Volatile Components of Calamondin Peel Oil

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Calamondin peel oil extract from two composite peel samples with hexane were each analyzed by gas chromatography−mass spectrometry (GC−MS), and 56 constituents were identified and quantified by GC peak area percent values. All except 5 of these components had been identified previously in citrus juices or oils. Composition of the peel oil components most resembled that reported earlier for kumquat, a member of the *Fortunella* species believed to be one of the parents of calamondin.

Keywords: *Citrus; gas chromatography; mass spectrometry; flavor; peel essential oil*

INTRODUCTION

Calamondin, or calamansi (*Citrus mitis* Blanco), possibly an orangequat from insect cross-pollination of sour loose-skinned mandarin orange and kumquat, is believed to be a hybrid of *Citrus reticulata* Blanco × *Fortunella* spp. It is grown in tropical and subtropical areas including the Philippines, Central America, Japan, China, Hawaii, and Florida (Hodgson, 1967; Morton, 1987; Mabesa, 1990). In the Philippines calamondin is the principal citrus fruit cultivated, where it is used primarily for its juice and as a substitute for lemon (Nisperos et al., 1982).

Studies have been reported on postharvest physiology, handling, and processing of calamondin fruit and on chemical and nutritional changes during processing and storage of juice (Mabesa, 1990; Nisperos et al., 1982; Mendoza and Pantastico, 1979). Volatile flavor constituents of the juice were reported by Mina (1980) and Nisperos-Carriedo et al. (1992), who also determined the sugars and organic acids. A few peel oil components have been previously reported (Anzaldo, 1980; Belingheri et al., 1991). This study was conducted to provide qualitative and quantitative data on the volatile constituents of the essential peel oil of calamondin and, thus, to better understand the flavor of this citrus hybrid.

MATERIALS AND METHODS

Sample Preparation. Calamondin fruit (100 fruit per composite sample) harvested in May 1992 and again in May 1993 from the Citrus Arboretum Division of Plant Industry, Florida Department of Agriculture and Consumer Services, Winter Haven, FL, was the source of the samples analyzed in this study. The thin peel was separated by hand from the fruit. For each sample 200 g of peel was blended for 30−60 s in an explosion-proof blender with 350 mL of HPLC-grade hexane (Wilson et al., 1990). The mixture was allowed to stand for 20 min and filtered through a coarse sintered-glass funnel. The flavedo was stirred with 2 × 250 mL of hexane and refiltered each time, and the combined extracts were dried over sodium sulfate. The dried extract was concentrated using a rotary evaporator at 55 °C under reduced pressure until the solvent was removed (no further weight loss to the residue), leaving the residual extracted peel oil sample.

Gas Chromatography (GC) of Peel Extracts. GC analyses of the extracts from two composite peel oil samples from calamondin were performed using a Hewlett-Packard Model 5880A instrument equipped with a flame ionization detector, a 50 m × 0.32 mm i.d. × 1.0 μm fused silica capillary cross-linked 5% phenylmethyl silicone column (Hewlett-Packard, Avondale, PA), and a capillary inlet system fitted with a split line that allowed the helium carrier gas flow to be split at 100:1. Helium flow through the column was 1.5 mL/min. Injection port and detector temperatures were 275 °C. The column temperature was held at 60 °C for 4 min and then programmed to 200 °C at 6 °C/min and held there for 45 min. The threshold was set at 1, peak width at 0.02, and chart speed at 1 cm/min. Peel oil samples (0.2 μL each) were injected manually. There were no substantial differences in the GC chromatograms of the two samples.

Mass Spectra. Identification of peel oil constituents was made by gas chromatography−mass spectrometry (GC−MS). A Hewlett-Packard Model 5970B, MSD, GC−MS was used with a 50 m × 0.32 mm i.d. × 1.0 μm fused silica column of cross-linked 5% phenylmethyl silicone. The initial oven temperature was held at 55 °C for 9 min and then programmed at 7.5 °C/min to 220 °C and held there for 30 min. Injection port and ionizing source were kept at 250 °C, and the transfer line was kept at 280 °C. Mass units were monitored from 25 to 350 at 70 eV. Mass spectral matches were made by comparison of mass spectra and retention times with those of authentic compounds except for eudesmol, which was identified by a mass spectral match of 98% with the NBS library spectrum.

RESULTS AND DISCUSSION

The peel essential oil in each citrus cultivar contributes to the characteristic flavor of the juice because some oil is introduced into the juice during extraction. Whole calamondin fruit are small enough to be consumed as such in specialty dishes (Morton, 1987). In these uses, the peel oil makes an even greater contribution to calamondin flavor since all of the oil is consumed.

In this study, 56 volatile components in calamondin oil extracted from peel and their relative proportions in extracted peel oil were determined as listed in Table 1. The compounds listed were identified by comparison of mass spectra and GC retention times with those of authentic samples. Only 4 of the 56 components identified had been reported earlier in calamondin peel oil (Anzaldo, 1980), as indicated in Table 1. Seventeen of the components had been reported in calamondin juice, and only 4 of these (limonene, α- and β-pinene, and γ-terpinene) had been found also in peel oil. It is possible that the water-soluble volatile components previously found in juice, acetaldehyde and acetone, were introduced into the peel oil from juice during the oil extraction process. Both of these compounds have been reported in other citrus peel oils, however (Maarse

Table 1. Volatile Components in Calamondin Peel Oil

component	RT[a]	quantity[b]
acetaldehyde[c]	5.1	0.003
acetone[c]	6.0	0.009
heptane[f]	10.7	0.001
3-hexanone[g]	13.5	0.005
2-hexanone	13.7	0.009
octane[f]	13.9	0.02
3-hexen-1-ol[d]	16.4	0.002
thujene[d]	19.5	0.001
α-pinene[c–e]	19.8	0.081
sabinene[d]	21.1	0.096
β-pinene[c–e]	21.3	1.36
myrcene[c,d]	21.4	0.274
octanal[c,d]	21.7	0.136
α-phellandrene[c,d]	22.2	0.05
cis-ocimene	22.4	0.063
limonene[c–e]	23.0	91.264
trans-ocimene[d]	23.3	0.15
2-octenal	23.5	0.01
γ-terpinene[c–e]	23.7	0.001
octanol[d]	23.9	0.149
linalool[c,d]	25.0	0.401
nonanal[c,d]	25.2	0.267
heptyl acetate	25.4	0.01
cis-1,8-p-menthadien-1-ol	26.2	0.016
trans-1,8-p-menthadien-1-ol	26.6	0.016
citronellal[d]	26.7	0.026
2-nonenal[d]	27.0	0.015
decanal[c,d]	28.1	0.294
α-terpineol[c,d]	28.3	0.352
cis-dihydrocarvone[g]	28.5	0.184
methyl salicylate[g]	28.7	0.001
2,4-nonadienal	28.8	0.016
trans-dihydrocarvone[g]	29.0	0.015
verbenone	29.3	0.008
neral[d]	29.7	0.013
nonanoic acid[d]	30.0	0.014
carvone[d]	30.2	0.318
geranial[d]	30.5	0.007
perillaldehyde[c]	30.9	0.006
nonyl acetate[d]	31.3	0.115
undecanal[d]	31.5	0.116
indole	31.7	0.313
2,4-decadienal	32.2	0.007
citronellyl acetate[d]	33.0	0.036
neryl acetate[c,d]	33.2	0.001
neryl propionate[d]	33.5	0.315
geranyl acetate[c,d]	34.1	0.525
decyl acetate[d]	35.0	0.162
dodecanal[d]	35.3	0.107
β-elemene[d]	35.8	0.099
valencene[c,d]	40.9	0.714
dodecanoic acid	42.4	0.023
elemol	44.3	0.298
eudesmol[g]	53.5	0.315
tetradecanoic acid	54.1	0.01
hexadecanoic acid	73.2	0.01

[a] RT, retention time in minutes. [b] Listed as averages of two runs for GC area percent for 1993 oil sample. Some loss of highly volatile compounds may have occurred during solvent removal. [c] Previously reported in calamondin juice (Mina, 1980; Nisperos-Carriedo et al., 1992). [d] Previously reported in kumquat peel oil (Maarse and Visscher, 1989). [e] Previously reported in calamondin peel oil (Anzaldo, 1980). [f] Possible artifact from extraction solvent. [g] Newly reported in citrus.

and Visscher, 1989). All of the compounds in Table 1 have been reported in fruit, and all but five (see footnote *g* of Table 1) have been reported in citrus juice or peel oil (Maarse and Visscher, 1989).

Although calamondin fruit have mandarin-like characteristics, they bear a greater resemblance to the kumquat, which is a member of the *Fortunella* genus (Hodgson, 1967), in fruit size, food uses, and flavor characteristics (sour juice with sweet-flavored peel and fruit often consumed whole). Thus, it is of interest to compare the components of calamondin peel oil with those listed earlier as present in kumquat peel oil (Maarse and Visscher, 1989). Many more components have been reported in kumquat peel oil (142 total) than in calamondin peel oil. Of those reported in kumquat, 33 were found in this study of calamondin.

Many of the 51 compounds listed in Table 1, which are previously identified citrus components, have been discussed earlier for their contributions to specific citrus flavors (Shaw, 1986, 1991). Of the five compounds found earlier in other fruit but not in citrus, Arctander (1969) described the use in synthetic flavors for three of these. Specifically, methyl salicylate is widely used in synthetic fruit flavors because of its "green" flavor note and in other flavors because of its minty flavor properties. Verbenone contributes a spicy-herb or resinlike aroma, and eudesmol contributes sweet-woody and warm notes. There is no one compound that can be considered a "flavor-impact" compound, just as is the case with orange and mandarin flavors (Shaw, 1991). Rather, a mixture of many components in the proper proportion is probably responsible for the characteristic calamondin flavor.

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