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Evaluation of headspace volatiles and sensory characteristics of ripe pawpaws (*Asimina triloba*) from selected cultivars

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Ripe fruit from four pawpaw cultivars (*Asimina triloba*) were analyzed for headspace volatiles and sensory properties. The volatile components of pawpaws were found to be mainly ethyl and methyl esters of fatty acids. Ethyl hexanoate was found to be in the highest concentration (31–65%) in fruit from all cultivars. Other esters found in substantial quantities were ethyl butanoate (3–11%), methyl hexanoate (1–4%), methyl octanoate (2–5%) and ethyl octanoate (4–31%). Fruit from the cultivar containing the highest total volatile concentration (101·8 ppm) and the highest ethyl hexanoate content (65%) had the highest tropical fruit-like aroma intensity.

INTRODUCTION

The pawpaw (*Asimina triloba*) is a member of the Annonaceae family which includes several tropical species such as the cherimoya (*Annona cherimola*) and the custard apple (*Annona squamosa*). Pawpaws are the largest wild fruit that are indigenous to the eastern half of the United States with the exceptions of New England, Florida and the Gulf Coast (Zimmerman, 1941). They are the only temperate zone member of the Annonaceae family (Zimmerman, 1941).

Pawpaws are large oval-to-peanut-shaped thin-skinned berries that range from three to six inches (~7·5–15 cm) in length. The fruit are green when immature, greenish yellow as they ripen and brown after falling from the tree (Bartholomew, 1962). The flesh of pawpaws is easily bruised and extremely perishable when fully ripe because of their thin skin. Pawpaw trees produce low yields of fruit, and the few that are harvested for fresh fruit consumption do not readily withstand transportation or commercial storage (Langworthy & Holmes, 1917). These characteristics have prevented pawpaws from becoming commercially available as a fresh fruit commodity (Peterson *et al.*, 1982). At present, there are no commercial pawpaw varieties or cultivars (Peterson, 1991). However, breeding and domestication studies have been undertaken to evaluate ways of improving problems associated with production of pawpaws such as poor pollination resulting in low yields, large numbers of seeds and thin skins (Sweintek, 1989; Peterson, 1991).

Shiota (1991) reported on the volatile components of pawpaw fruit, and various toxicological investigations on *Asimina* species (Leboeuf *et al.*, 1982) have been reported. Peterson *et al.* (1982) investigated the nutritional properties of pawpaw fruit. Proximate analysis indicated that pawpaws were high in protein, fat, fiber and carbohydrates in comparison to other temperate fruits such as peaches. Fatty acid analysis indicated high levels of linolenic, linoleic and oleic acids (Peterson *et al.*, 1982).

Selection of cultivars exhibiting high intensities of fruit-like flavors and aromas could prove to be beneficial in breeding new pawpaw cultivars that can be commercialized for use in the manufacture of natural tropical fruit flavor extracts or as a fresh fruit commodity. Therefore, the purpose of this study was to investigate the differences in chemical and sensory properties of selected pawpaw cultivars.

MATERIALS AND METHODS

Sample acquisition

Pawpaws were grown at the University of Maryland Wye Research and Education Center (Wye, MD). Each pawpaw tree from the University of Maryland collection was a different cultivar. Ripe pawpaws from four trees representing four different cultivars (designated as 1-59, 3-61, 4-39, and 7-54) were picked during the 1991

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growing season. Eight to eleven fruit ranging from 45 to 95 g were harvested from each cultivar when ripe and immediately analyzed for external skin color and hardness. Samples were then vacuum packaged (Multivac A300 Vacuum Packager, Wolfertschwenden, Germany) in oxygen barrier pouches (3·2 oxygen transmission, Winpak Vak 3-R, 0·08 mil Nylon/2·4 mil EVA copolymer, Holly Sales and Service Inc., Elkridge, MD) and stored at −20°C (±2°C) until further analysis.

Physical and chemical Analysis

Hardness

All fruit samples were analyzed for hardness using an Instron testing machine (Model 1026; Instron Corporation, Canton, MA) equipped with either a 50 kg or 2000 g load cell, depending upon the softness of the fruit. A cross-head speed of 5 cm/min, chart speed of 1 cm/min, and a 12 mm diameter cylindrical probe was employed. Samples were punctured to a 10 mm depth where the skin had been carefully peeled away. At least three fruit from each cultivar were evaluated for hardness, and measurements were taken from three areas of each fruit. Mean values reported for each cultivar represent an average of all replications.

External skin colour

Skin color of the fruit was analyzed by the Spectroguard Color System (Pacific Scientific, Silver Spring, MD) which was calibrated using a white plate (L = 92·3, a = −1·3, b = 0·1). At least three fruit from each cultivar were evaluated for color and Hunter difference values were obtained from three areas of each fruit. Hunter color data were converted to hue angles θ, where $\theta = \tan^{-1}(b/a)$ (Little, 1975). Mean values reported for each cultivar represent an average of all replications.

Soluble solids

Soluble solids content was determined by the AOAC (1980) refractometer method using a temperature-compensated refractometer (Milton Roy Co., Model 4L) operated at 20°C (±0·5°C). Samples of pawpaw fruit pulp were pressed through cheese-cloth to express serum. The soluble solids in the serum were measured as degree Brix. Values reported for each cultivar reflect the mean of two extractions from three fruit.

Lipid

Lipids were extracted from pawpaw cultivars 1-59 and 3-61 using a modified Bligh and Dyer (1959) method. Three-fruit composite samples were employed because of small fruit size and low lipid contents (≤0·5%). Fruit pulp (100 g) was homogenized in a Waring Blendor (Waring Products, New Hartford, CT) with a 2:1 mixture of methanol:chloroform. Diatomaceous earth (20 g) (Sigma Chemical Co., St Louis, MO) and 20 g of anhydrous sodium sulfate (J. T. Baker Inc., Phillipsburg, NJ) were added to the mixture to prevent emulsification (Smith *et al.*, 1964). After filtering the slurry, the remaining filter cake was rewashed with chloroform to remove any residual lipid. After total filtrate volume was recorded, 50 ml aliquots were vacuum-evaporated using a Rotovapor (Model RE-111; Buchi, Flawil, Switzerland). Lipid extracts were immediately removed from the vacuum evaporator, placed in open glass vials, vacuum-packaged in the same oxygen barrier pouches as stated above, and frozen (−20 ± 2°C) until analyzed for fatty acid content.

Fatty acid analysis

The fatty acid profiles of three-fruit composite lipid extracts from cultivars 1-59 and 3-61 were determined as methyl esters of fatty acids from saponified triacylglycerols using the method described by Metcalf and Schmidt (1966). Approximately 150 mg of lipid was saponified using 5 ml anhydrous 1·5N methanolic sodium hydroxide (J. T. Baker, Phillipsburg, NJ) and heated in a 100°C waterbath for 3 min. The mixture was esterified using BF_3 in methanol solution (approximately 50% by weight; Aldrich Chemical Co., Milwaukee, WI).

Methyl esters of fatty acids were separated by injecting a 0·2 μl sample into a gas chromatograph (Hewlett Packard 5890 Series II, Hewlett Packard, Inc., Avondale, PA) operated with a 1:50 split ratio and fitted with a permanently bonded polyethylene glycol-fused silica capillary column (Supelcowax 10; 30 m × 0·32 mm i.d. 0·25 μm film thickness; Supelco, Inc., Bellfonte, PA). Helium was used as the carrier gas at a flow rate of 2 ml/min. An injector temperature of 200°C, a detector temperature of 250°C, and an oven temperature program rate of 195°C (8 min hold) to 240°C at 3°C/min was employed. Identification of fatty acid methyl esters was achieved using positions of eluting methyl ester standards (Supelco, Inc.; Aldrich Chemical Co.) run on the same Supelcowax 10 column using the same program conditions as employed for sample analysis. Peak areas were integrated using a Hewlett Packard computing integrator (HP 3396A, Hewlett Packard, Inc.) and concentrations of each methyl ester were quantified based on the per cent of the total identified fatty acid concentrations of each lipid sample.

Analysis of headspace volatiles

Headspace volatiles of pawpaw fruit were collected onto Tenax GC^R traps using the method outlined by Olafsdottir *et al.* (1985) with modifications. Samples (50 g) of fruit pulp were blended with 200 ml saturated NaCl for 30 s at high speed in a Waring Blendor (Waring Products, New Hartford, CT). Sample slurries were poured into 500 ml flasks along with 200 μl of a 830 ppm ethyl heptanoate (Aldrich Chemical Co.) internal standard. The flasks were fitted with purge heads and headspace volatiles were collected and concentrated by purging agitated samples under a steady stream of nitrogen (300 ml/min) for 2 h at room temperature (21°C) on to Tenax GC^R traps. Tenax GC^R

traps were prepared by packing a pasteur pipet with 0·15 ± 0·02 g of adsorbent. Volatile compounds were eluted from the Tenax GC^R traps using approximately 1 ml of anhydrous diethyl ether (99%+, Aldrich Chemical Co.) and were concentrated under a slow stream of nitrogen to approximately 15 μl prior to gas chromatographic analysis.

Concentrated extracts of headspace volatiles were analyzed using capillary column gas chromatography (GC) for compound quantification. Compound identification was achieved by odor-assessing peak areas from a packed GC column in addition to capillary GC in conjunction with mass spectrometry (GC–MS). Capillary GC separation of volatile compounds was achieved by injecting a 1 μl sample into a gas chromatograph (Hewlett Packard Model HP 5890A Series II) operated with a 1:50 split ratio and equipped with HP-5 (cross-linked 5% phenyl, methyl silicone) 25 m × 0·20 mm × 0·5 μm film thickness capillary column (Hewlett Packard, Sunnyvale, CA). Helium was used as the carrier gas at a flow rate of 1 ml/min. An injector temperature of 200°C, detector temperature of 250°C, and an oven temperature program rate of 50°C (4 min hold) to 250°C at 4°C/min was employed. Chromatographic data were processed using a computing integrator (Hewlett Packard Model HP 3396A).

Ether extracts were odor assessed to identify qualitative characteristics of eluting peaks off a packed column. Odor assessments were achieved using a Varian 3700 gas chromatograph (Varian Associates, Palo Alto, CA) equipped with a variable effluent splitter assembly (SGE, Houston, TX) that was set at 100:1 in favor of the exit port. Packed column separations were carried out with a 3 m × 2 mm i.d. silane-deactivated glass column containing 10% SE-54 on Supelcoport 80/100 (Supelco, Inc.). An injector temperature of 200°C, detector temperature of 250°C, and an oven temperature program rate of 50°C (4 min hold) to 240°C at 4°C/min was employed. Helium was used as the carrier gas at a flow rate of 30 ml/min. The sample size for each injection was approximately 5–8 μl.

Mass spectra were obtained using an Hewlett Packard 5970 mass spectrometer fitted with the same HP-5 column using a temperature program rate of 50°C (4 min hold) to 240°C at 4°C/min. Identification of peaks was achieved by matching electron impact (70/eV) mass spectral data to those of authentic compounds. Coincidence of retention indices of unknown compounds (I_E; Van den Dool & Kratz, 1963) with authentic compounds and odor quality of peak areas were also employed for compound identification. Standard compounds were obtained from either Aldrich Chemical Co. (Milwaukee, WI), or Bedoukian Research, Inc. (Danbury, CT) to confirm retention indices of unknown compounds.

Taste panel procedures

Samples (10 g) of fresh frozen pawpaw pulp were thawed the day of the panel, then placed into three-digit randomly coded glass screw cap vials (3 × 1·5 in or 7·6 × 3·8 cm) and equilibrated to room temperature (21 ± 3°C) until presentation to the panelists.

Sensory analysis testing was conducted in the sensory analysis testing laboratory. Thirty panelists were recruited for each panel session from the students, staff, and faculty. Training procedures for panel members generally followed those described by Meilgaard *et al.* (1991). Prior to sample testing, panelists were familiarized with attribute descriptions, anchor points ranging from imperceptible to very pronounced and instructions relating to the completion of descriptive ballots. Pretests were undertaken with selected pawpaw samples to familiarize panelists with test samples as well as the measurement tool.

Panelists were seated in individual booths equipped with standard indoor fluorescent lighting (400 Lux). Panelists were presented with a tray of three-digit randomly coded pawpaw samples, and a descriptive odor analysis ballot consisting of unmarked seven-point linear scales for each attribute (Meilgaard *et al.*, 1991). Panelists were asked to evaluate each sample for overall fruity aroma, tropical fruit aroma, sweet aroma, green apple aroma, and fermented aroma intensities. The attributes used in the sensory panels to describe pawpaw aroma were determined by a group familiar with pawpaw aroma. Panelists were allowed to choose the order of sampling which randomized sampling order.

Statistical analysis

Chemical and sensory data were statistically analyzed by analysis of variance (ANOVA) using the general linear model (GLM) procedure (SAS Institute Inc., Cary, NC) to accommodate unbalanced data. Least significant difference tests (LSD) at the 0.05 level of significance were used to separate means when significant differences were found (SAS Institute).

RESULTS AND DISCUSSION

Concentrations of volatile esters contributing to pawpaw aroma from selected cultivars

A typical chromatogram illustrating the volatile headspace profile of tree-ripened pawpaw fruit is shown in Fig. 1. The identities of selected compounds that contribute to pawpaw aroma are reported in Table 1. All compounds listed in Table 1 were previously identified by Shiota (1991) when simultaneous distillation–extraction procedures were employed. Concentrations of individual compounds reported in Table 1 for each cultivar were obtained from ripe pawpaws. All fruit were assessed for ripeness based upon their hardness and color values and soluble solids content. Previous work with pawpaw fruit indicated that fruit exhibiting hardness values less than 1·0 kg, color values calculated as hue angle less than 100, and soluble solids contents greater than 20°Brix were ripe (McGrath & Kara-

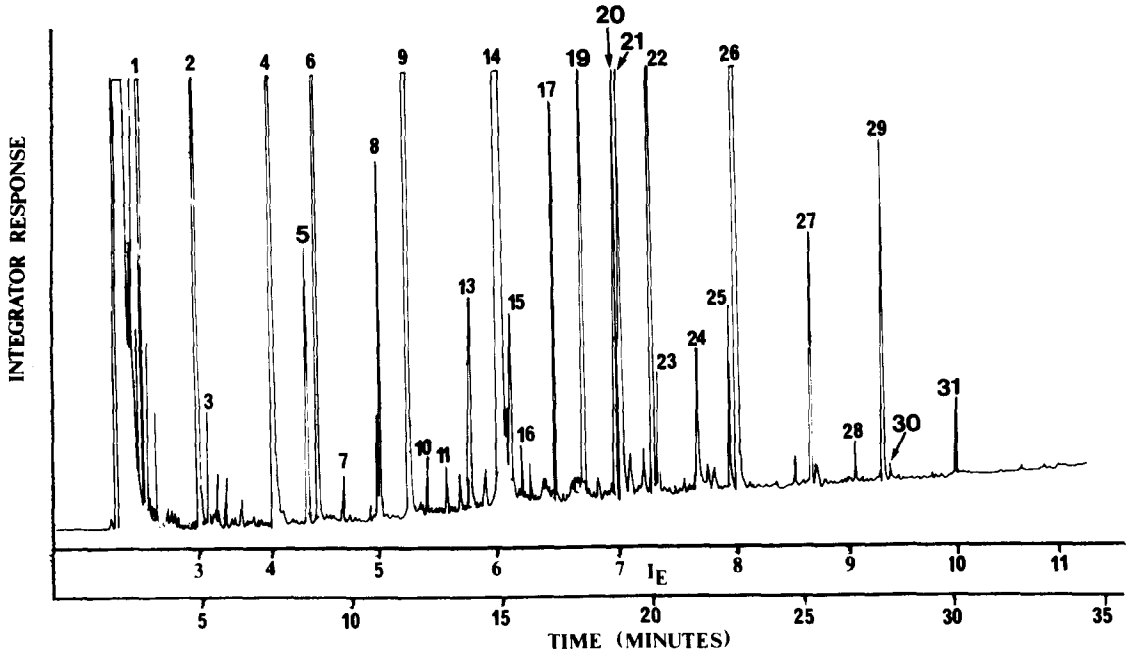

Fig. 1. Capillary gas chromatogram of headspace volatiles from typical tree-ripened pawpaw (*Asimina triloba*) using a fused silica 25 m HP-5 capillary column. The identity of selected peaks are listed in Table 1.

hadian, 1994). All fruit evaluated for this study met these criteria (Table 2).

Headspace volatiles from all pawpaw cultivars contained ethyl esters in highest concentrations with contents ranging over 46·1–90·2% of the total volatile content and ethyl hexanoate ranging over 31·4–65·9% (Table 1). These findings were in agreement with those observed by Shiota (1991) who reported 83·1% of the volatile aroma compounds to be derived from ethyl esters. However, it appeared that large variations existed among cultivars (Table 1). Specific acid precursors involved in ester formation can be derived from either the hydrolysis of short chain fatty acids from triacylglycerols, beta-oxidation of long chain fatty acids or the oxidation of short chain aldehydes that develop during the ripening process (Eriksson, 1975; Buttery,

Table 1. Concentrations of selected headspace volatiles from four cultivars of tree-ripened pawpaw (*Asimina triloba*) fruit

Compound	Peak no.	HP-5 I_E[a]	Cultivar identification				Identification[b]	Odor description[c]
			1-59	4-39	7-54	3-61		
			Concentration[d] (ppb)					
Ethyl acetate	1	2·00	30	61	155	246	a,b,c	Ethereal, fruity, banana-like
Acetoin	2	3·00	1320	140	41	310	a,b,c	Creamy, butter-like
Methyl butanoate	3	3·14	48	50	145	207	a,b,c	Pungent, acrid
Ethyl *n*-butanoate	4	4·00	1560	4455	2499	11 136	a,b,c	Banana, pineapple
Ethyl 2-butenoate	6	4·42	193	748	56	3013	a,b,c	Sour, caramellic, fruity
Methyl hexanoate	9	5·24	—[e]	723	1520	3900	a,b,c	Ether-like, reminiscent of pineapple
Ethyl 3-hydroxy-butanoate	10	5·35	7	65	3	13	a,b	Pleasant, tropical-fruit-like
Ethyl hexanoate	14	6·00	28 990	39 085	11 765	67 056	a,b,c	Powerful, fruity, pineapple, banana
Gamma-Hexalactone	19	6·62	4	7	24	82	a,b	Warm, herbaceous, sweet
Ethyl heptanoate	21	7·00					(Internal standard)	
Methyl octanoate	22	7·28	2280	1275	1945	1907	a,b,c	Power, fruity, orange-like
Ethyl octanoate	26	8·00	6000	23 575	2825	3715	a,b,c	Pleasant, fruity, floral
Methyl decanoate	29	9·30	676	449	544	750	a,b,c	Pleasant, fruity, floral
Methyl geranate	30	9·37	3	5	1	16	a,b	Fresh, green, leafy
Ethyl decanoate	31	10·00	57	33	46	13	a,b	Sweet, brandy-like

[a] Retention indices; Van den Dool & Kratz (1963); HP-5 capillary column.
[b] a, Retention index; b, mass spectrometry; c, odor assessment
[c] Odors described by Fenaroli (1975).
[d] Values reflect the mean of three extractions from each cultivar and are within 20% variance of the mean. Concentration calculated using ethyl heptanoate as the internal standard and assuming a one-to-one recovery of measured compounds compared to the internal standard.
[e] None detected.

Table 2. Physical and chemical properties of tree-ripened pawpaw (*Asimina triloba*) from selected cultivars

Property	Cultivar identification			
	1-59	3-61	4-39	7-54
	Mean values[a]			
Physical:				
hardness (kg)	0·2a	0·2a	0·3a	0·4a
flesh color (hue angle)[b]	75·5a	87·3b	79·9a,b	87·8b
Chemical:				
soluble sugars (°Brix)	21·9a	25·9b	21·2a	21·7a
concentration of total headspace volatiles (ppm)	47·8	101·8	75·4	37·6

[a] Values reflect the mean of at least 2 replicates from at least 3 fruit per cultivar and are within 20% variance of the mean.
[b] Hue angle $\theta = \tan^{-1}(b/a)$; Little (1975).
a,b, Mean values in the same row with different following letters are significantly different ($P < 0.05$).

1981; Tressl *et al.*, 1981). In general, the absence of aldehydes and alcohols in the volatile profile of pawpaw fruit (Table 1) would suggest that the conversion of these compounds to esters is a rapid process. Differences in fatty acid compositions as well as enzymes responsible for these biochemical processes can account in part for the observed differences in ester distribution between cultivars.

Fatty acid profiles of pawpaws previously determined by Peterson *et al.* (1982) quantified concentrations of $C_{14:0}$, $C_{16:0}$, $C_{16:1n7}$, $C_{18:1n9}$, $C_{18:2n6}$, and $C_{18:3n3}$ and reported trace amounts of $C_{8:0}$, $C_{10:0}$, and $C_{12:0}$ from four cultivars. Fatty acid contents of lipids extracted from pawpaws harvested from cultivars 1-59 and 3-61 were determined from capillary gas chromatographic separations (Table 3). In addition to longer chain fatty acids, the data show quantitative amounts of hexanoic, octanoic, decanoic and lauric acids which were not reported earlier. Greater resolution and increased sensitivity of capillary GC analyses compared to packed column GC analyses employed in the earlier study allowed us to develop more quantitative fatty acid data for pawpaws.

Table 3. Fatty acid profiles for two cultivars of tree-ripened pawpaw (*Asimina triloba*) fruit

Fatty acid	Cultivar identification	
	1-59[a]	3-61[b]
	% Total fatty acids[c]	
6:0	4·16 (0·11)[d]	4·72 (1·00)
8:0	21·07 (0·42)	26·85 (1·70)
10:0	1·77 (0·34)	2·48 (0·95)
12:0	1·40 (0·25)	1·80 (0·16)
14:0	6·99 (0·07)	7·34 (1·98)
16:0	13·30 (0·45)	12·21 (0·86)
16:1n7	7·38 (0·18)	8·16 (3·05)
18:0	1·25 (0·06)	1·09 (0·10)
18:1n9	9·23 (0·25)	8·36 (0·57)
18:1n7	11·13 (0·14)	9·97 (0·71)
18:1n5	1·18 (0·10)	0·89 (0·26)
18:2n6	3·86 (0·16)	3·54 (0·28)
18:3n3	7·35 (0·28)	6·91 (1·33)

[a] Mean scores reflect duplicate analyses of a single lipid extract of a three-fruit composite sample.
[b] Mean scores reflect duplicate analyses of duplicate lipid extracts of three-fruit composite samples.
[c] Per cent concentration = peak area/total peak area of identified peaks.
[d] Standard deviations reported in parenthesis.

Although fatty acid data show cultivar 1-59 to be somewhat lower in short and intermediate chain fatty acids and higher in longer chain fatty acids compared to cultivar 3–61 (Table 3), substantial variations within cultivars would suggest that there were no differences between the two profiles. From the data, it appeared that saturated short and intermediate length fatty acids as well as unsaturated longer chain fatty acids could be precursors of volatile ester formation. Elevated concentrations of specific short chain fatty acids found in the total fatty acid profile (Table 3) did not always parallel the relative abundance of their corresponding esters (Table 1). However, total fatty acid data are not always accurate predictors of available free fatty acid precursors. If enzyme-mediated hydrolysis of fatty acids from triacylglycerols were site- or fatty-acid-specific, concentrations of free fatty acids available for esterification reactions would likely differ from that observed in the total fatty acid profile. Further studies to assess the relationship between triacylglycerol composition in relation to enzyme-specific hydrolysis would provide more definitive information as to the mechanism of ester formation in pawpaws.

In addition to variations in total volatile and ethyl hexanoate content, concentrations of other fruit-like esters found in relatively high concentrations also varied among cultivars (Table 1). These compounds included methyl butanoate, ethyl butanoate, ethyl 2-butanoate, methyl hexanoate, methyl octanoate, ethyl octanoate, and methyl decanoate (Table 1). When the relative abundance of these esters were compared in fruits from the four sampled cultivars, a notable difference was observed. Higher concentrations of ethyl octanoate were observed in fruit from cultivars 1-59, 4-39, and 7-54 as compared to ethyl butanoate. Fruit from cultivar 3-61 had substantially higher concentrations of ethyl

Table 4. Mean scores for the descriptive sensory analysis of tree-ripened pawpaw (*Asimina triloba*) fruit from four selected cultivars

Cultivar identity	Sensory attributes of pawpaws				
	Fruity[a] aroma intensity	Tropical[a] aroma intensity	Sweet[b] intensity	Green-apple[a] aroma intensity	Fermented[a] aroma intensity
	Mean scores[c]				
Session I					
1-59	3·84a[d]	3·54a	3·64a	3·38a	3·89a
4-39	3·46a	3·24a	3·05a	3·06a	3·83a
7-54	4·55b	4·68b	4·83b	4·32b	3·36a
LSD	0·59	0·62	0·60	0·67	NS
Session II					
3-61	4·84a	4·80a	4·25a	3·83a	3·58a
1-59	3·91b	3·51b	3·51b	3·04b	3·33a
LSD	0·54	0·55	0·60	0·65	NS

[a] Scale: 1 = imperceptible; 7 = very pronounced.
[b] Scale: 1 = not sweet; 7 = very sweet.
[c] $n = 30$.
[d] a,b, Mean scores in the same column within a session with different following letters are significantly different ($P < 0·05$).

butanoate compared to ethyl octanoate. Although both of these ethyl esters exhibit fruity aroma characteristics, ethyl butanoate appeared to be more reminiscent of tropical fruit aromas such as those of bananas and pineapples (Table 1).

Data from aroma panels show that fruit from cultivar 3-61 exhibited the highest intensity of fruit-related aromas of all cultivars tested (Table 4). Fruit from this cultivar contained the highest concentration of total volatiles (101·8 ppm; Table 2) as well as the highest concentrations of ethyl hexanoate and ethyl butanoate, two potent fruity aroma compounds (Table 1). It would appear that fruit from cultivar 3-61 would be a good tropical fruit flavor source because of its high ester content and intense fruity aroma characteristics (Tables 1 and 4).

When fruit from the other cultivars were evaluated for fruity aromas, it was noted that cultivar 7-54 also appeared to exhibit high fruity aroma intensities. These findings seemed somewhat contradictory because of the relatively low total volatile content measured in the fruit (37·6 ppm; Table 2). Upon evaluating the per cent distribution of some selected esters other than ethyl hexanoate, it was observed that a more equal distribution of esters existed in the volatile headspace of fruit from this cultivar (6·6% ethyl butanoate; 0·4% methyl butanoate; 4·0% methyl hexanoate; 5·2% methyl octanoate; 7·5% ethyl octanoate; Table 1). Since concentrations of ethyl butanoate (2499 ppb), methyl butanoate (145 ppb), methyl hexanoate (1520 ppb), and methyl octanoate (1945 ppb) in cultivar 7-54 (Table 1) were all above their threshold levels (1, 60, 70, 1, and 200 ppb, respectively; Takeoka *et al.*, 1989), the overall blending of compounds could have been perceived as an intense fruity character by panelists (Table 4).

Sensory data indicate that fruit from cultivars 1-59 and 4-39 exhibited lower scores for overall fruity and tropical aroma intensities (Table 4). Although moderate concentrations of total headspace volatiles were observed in cultivars 1-59 and 4-39 (47·8 and 75·4 ppm, respectively; Table 2), the distribution of volatiles from these cultivars reflected lower quantities of ethyl butanoate (3·3 and 5·9%), methyl butanoate (0·01 and 0·07%), and methyl hexanoate (0 and 1·0%) compared to that observed for ethyl octanoate (12·6 and 31·3%; Table 1). Concentrations of methyl butanoate (48 ppb) and methyl hexanoate (none detected) in cultivar 1-59 (Table 1) were below their threshold levels (Takeoka *et al.*, 1989) which would likely lower the overall intensity of fruity aromas (Table 4). The per cent distribution of esters as well as other aroma-contributing compounds appeared to impact for the overall aroma intensity of pawpaw fruit (Table 4).

Many of the esters found in pawpaws that are strong contributors to tropical fruit aromas have also been found in a variety of other tropical and subtropical fruits (Flath & Forrey, 1977; MacLeod & Snyder, 1985; Suarez & Duque, 1992; Umano *et al.*, 1992). Methyl and ethyl esters similar to those found in pawpaws have been identified as important contributors of tropical fruit flavors in pineapples (*Ananas comosus*; Umano *et al.*, 1992), passion fruit (*Passiflora edulis flavicarpa* and *P. edulis sims*; Shibamoto & Tang, 1990), soursop (*Annona muricata*; Young & Paterson, 1990), guava (*Psidium guajava*; Shibamoto & Tang, 1990), papaya (*Carica papaya*; Flath & Forrey, 1977), and lulo fruit (Suarez & Duque, 1992). Since many tropical fruits contain methyl and ethyl esters that are common to pawpaws, the distribution of these fatty acid esters is important in distinguishing between tropical fruit varieties.

Other less-abundant volatiles contributing to pawpaw aromas from selected cultivars

Several other volatile compounds have been found to contribute to pawpaw flavor and aroma. Many lactone

compounds have been characterized as providing creamy, fruity flavors and aromas (Flath & Forrey, 1977; Shibamoto & Tang, 1990; Young & Patterson, 1990; Shiota, 1991). Although concentrations of lactones are much lower in pawpaws compared to the ester component (Table 1), their presence is important in providing the underlying sweet, creamy, aroma and flavor character of this fruit. Fruit from cultivars 3-61 and 7-54 had the highest concentrations of gamma-hexalactone (Table 1). Elevated concentrations of this compound may have contributed to the intensity of fruity aromas in these fruits Table 4).

Although sulfur-containing compounds have not been identified in pawpaws, these compounds are known to contribute to the flavor and aroma of many tropical fruits (Flath & Forrey, 1977; Idstein & Schreier, 1985; Takeoka *et al.*, 1989). Typically, sulfur-containing compounds exhibit very low threshold concentrations. Although they may be difficult to detect analytically, their impact can be very pronounced. Further studies designed to identify low threshold, character-contributing compounds in pawpaws will be necessary to characterize completely this tropical-flavored fruit.

In summary, ethyl hexanoate, methyl hexanoate, ethyl butanoate, methyl butanoate, ethyl octanoate and methyl octanoate appear to be primary esters that contribute to the tropical fruit-like aroma of pawpaws. The presence of elevated levels of short chain fatty acids as well as long chain linoleic and linolenic acids in pawpaw fruit provides the necessary precursors to form these volatile esters. Cultivar 3-61 exhibited the highest intensity of fruit-related aromas and had the highest total volatile concentration. Fruit from cultivar 3-61 also possessed a higher ratio of ethyl butanoate to ethyl octanoate compared to other cultivars. Results from this study would indicate that fruit from cultivar 3-61 would be a good source of tropical fruit flavor because of its high total volatile content and intensity of fruit-like aromas.

It was also noted that fruit from cultivar 7-54 exhibited the lowest total volatile concentration, but scored high for fruity aroma intensity. Upon further examination, it was found that the fruit from this cultivar possessed a more equal distribution of esters compared to cultivars exhibiting lower fruity aroma intensities. Therefore, it would appear that the distribution of esters as well as high concentration of volatiles are both important to the assessment of pawpaw fruit characteristics. These factors should be considered when selecting cultivars for breeding and commercialization of pawpaws.

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