Comparison of Three Lychee Cultivar Odor Profiles Using Gas Chromatography–Olfactometry and Gas Chromatography–Sulfur Detection

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Odor volatiles in three major lychee cultivars (Mauritius, Brewster, and Hak Ip) were examined using gas chromatography−olfactometry, gas chromatography−mass spectrometry, and gas chromatography−pulsed flame photometric detection. Fifty-nine odor-active compounds were observed including 11 peaks, which were associated with sulfur detector responses. Eight sulfur volatiles were identified as follows: hydrogen sulfide, dimethyl sulfide, diethyl disulfide, 2-acetyl-2-thiazoline, 2-methyl thiazole, 2,4-dithiopentane, dimethyl trisulfide, and methional. Mauritius contained 25% and Brewster contained 81% as much total sulfur volatiles as Hak Ip. Cultivars were evaluated using eight odor attributes: floral, honey, green/woody, tropical fruit, peach/apricot, citrus, cabbage, and garlic. Major odor differences in cabbage and garlic attributes correlated with cultivar sulfur volatile composition. The 24 odor volatiles common to all three cultivars were acetaldehyde, ethanol, ethyl-3-methylbutanoate, diethyl disulfide, 2-methyl thiazole, 1-octen-3-one, *cis*-rose oxide, hexanol, dimethyl trisulfide, α-thujone, methional, 2-ethyl hexanol, citronellal, (*E*)-2-nonenal, linalool, octanol, (*E*,*Z*)-2,6-nonadienal, menthol, 2-acetyl-2-thiazoline, (*E*,*E*)-2,4-nonadienal, β-damascenone, 2-phenylethanol, β-ionone, and 4-vinylguaiacol.

KEYWORDS: ***Litchi chinensis*; subtropical fruits; olfactometry; sulfides; headspace SPME**

INTRODUCTION

Lychee (*Litchi chinensis* Sonn.) is a subtropical fruit native to southern China and is also known as litchi. It is the most commercially significant member of the soapberry family, Sapindaceae. World production of lychee is estimated to be approximately 2.11 million tons, with more than 95% of the world cultivation produced in Asia (*1*). The fruit is found in loose, pendent clusters of 2−10 bright red oblong fruit about 2.5−3 cm wide. Lychee flesh consists of a white, juicy aril (fleshy appendage of the seed coat) surrounding a large brown seed. At full maturity, lychees are covered with a thin, red, leathery peel, which degrades to a dull brown in as little as 3 days after harvest. Typically, lychees are peeled and eaten fresh, but peeled lychees are also commercially canned or frozen.

Lychee flesh is aromatic with a distinctive flavor and consistency whose aroma has been described as "rose- and fruity-floral cherry-like" (*2*). Other investigators (*3*, *4*) have described its odor/aroma as sweet, rose-floral, and citrus-like. Previous studies identified many of the free or neutral volatiles in this fruit (*3*−*6*). Johnston and co-workers (*3*) identified 42 volatiles in freshly macerated lychee from Florida. Subsequent investigators (*5*) identified 75 volatiles in peeled lychee whose source was not identified. Froehlich and Schreier (*6*) identified an additional 34 volatiles in macerated lychee from South Africa. An investigation into bound lychee volatiles (*7*) found that the major bound volatiles consisted primarily of geraniol (73.7%) and geranial (7.95%). Ong and Acree (*4*) observed over 60 aroma-active volatiles in macerated lychees grown in China using gas chromatography−olfactometry (GC-O).

Unfortunately, few prior lychee studies have identified the specific lychee cultivar examined and, in all cases, only examined a single cultivar. There are at least 49 distinct lychee cultivars (*8*) grown throughout the subtropical regions of the world. In the United States, Mauritius is the major commercial cultivar followed by Brewster. Mauritius is one of the three horticulturally distinctive lychee cultivar types and was originally known as Kwai Mi in China. Brewster is a centuries-old

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cultivar known as Chen-Tze or Royal Chen Purple. It has fruit of soft flesh and is slightly more acidic than that of Mauritius (Kwai mi). Hak Ip, or Hei yeh (black leaf), has medium-red fruit with a thin, soft skin. The flesh is occasionally pinkish and is crisp and sweet. These three distinctly different flavored cultivars were imported into Florida sometime between 1903 and 1910 (*9*). In Southeast Asia, the commercial markets value the flavor quality of some cultivars more than others. For example, the Maritius (Kwai Mi) cultivar is highly prized and on average sells for 2.5 times the price of Hak Ip (*10*).

The warm, tropical, fruity flavor of freshly picked lychee is strongly suggestive of sulfur compounds, but few lychee sulfur volatiles have been identified. Johnston and co-workers (*3*) reported finding benzothiazole, which smells like rubber. They reported that "it is well-known by those who consume it that freshly picked litchi is very noticeably sulfurous and that this well recognized characteristic of the fruit rapidly diminishes on standing" and concluded that benzothiazole was not likely responsible for this sulfurous note. Subsequent studies reported finding 3-methylthiopropan-l-ol (methionol), which possesses a cooked potato aroma (*6*), and 2-acetyl-2-thiazoline, which possesses a nutty-woody aroma (*4*). None of the identified sulfur compounds could be responsible for the distinct sulfurous note in fresh lychee.

The goals of this study were to identify which odor components contribute to common lychee odor as well as determine which odor volatiles might be responsible for perceived odor differences between three lychee cultivars. An additional objective was to examine sulfur volatiles in the three lychee cultivars and determine if they might contribute to the overall odor and flavor found in these cultivars.

MATERIALS AND METHODS

Fruit Samples. Lychee cultivars (Mauritius, Brewster, and Hak Ip) were obtained from the Tropical Research and Education Center, University of Florida (Homestead, Florida). They were stored at 5 °C and evaluated within 72 h of being harvested.

Chemicals. Acetone, hexanol, dimethyl trisulfide, neral, geranial, geraniol, and dimethyl trisulfide were purchased from Across Organics. Acetaldehyde, 2-methyl butanal, 3 methyl butanal, ethyl-2-methylbutanoate, hexanal, isoamyl acetate, β-myrcene, diethyl disulfide, acetoin, octanal, 1-octen-3-one, nonanal, 1-octen-3-ol, methional, (*E*)-2-nonenal, (*Z*)-2-nonenal, linalool, octanol, (*E*,*Z*)-2,6-nonadienal, (*E*,*E*)-2,4-nonadienal, phenylacetaldehyde, 3-methyl-butyric acid, 2-acetyl-2-thiazoline, nerol, Furaneol, 4-vinyl-guaiacol, dimethyl sulfide, (*E*)-2-hexenal, *p*-cymene, β-ionone, allyl propyl sulfide, methyl propyl disulfide, and ethyl-2-mercaptopropionate were obtained from Aldrich Chemical Co. β-Damascenone was a gift from Danisco; diallyl sulfide and diallyl disulfide were gifts from Treatt, and neryl acetate was from SunPure. Ethyl-3-methylbutanoate, *cis*-rose oxide, *cis*-thujone (α-trujone), *cis*-linalool oxide, 2-ethyl hexanol, (*Z*)-β-ocimene, menthol, and allyl isothiocyanate were obtained from Fluka. 2-Phenylethanol was purchased from ICN, and allyl methyl trisulfide was from Oxford Chemicals. Citronellal was obtained from the Kodak Chemical Co. Hydrogen sulfide gas obtained from Matheson Gas Products.

Headspace Sampling. Headspace volatiles were extracted and concentrated using SPME headspace sampling of the freshly peeled fruit. Fifteen fruits of each cultivar were blended, and 10 g of puree was added to 40 mL screw cap glass vial Teflon-coated septa, containing a microstir-bar and the headspace purged with nitrogen. The vial containing the sample was placed in a water bath, and after headspace volatiles were equilibrated for 15 min at 35 °C, a SPME fiber (50/30 μm DVD/Carboxen/PDMS on a 2 cm StableFlex fiber, Supelco Bellefonte, PA) was manually inserted into the headspace of the sample and exposed for 45 min. Subsequently, the SPME fiber was thermally desorbed in the GC injector port for 5 min (220 °C).

GC−Flame Ionization Detection (FID)/Olfactometry. Separation was accomplished with a HP-5890 GC (Palo Alto, CA) using either a DB-5 or DB-wax column (30 m × 0.32 mm. i.d. × 0.5 μm, J&W Scientific; Folsom, CA). The column oven temperature (for DB-5) was programmed from 40 to 265 °C (but from 40 to 240 °C for DB-wax) at 7 °C/min with a 5 min hold. Helium was used as the carrier gas at a flow rate of 1.55 mL/min. Injector and detector temperatures were 220 and 290 °C, respectively. A 0.75 mm injector liner was employed to improve the peak shape and chromatographic efficiency. Injections were splitless. The GC column effluent was split between a FID and olfactometer. As previously described (*11*), a time-intensity approach was used to evaluate odor quality and intensity at the sniffing port under GC conditions. Two trained assessors separately evaluated each sample in triplicate, thus producing six individual time-intensity aromagrams in each column. Intensities of odor-active compounds of each GC-O run were normalized so the highest intensity was given a score of 10. Normalized intensities were averaged, provided that a similar odor activity was detected at that retention time in at least half of the panel responses. If the compound was not detected in one run, its value was treated as zero. To make comparisons between odor intensities easier, intensities listed in **Table 1** represent a condensed three point scale, where normalized scores from 1 to 3 were listed as 1, normalized scores from 4 to 7 were given a value of 2, and normalized scores from 8 to 10 were given a value of 3. Chromatograms and aromagrams were recorded and integrated using Chromperfect version 5.0, Justice Laboratory Software (Palo Alto, CA). Initial identification of odor-active components was based on the combination of sensory descriptors and linear retention index (LRI) values on DB-wax and DB-5 columns (C_5-C_{25}). All odor-active compounds were confirmed by comparison with standards on both columns and with GC-MS and/or gas chromatography−sulfur (GC-S).

Mass Spectrometry. GC-MS was employed to confirm the identities of the odor-active volatile identified in the GC-O experiments. SPME volatiles were separated and analyzed using a 60 m × 0.25 mm id carbowax column. Helium was used as the carrier gas at 2 mL/min. The oven temperature program consisted of a linear gradient from 40 to 240 °C at 7 °C/min. The MS was set to scan from *m*/*z* 40 to 300 in the positive ion mode. Chromatographic peaks were identified using NIST 2005. Only those compounds with spectral fit values equal to or greater than 800 were considered positive identifications. Final identification was based on the combination of spectral matches and standardized alkane retention index values (*12*) and odor characteristics. Standards were used to confirm identification, by comparing the resulting fragmentation pattern, retention index value, and odor descriptor (*13*).

Gas Chromatography−Pulsed Flame Photometric Detection (GC-PFPD). Sulfur compounds were separated using a DB-5 column and DB-wax column (30 m × 0.32 mm. i.d. × 0.5 μm, J&W Scientific) with a HP-5890 GC using the same oven temperature program as for the GC-O. The injector temperature was 220 °C. A sulfur-specific PFPD, OI Analytical model 5380 PFPD (OI Analytical Co., College Station, TX), was used to detect sulfur volatiles. The detector temperature was set at 250 °C, and the sulfur gate time was 6−24.9 ms.

Sensory Analysis. Three trained assessors (two females and one male) of the Citrus Research and Education Center (United States) with 50 h of training in descriptive analysis of fruit juices participated in this project. Odor (orthonasal) lexicons were selected from sensory literature (*14*) as well as lychee aroma studies (*2*−*4*). Eight consensus attributes (see **Figure 1**) were scored for each cultivar using a five-point category scale ranging from one (very slight perception) to five (very intense). Samples were randomly taken from the batch of fruits and were served at room temperature on plastic dishes. Each assessor received two fruits (whole fruit, with peel) for the sensory test and mineral water to cleanse the palate between samples. All of the tests were carried out in triplicate.

Identification Procedures. Identifications were based on matching the totality of data from retention index values on polar and nonpolar columns, sensory descriptors, sulfur selective detector (PFPD) response, and MS fragmentation patterns of target substances with those of authentic standards in the author's labs. Those aroma-active compounds, which could meet some but not all of the above criteria, were labeled

Table 1. Lychee Aroma-Active Volatiles for Mauritius (M), Brewster (B), and Hak Ip (H)

	identification[a]	CAS no.	previous reports[b]	sensory description	LRI		cultivars			detection/ identification
					Wax	DB-5	M	B	H	
1	**hydrogen sulfide**[c]	7786-06-4		sulfur, fetid	691	584	0	2	3	LRI, OD, PFPD
2	***acetaldehyde***	75-07-0		solvent like	714	528	2	2	2	LRI, OD, MS
3	**dimethyl sulfide**	75-18-3		cabbage		690	2	0	3	LRI, OD, PFPD, MS
4	**acetone**	67-64-1	*3*	nail polish, solventy	809	716	0	2	2	LRI, OD, MS
5	***ethanol***	64-17-5		ethanol like, fruity	937	579	2	2	2	LRI, OD, MS
6	**2-methyl butanal**	96-17-3		fruity, sweet	961		1	0	0	LRI, OD,MS
7	**3 methyl butanal**	590-86-3	*5*	candy, caramel	974		2	0	0	LRI, OD,MS
8	**ethyl-2-methylbutanoate**	7452-79-1	*4*, *16*	fruity	1041	840	1	3	0	LRI, OD, MS
9	***ethyl-3-methylbutanoate***	108-64-5		fruity	1056	858	2	2	2	LRI, OD, MS
10	unknown			tropical fruit	1072		3	0	0	
11	**hexanal**	66-25-1	*4*, *5*, *16*	green	1088		0	2	0	LRI, OD, MS
12	unknown			nutty roasted	1091		0	3	2	
13	unknown sulfur			burning rubber, garlic	1106	1162	0	3	2	PFPD
14	**isoamyl acetate**	123-92-2	*3–5*, *16*	fruity, banana-like	1143	878	0	1	0	LRI, OD, MS
15	**β-myrcene**	123-35-3	*3*, *5*, *7*	green burning, green	1155	986	2	2	0	LRI, OD, MS
16	***diethyl disulfide***[c]	110-81-6		moldy, sulfur	1215	932	3	2	3	LRI, OD, PFPD
17	**acetoin (3-hydroxy-2-butanone**	513-86-0	*3*, *5*, *7*	sweaty, sour	1231	743	3	0	0	LRI, OD, MS
18	**(*Z*)-β-ocimene**	3338-55-4	*5*, *7*	citrus, minty		1038	1	2	0	LRI, OD, MS
19	***2-methyl thiazole***[c]	3581-87-1		fresh garlic spice	1268	859	3	3	3	LRI, OD, PFPD
20	***p*-cymene**	99-87-6	*3*, *5*, *7*	citrus, green		1024	0	0	1	LRI, OD, MS
21	**2,4-dithiopentane**[c]	4038-08-8		burning tire, cabbage	1290	892	0	3	3	LRI, OD, PFPD, MS
22	**octanal**	124-13-0	*4*, *7*, *16*	fruity, citrus	1295	1002	2	1	0	LRI, OD, MS
23	***1-octen-3-one***	4312-99-6		mushroom	1308	983	2	3	3	LRI, OD, MS
24	***cis-rose oxide***	3033-23-6	*4*, *5*, *7*, *16*	floral, Lychee-like	1358	1157	2	2	3	LRI, OD, MS
25	***hexanol***	111-27-3	*3*, *5*, *7*	green leaf, green- burning	1379		3	3	3	LRI, OD, MS
26	***dimethyl trisulfide***[c]	3658-80-8		cabbage, sulfur	1383	993	2	3	3	LRI, OD, PFPD
27	**nonanal**	124-19-6	*4*, *5*, *7*, *16*	fruity	1398		2	0	2	LRI, OD, MS
28	***α-thujone***	76231-76-0	*3*	woody, earthy, green, burnt	1438	1100	3	3	3	LRI, OD, MS
29	***cis*-linalool oxide**	5989-33-3	*3*, *4*, *16*	floral, green	1451	1214	0	2	3	LRI, OD, MS
30	**1-octen-3-ol**	3391-86-4	*3*, *4*, *16*	mushroom	1459	981	0	2	2	LRI, OD, MS
31	***methional***[c]	3268-49-3		cooked potato	1465	894	3	3	2	LRI, OD, PFPD
32	*2-ethyl hexanol*	104-76-7		minty	1488		2	1	2	LRI, OD, MS
33	***citronellal***	106-23-0	*6*	solvent, lemon	1495		2	2	2	LRI, OD, MS
34	**(*Z*)-2-nonenal**[c]	60784-31-8	*4*, *16*	metallic	1513		2	2	0	LRI, OD
35	**(*E*)*-2-nonenal***	18829-56-6	*4*, *16*	metallic	1544	1166	3	3	2	LRI, OD, MS
36	***linalool***	78-70-6	*3*, *4*, *7*, *16*	floral	1555	1113	3	3	3	LRI, OD, MS
37	***octanol***	111-87-5	*6*	green herbal	1560		2	2	2	LRI, OD, MS
38	***(E,Z)-2,6-nonadienal***	557-48-2	*4*	green	1595		3	3	3	LRI, OD, MS
39	unknown			nutty roasted	1636		0	2	2	
40	**phenylacetaldehyde**	122-78-1		dry rose, floral	1657	1050	0	2	2	LRI, OD, MS
41	unknown sulfur			sulfur, cabbage	1668	1407	0	3	3	PFPD
42	***menthol***	1490-04-6	*3*	minty		1178	2	2	2	LRI, OD, MS
43	**3-methyl-butyric acid**[c]	503-74-2	*7*	sour, sweaty, butyric acid	1679		2	0	0	LRI, OD
44	**neral**	106-26-3	*3*, *7*	lemon, citrus, green	1696	1242	3	0	2	LRI, OD, MS
45	***2-acetyl-2-thiazoline***[c]	29926-41-8	*4*, *16*	dry fruit, nutty	1712		2	3	3	LRI, OD, PFPD
46	**neryl acetate**	141-12-8	*6*	sweet, candy, fruity	1737	1365	2	0	3	LRI, OD, MS
47	**geranial**	141-27-5	*3*	citrus, citric fruit	1747	1290	0	2	3	LRI, OD, MS
48	(***E,E*)-2,4-nonadienal**[c]	5910-87-2		fatty, citrus	1779	1195	2	3	3	LRI, OD
49	**nerol**	106-25-2	*3*, *4*, *16*	sweet, dry fruit	1826	1225	3	2	0	LRI, OD, MS
50	***β-damascenone***	23726-93-4	*4*, *16*	floral, sweet, honey	1834	1391	3	3	2	LRI, OD, MS
51	**geraniol**	106-24-1	*3–5*, *7*, *16*	lemon, citrus	1860		0	3	3	LRI, OD, MS
52	unknown			fatty, sweet	1890		2	0	2	
53	***2-phenylethanol***	60-12-8	*3*, *4*, *7*, *16*	floral, sweet	1924	1120	2	3	2	LRI, OD, MS
54	unknown			green, pungent oil	1942		0	2	2	
55	***β-ionone***	14901-07-6		floral, raspberry		1496	2	2	2	LRI, OD, MS
56	unknown sulfur			cabbage, sulfur	2013	1407	0	0	3	PFPD
57	*unknown*			solventy, fatty	2017		2	3	2	
58	**furaneol**[c]	3658-77-3	*4*, *6*, *16*	caramel	2048		0	0	3	LRI, OD
59	***4-vinyl-guaiacol***[c]	7786-61-0		spice, toast	2212		2	2	3	LRI, OD

[a] Compounds identified in bold font were identified by comparing analytical data of target molecules with reference compounds in the author's lab. Compounds in italics were found in all three cultivars. [b] Numbers in this column indicate reference numbers. [c] Identifications should be considered tentative.

"tentatively identified". Compounds whose data could not be matched with known standards or literature values were labeled "unknown".

RESULTS AND DISCUSSION

Odor Profiles. The comparison of the individual intensities of eight odor characteristics from the three lychee cultivars is shown in **Figure 1**. Eight different odor attributes were identified from sensory descriptive analysis: floral, honey, green/woody, tropical fruit, peach/apricot, citrus, cabbage, and garlic. In comparing all three cultivars as a whole, floral, honey, citrus, and peach were the most intense odor attributes followed by cabbage and garlic. Although the floral, honey, and citrus odors were expected, the garlic and cabbage odor attributes were unanticipated. The garlic odor was most intense for Brewster and Hak Ip and virtually absent in Mauritius. Mauritius had the most intense floral, honey, citrus, and peach/apricot attributes

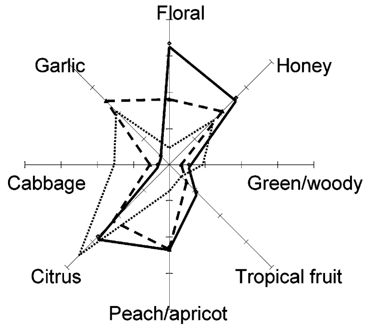

Figure 1. Sensory panel descriptive analysis average scores for three lychee cultivars: Mauritius (solid line), Brewster (dotted line), and Hak Ip (dashed line).

and essentially no garlic or cabbage notes. It also had very low odor intensities for tropical fruit and low green/woody scores. In contrast, Brewster showed the highest citrus and cabbage notes and strong garlic odors. Brewster exhibited weak floral, green/woody, tropical fruit, and peach/apricot odors. Hak Ip possessed a strong garlic odor but weak cabbage notes.

It is worth noting that when NaCl was immediately added to the macerated or freshly peeled fruit to inhibit enzyme reactions, the sulfurous and garlic odors were greatly diminished or absent, suggesting that the garlic odors were enzymatically produced similar to the way they are in fresh garlic. We consciously chose to allow the possibility of enzyme reactions in the sample preparation because this is the way the fresh fruit would be experienced by those consuming it.

Flame Ionization vs Olfaction Responses. A comparison of the FID and olfactory responses from a single SPME headspace sample from Hak Ip is shown in **Figure 2**. It is interesting to note that the FID chromatogram is relatively uncomplicated, with a few large peaks and many minor peaks, whereas the aromagram for this single run has 40 odor-active peaks. Many of the minor FID peaks produced intense odor peaks. Furthermore, several intense odor peaks (e.g., odor peaks 13−15) were observed in regions where little if any FID activity was evident. The major early eluting FID peaks included ethanol and acetaldehyde, which have been previously reported as components associated with ripening in lychee (*15*). Other noteworthy FID peaks observed include hexanal, cis-rose oxide, citronellal, linalool, geraniol, and 2-phenyl ethanol. These volatiles have been reported in at least one of the earlier GC-MS studies (*3*, *5*, *6*). However, compounds that produced small FID peaks without characteristic MS spectra such as (*E*)-2-nonenal and (*E*,*E*)-2,4-decadienal were not reported until GC-O was employed (*4*). Although limonene has been reported to be responsible for the citrus aroma (*3*), it was not listed as having odor activity in the first GC-O lychee study (*4*). As shown in **Figure 2**, a small odor peak was associated with the significant limonene FID peak. The odor of this peak was described as "green", which is not typically associated with limonene.

The odor components responsible for the fruity, honey, floral, garlic, and cabbage sensory attributes were more difficult to measure and identify as they produced little if any corresponding FID response. This suggests that the compounds responsible for these odor attributes are present at trace levels and that they are extremely potent.

Odor-Active Compounds. Fifty-nine odor-active components were observed between all three cultivars although no single cultivar contained more than 48 odor volatiles. LRI values on DB-5 and DB-wax columns along with identifications, odor descriptors (OD), MS, and GC-PFPD responses are presented in **Table 1**. Nine of the 59 volatiles listed in **Table 1** could not be identified. Eleven volatiles, which could not be confirmed by GC-MS, are denoted with footnote *c*, and identifications should be considered tentative. Thirty-four of the 50 identified odor-active compounds have been reported in previous lychee studies. Eleven odor-active peaks seemed to contain sulfur as their odor activity was associated with a sulfur peak from the PFPD.

In this study, 17 odor compounds are reported in freshly peeled lychee for the first time. Seven of these 17 compounds were sulfur compounds. Newly reported nonsulfur compounds shown in **Table 1** include acetaldehyde (**2**), ethanol (**5**), 2-methyl butanal (**6**), ethyl-3-methylbutanoate (**9**), 1-octen-3-one (**23**), 2-ethyl hexanol (**32**), phenylacetaldehyde (**40**), (*E*,*E*)-2,4-nonadienal (**48**), β-ionone (**55**), and 4-vinyl guaiacol (**59**). As indicated in **Table 1**, the identification of most of these compounds was confirmed by GC-MS. However, five nonsulfur volatiles were tentatively identified on the basis of odor descriptor and retention index data only. The matching of retention and sensory characteristics with authentic standards on polar and nonpolar columns supported these tentative identifications.

Earlier GC-MS studies (*3*) suggested that the citrus note in lychee was due to limonene, geranial, and neral, and its floral character was due primarily to 2-phenylethanol and its derivatives. Subsequent GC-MS studies (*5*) added rose oxide, nonanal and decanal, citronellyl and geranyl alcohols, and acetates to the list of compounds, which might be responsible for lychee fruity-floral and citrus notes. A GC-O study (*4*) reported that 2-phenylethanol, *cis*-rose oxide, and phenethyl acetate were responsible for the rose-floral notes and that geraniol contributed to the citrus-fruity odor in lychee.

As seen in **Table 1**, many of the previously reported lychee character impact compounds were observed in this study. Individual volatiles contributing to the floral sensory attribute would include *cis*-rose oxide and 2-phenylethanol as previously reported. However, other volatiles such as linalool, phenylacetaldehyde, *cis*-linalool oxide, and β-ionone would also contribute to the floral perception. In contrast, only a few components directly contribute to the honey odor attribute, but β-damascenone, Furaneol, and nerol are probably major contributors. Green/woody odors are due to volatiles such as hexanal, myrcene, 1-octen-3-one, and (*E*,*Z*)-2,6-nonadienal.

Fruity is a sensory descriptor commonly used in the literature to describe the odor of lychee. However, there exists a wide range of fruity odors, so instead of the general term fruity, specific fruit odors such as tropical fruit, peach/apricot, and citrus fruit odors were observed and scored. Tropical fruit was due to isoamyl acetate and to a potent unidentified volatile (wax LRI 1072). Citrus odor was due, in part, to ocimene, citronellal, neral, geranial, octanal, and nonanal. Both cabbage and garlic odor attributes are associated with sulfur compounds and will be discussed in a separate section.

Sulfur Compounds. Early studies had noted sulfur-like aroma attributes in lychee (*3*, *4*) but only identified a single sulfur volatile in each case. In this study, the PFPD was able to detect 11 sulfur peaks in the three lychee cultivars. Of the 11 compounds, eight were tentatively identified in lychee for the first time, one (2-acetyl-2-thiazoline) was previously reported (*4*), and three could not be identified. Because concentrations of these sulfur volatiles were so low, MS spectral confirmation was generally unobtainable. Tentative identifications were based upon retention time matches and sensory similarities with that of standards on two chromatographic column types (wax and

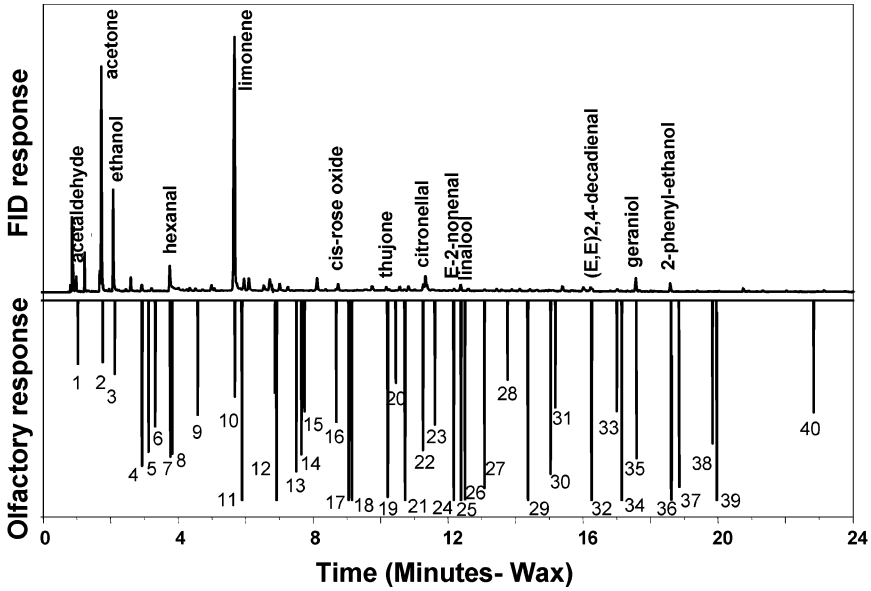

Figure 2. Comparison of FID response and olfactory response for Hak Ip. Olfactory descriptors: 1, solventy; 2, nail polish, solventy; 3, ethanol-like, solventy; 4, fruity; 5, fruity; 6, fruity; 7, green; 8, nutty roasted; 9, banana-like, fruity; 10, green; 11, moldy, sulfur; 12, fresh garlic spice; 13, burning tire, sulfur; 14, fruity, citrus; 15, mushroom; 16, floral; 17, green leaf; 18, cabbage, sulfur; 19, green, earthy; 20, floral, green; 21, cooked potato; 22, solvent, lemon; 23, metallic; 24, metallic; 25, floral; 26, green herbal; 27, green; 28, nutty roasted; 29, sulfur, cabbage; 30, nutty; 31, citrus, minty; 32, green, citrus; 33, sweet dried, fruit; 34, sweet, floral, honey; 35, citrus, lemon; 36, floral, sweet; 37, green, pungent oil; 38, cabbage, sulfur; 39, solvent, fatty; and 40, caramel, toasted.

Table 2. Retention and Sensory Properties of Sulfur Standards Reported to Have Garlic Character Obtained from the Author's Laboratory

LRI			
Wax	DB5	standard	odor description
1099	875	allyl propyl sulfide	alliaceous-like
1148	862	diallyl sulfide	fresh garlic
1238	946	methyl propyl disulfide	roasted garlic
1250	852	2-methylthiazole	roasted garlic
1339	925	ethyl-2-mercaptopropionate	alliaceous-like
1369	892	allyl isothiocyanate	fresh garlic, pungent
1463	1082	diallyl disulfide	fresh garlic
1592	1142	allyl methyl trisulfide	roasted garlic

DB-5). The 11 sulfur compounds are included in **Table 1** and consist of hydrogen sulfide (**1**), dimethyl sulfide (**3**), diethyl disulfide (**16**), 2-methyl thiazole (**19**), 2,4-dithiopentane (**21**), dimethyl trisulfide (**26**), methional (**31**), 2-acetyl-2-thiazoline (**45**), and three unknowns (**13**, **41**, and **56**).

Two peaks in **Table 1** were described as garlic smelling and also produced a sulfur response at the same retention times. Because meaningful MS spectra could not be obtained for these peaks, a series of sulfur standards reported to have garlic sensory attributes were evaluated to identify the two garlic peaks based upon retention and sensory matches. The eight sulfur standards with reported garlic odor are shown in **Table 2** and are presented in terms of increasing retention index values (Wax) with corresponding DB-5 LRI values. The garlic peak at 1106 matches well with allyl propyl sulfide Wax data (LRI 1099) and possessed a similar sensory descriptor, but the corresponding DB-5 is too dissimilar (1162 vs 875 for the standard) to be considered a match. Therefore, this compound (**13**) has been listed as an unknown as there were no other appropriate retention index matches. In a similar fashion, the garlic peak at LRI 1268 matches with both Wax (1268 unknown vs 1250 standard) and DB-5 (859 unknown vs 852 standard) retention characteristics

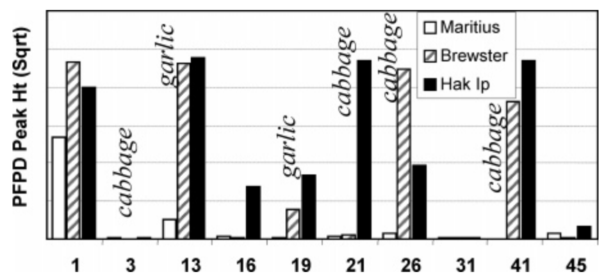

Figure 3. Distribution of sulfur volatiles between the three lychee cultivars. Numbers refer to the identifications in **Table 1**.

of standard 2-methylthiazole; therefore, it has been tentatively identified as 2-methylthiazole.

Five peaks in **Table 1** were reported to smell like cabbage and also produced a sulfur detector response (shown in **Figure 3**). However, only three of them could be tentatively identified from matching sensory and retention characteristics with standards. Three alkyl sulfides were identified as follows: dimethyl sulfide (**3**), diethyl disulfide (**16**), and dimethyl trisulfide (**26**). Two of these, dimethyl sulfide (**3**) and dimethyl trisulfide (**26**), are typically described as possessing cabbage odor attributes. The third cabbage volatile has been identified as 2,4-dithiopentane, which in addition to retention time and sensory matching, was also confirmed from its MS spectrum. Unfortunately, two of the late-eluting cabbage odors peaks could not be identified. The identification of most sulfur volatiles helps explain the cabbage and garlic notes observed in the sensory study.

Similarities and Differences between Cultivars. One of the most striking differences between the cultivars can be seen in the cabbage and garlic sensory attributes shown in the odor profile (**Figure 1**). Brewster exhibited strong garlic and cabbage notes, Hak Ip had strong garlic with moderate to low cabbage odor attributes, whereas Mauritius had weak garlic and weak cabbage notes. To partially explain these observations, the sulfur peak heights (which should be directly proportional to concentration in the square root mode) for 10 of the 11 sulfur volatiles from each cultivar are shown in **Figure 3**. Brewster and Hak Ip contained appreciable amounts of sulfur volatiles whereas Mauritius contained small amounts sulfur volatiles. If all of the sulfur responses for each cultivar are totaled, then Mauritius contained only 25% as much as Hak Ip and Brewster contained 81% as much as Hak Ip.

The two peaks specifically labeled garlic (**13** and **19**) show that Hak Ip contained the highest levels of these compounds. Relative sulfur levels for these volatiles explain why Hak Ip and Brewster exhibited the strongest odor profile responses for the garlic attribute. Conversely, it is worth noting that Mauritius produced small "garlic" peaks and produced weak garlic sensory responses. Hak Ip produced the strongest olfactory response closely followed by Brewster in the odor profile experiments, which corresponds with the PFPD sulfur peak responses shown in **Figure 3**.

Of the three major odor peaks with cabbage attributes, Brewster was only the highest for dimethyl trisulfide (**26**), it had a slightly lower response than Hak Ip for one of the unidentified cabbage peaks (**41**) but essentially no response as compared to Hak Ip for the 2,4-dithiopentane (**21**). A possible explanation would be that although Hak Ip contains approximately 10 times as much 2,4-dithiopentane as Brewster; these compounds may not be as potent as the other cabbage odor compounds. Hydrogen sulfide may also be a component of cabbage odor, and Brewster contains more of this compound than Hak Ip. It should be mentioned that the 11th sulfur volatile (**56**) was cabbage smelling but its sulfur peak heights were so small that they were almost indistinguishable as compared to baseline and thus not graphed.

It would not be unreasonable to assume that the character impact compounds for lychee would be found in the group of 24 volatiles common to all three cultivars. The names of these 24 volatiles have been listed in italics in **Table 1** and include acetaldehyde, ethanol, ethyl-3-methylbutanoate, diethyl disulfide, 2-methyl thiazole, 1-octen-3-one, *cis*-rose oxide, hexanol, dimethyl trisulfide, α-thujone, methional, 2-ethyl hexanol, citronellal, (*E*)-2-nonenal, linalool, octanol, (*E*,*Z*)-2,6-nonadienal, menthol, 2-acetyl-2-thiazoline, (*E*,*E*)-2,4-nonadienal, *β*-damascenone, 2-phenylethanol, *β*-ionone, and 4-vinyl-guaiacol. Twelve of the common 24 volatiles have been previously reported. Compounds such as *cis*-rose oxide, hexanol, citronellal, (*E*)-2-nonenal, linalool, octanol, (*E*,*Z*)-2,6-nonadienal, *β*-damascenone, 2-phenylethanol, 2-acetyl-2-thiazoline, and α-thujone obviously are lychee odor impact compounds. Interestingly, four of the newly reported common lychee volatiles were sulfur compounds such as diethyl disulfide, 2-methyl thiazole, dimethyl trisulfide, and methional and are primarily responsible for the sulfurous character observed but not explained in previous studies.

ABBREVIATIONS USED

GC-O, gas chromatography−olfactometry; GC-PFPD, gas chromatography−pulsed flame photometric detection; LRI, linear retention indices; GC-S, gas chromatography−sulfur.

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