these compounds were unchanged, four were appreciably diminished, and four were lost completely as a result of thermal concentration. The relative aroma contribution of these compounds is emphasized or "unmasked" during concentration because of the loss of many of the grapefruit character impact compounds in the sulfury/grapefruit and fresh/citrusy categories. In the original juice, the overall sensory impact from the green/fatty/metallic group was more of a secondary contribution, but in the concentrated juice they became the primary aroma-impact group.

Cooked/Meaty Compounds. All three compounds in this group contain sulfur. Methional smells like cooked potato. The increased level of methional in the thermally concentrated juice is probably due to the Strecker degradation of methionine. 2-Methyl-3-furanthiol, and its dimer bis-(2-methyl-3-furyl)-disulfide, were found in the original juice but not in the concentrated juice. Since 2-methyl-3-furanthiol has been observed in fresh orange juice where its concentration increased as the result of thermal concentration (27), it is more likely MFT was lost through evaporation.

This study has shown that the process of making concentrated grapefruit juice removes >90% of the volatiles, but many aroma compounds remain. Not all aroma compounds are affected to the same degree by thermal concentration. Some aroma compounds are lost completely, and a few new ones are produced because of the concentration process. Most of the compounds in the fresh/citrusy and sulfury/grapefruit groups are lost, whereas almost all of the green/fatty/metallic and the

fruit/sweet are retained. In the past, it was assumed that all aroma compounds were lost during thermal concentration. This study has demonstrated that aroma losses are very unequal, and the information should be of value for those attempting to restore the original aroma to grapefruit juice. This work has demonstrated how GC−O can be used to identify which aroma compounds need to be restored and which newly formed compounds may need to be masked. Considering this study involved a single juice, the list of aroma compounds formed or lost should not be considered definitive, but rather as a first approximation. Additional samples need to be analyzed using these same techniques before a definitive list can be generated.

ACKNOWLEDGMENT

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