

# Evaluation of Physical, Chemical, and Sensory Properties of Pawpaw Fruit (*Asimina triloba*) as Indicators of Ripeness<sup>†</sup>

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Total headspace volatiles, soluble solids content, fruit hardness, skin color, and sensory attributes were monitored in ripening pawpaw (*Asimina triloba*) fruit. A rapid rise in concentration of volatile headspace compounds was observed when fruit were fully ripe. This coincided with an increase in fruity aroma intensity and soluble solids content and a decrease in hardness and hue angle. Although postharvest mature unripe fruit ripened more rapidly than fruit ripened on the tree, all ripe fruit exhibited soluble solids contents of greater than 20 °Brix, hardness values of less than 1.0 kg, and hue angles of less than 100.

## INTRODUCTION

The pawpaw (*Asimina triloba*) is the largest wild fruit native to North America (Zimmerman, 1941). It grows over most of the eastern half of the United States with the exceptions of New England, Florida, and the Gulf Coast (Thomson, 1974). The pawpaw belongs to the Annonaceae family, which contains over 2000 species, many of which possess edible fruit (Young and Paterson, 1990). Several tropical fruits including the cherimoya (*Annona cherimola*), sweetsop (*Annona squamosa*), soursop (*Annona muricata*), and custard apple (*Annona atemoya*) are all related to the pawpaw; however, the genus *Asimina* to which the pawpaw belongs is the only temperate zone member of this tropical family (Zimmerman, 1941).

Pawpaws can grow in many parts of the United States. It is a lesser known fruit variety among consumers because of its limited supply and highly perishable nature. Typically, each tree produces a limited number of fruit (Peterson, 1991); once picked, its rapid rate of ripening has prevented successful distribution through commercial food chains for fresh-market sales (Peterson, 1991). Although their rapid rate of ripening may prevent pawpaws from being a high-volume fresh-market commercial fruit, its intense natural tropical fruit-like aromas and flavors (Shiota, 1991) make it a potential source of natural fruit flavor.

The fruit itself is a large, thin-skinned berry with two rows of almond-sized seeds. Its shape can vary from oval to oblong to peanut-shaped and can range between 3 and 6 in. in length (Bartholomew, 1962). Because of its desirable tropical fruit-like aromas and flavors (Shiota, 1991), research efforts to domesticate pawpaws have been undertaken (Peterson et al., 1982; Peterson, 1986; Callaway, 1992). Even though some physiological characteristics and genetic information have been obtained (Zimmerman, 1941; Lebouef et al., 1982; Peterson et al., 1982), commercial varieties and cultivars have yet to be developed (Peterson, 1991).

Pawpaws, like many climacteric fruits (Peterson, 1991), undergo a variety of physical and chemical changes after

harvest (Shiota, 1991). Because the stage of fruit ripeness at the time of harvest determines the final quality of ripe fruit (Ben Arie and Lurie, 1986), many studies designed to index ripening parameters have been undertaken for commercial fruit (Wills et al., 1989). It has been well established that many fruit varieties undergo physical changes upon ripening that cause greater perishability and reduced shelf life (Do et al., 1969; Brown, 1987; Chapman et al., 1990).

Researchers have identified indicators of fruit maturity for many commercial varieties. These indicators have been used to determine harvest times of fruit with acceptable flavor characteristics and structural integrity (Wills et al., 1989; Meredith et al., 1989; Robertson et al., 1990a). They have included skin color, fruit firmness, soluble solids content, acid content, and concentration of volatile compounds as well as changes in other chemical constituents (Ben Arie and Lurie, 1986; Chapman et al., 1990, 1991).

Little information is available as to the relationship between changes in physical, chemical, and sensory properties of ripening pawpaws and how these changes can be used to index fruit ripeness. Therefore, this research was undertaken to investigate the relationship between volatile flavor development in tree-ripened and postharvest-ripened mature green pawpaws and changes in soluble solids content, skin color, fruit hardness, and sensory attributes as it relates to fruit ripeness. These parameters were evaluated as to their usefulness as indicators of pawpaw fruit maturity.

## MATERIALS AND METHODS

**Sample Acquisition.** Pawpaw fruit 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. Pawpaw fruit from four different cultivars designated 1-59, 3-61, 4-39, and 7-54 were picked during the 1991 growing season at each stage of ripeness ranging from mature unripe to ripe. The harvested fruit were immediately tested for external skin color, hardness, and moisture content prior to vacuum packaging (Multivac A300 vacuum packager, Wolfertschwenden, Germany) in oxygen barrier pouches (3.2 oxygen transmission, Wipak Vak 3-R, 0.08 mil of nylon/2.4 mil of EVA copolymer, Holly Sales and Service Inc., Elkridge, MD). Vacuum-packaged fruit were stored at  $-20 \pm 2$  °C until further analysis. Laboratory-ripened pawpaws were picked from the same four cultivars during the 1990 growing season at the mature unripe stage and were allowed to ripen on the benchtop

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and open to the air at room temperature ( $21 \pm 3^\circ\text{C}$ ). At 4-day intervals, two to five pawpaws from each group were tested for skin color, hardness, and moisture content. After these analyses were complete, samples were vacuum packaged in the same oxygen-impermeable pouches and frozen at  $-20 \pm 2^\circ\text{C}$  until further analysis.

**Physical and Chemical Analysis. Hardness.** Fruit samples were analyzed for hardness using an Instron Model 1026 testing machine (Instron Corp., Canton, MA) equipped with either a 50-kg or a 2000-g load cell, depending upon the softness of the fruit. A crosshead speed of 5 cm/min, a chart speed of 1 cm/min, and a 12-mm-diameter cylindrical probe were 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 at each sampling interval, and measurements were taken from three areas of each fruit. Values reported for each cultivar reflect the mean of all replicate readings.

**External Skin Color.** 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 at each sampling interval. Hunter difference value readings were taken from three areas of each fruit. Hunter color data were converted to hue angles,  $\theta$ , where  $\theta = \tan^{-1}(b/a)$  (Little, 1975). Mean values reported for each cultivar at each sampling interval represent an average of all replications.

**Soluble Solids.** Soluble solids content was determined according to the AOAC (1980) refractometer method using a temperature-compensated refractometer (Milton Roy Co., Model 4L) operated at  $20 \pm 0.5^\circ\text{C}$ . Samples of pawpaw fruit pulp were pressed through cheesecloth to express serum. The soluble solids in the serum were measured directly as degrees Brix. Values reported for each cultivar at each sampling interval reflect the mean of two extractions from three fruit.

**Protein Analysis.** Protein content was determined according to the Kjeldahl method (AOAC, 1980). Quantification of nitrogen was automatically determined using the Buchi distillation and titration system (Buchi, Flawil, Switzerland). Protein content was determined by multiplying grams of nitrogen by 6.25 (AOAC, 1980). Values reported reflect the mean of three analyses from three cultivars at each stage of ripeness.

**Ash.** Ash was determined using the AOAC (1980) muffle furnace method. About 2 g of dehydrated sample was ashed in a muffle furnace (Lindberg, Model 51894, Watertown, WI) for at least 3 h at  $600^\circ\text{C}$ . Values reported reflect the mean of three analyses from three cultivars at each stage of ripeness.

**Moisture.** Moisture was analyzed using the AOAC (1980) vacuum oven method. Samples were dried for 5 h at  $100^\circ\text{C}$  and at 686 mmHg in a vacuum oven. At least three fruit from each cultivar were evaluated for moisture at each stage of ripeness. Two measurements were obtained from each fruit, and values reported reflect the mean of all replications at each stage of ripeness.

**Lipid.** Lipid content was determined using a modified Bligh and Dyer (1959) method. Composite samples consisting of three fruit from each cultivar were employed because of small fruit size and low lipid contents. One hundred grams of fruit pulp was homogenized in a Waring Blendor (Waring Products, New Hartford, CT) with 300 mL of a 2:1 methanol/chloroform mixture. Twenty grams of diatomaceous earth (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 the slurry was filtered, the remaining filter cake was washed with chloroform to remove any residual lipid. After total filtrate volume was recorded, 50-mL aliquots were vacuum evaporated using a vacuum evaporator (Rotovapor, Model RE-111; Buchi). Lipid contents were calculated on the bases of the amount of starting material. Values reported reflect the mean of three extractions from three cultivars at each stage of ripeness.

**Volatile Headspace Analysis.** Headspace volatiles of pawpaw fruit were collected onto Tenax GC (Alltech Associates, Deerfield, IL) traps using the method outlined by Olafsdottir et al. (1985) with modifications. Fifty-gram samples of fruit pulp were blended with 200 mL of saturated NaCl solution for 30 s at high speed in a Waring Blendor. Sample slurries were poured into

500-mL flasks along with 200  $\mu\text{L}$  of a 830 ppm of ethyl heptanoate (Aldrich Chemical Co., Milwaukee, WI) 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 ( $21^\circ\text{C}$ ) onto Tenax GC traps. Tenax GC traps were prepared by packing a Pasteur pipet with  $0.15 \pm 0.02$  g of adsorbent. Volatile compounds were eluted from the Tenax GC traps using approximately 1 mL of anhydrous diethyl ether (99% up, Aldrich Chemical Co.) and were concentrated under a slow stream of nitrogen to approximately 15  $\mu\text{L}$  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 and sample analysis using capillary GC in conjunction with mass spectrometry (GC-MS). Capillary GC separation of volatile compounds was achieved by injecting a 1- $\mu\text{L}$  sample into a gas chromatograph (Hewlett-Packard Model HP 5890A Series II, Avondale, PA) operated with a 1:50 split ratio and equipped with an HP-5 (cross-linked 5% phenyl methyl silicone; 25 m  $\times$  0.2 mm  $\times$  0.5  $\mu\text{m}$  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  $200^\circ\text{C}$ , a detector temperature of  $250^\circ\text{C}$ , and an oven temperature program of  $50^\circ\text{C}$  (4-min hold) to  $250^\circ\text{C}$  at  $4^\circ\text{C}/\text{min}$  were employed. Data were processed using a Hewlett-Packard 3396A computing integrator.

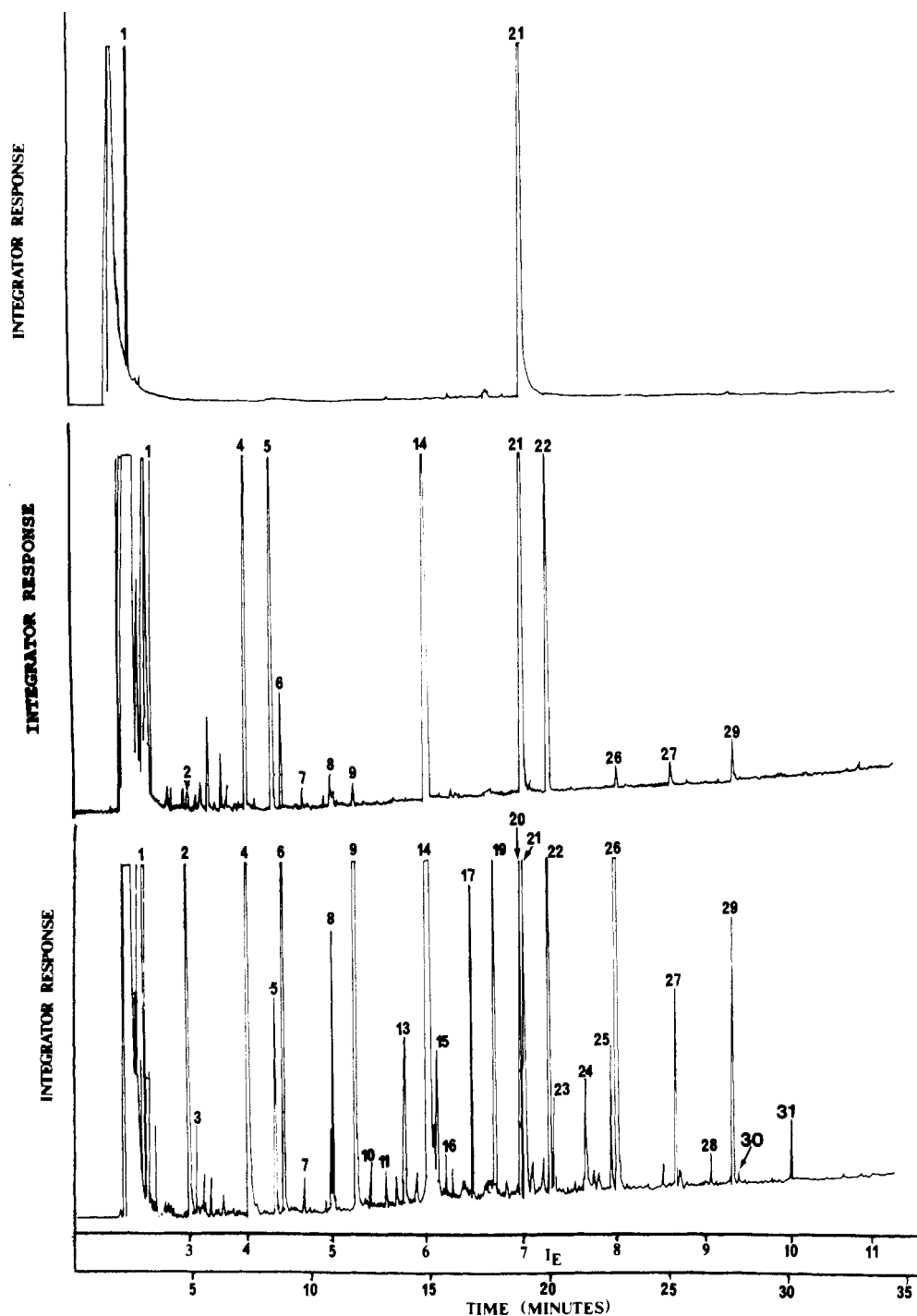
Ether extracts were odor assessed to identify qualitative characteristics of eluting peaks off a packed column. Odor assessments were achieved using a Varian 3700 gas chromatograph (Varian Associates, Palo Alto, CA) equipped with a variable effluent splitter assembly (SGE, Houston, TX) that was set at 100:1 in favor of the exit port. Packed column separations were carried out with a 3 m  $\times$  2 mm i.d. silane-deactivated glass column containing 10% SE-54 on Supelcoport 80/100 (Supelco, Inc., Bellefonte, PA). An injector temperature of  $200^\circ\text{C}$ , a detector temperature of  $250^\circ\text{C}$ , and an oven temperature program of  $50^\circ\text{C}$  (4-min hold) to  $240^\circ\text{C}$  at  $4^\circ\text{C}/\text{min}$  were 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  $\mu\text{L}$ .

Mass spectra were obtained using a Hewlett-Packard 5970 gas chromatograph-mass spectrometer fitted with the same HP-5 column and using a temperature program of  $50^\circ\text{C}$  (4-min hold) to  $240^\circ\text{C}$  at  $4^\circ\text{C}/\text{min}$ . 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 and 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. or Bedoukian Research, Inc. (Danbury, CT) to confirm retention indices of unknown compounds.

**Taste Panel Procedures.** Ten-gram samples of fresh frozen pawpaw pulp were thawed the day of the panel and placed into three-digit randomly coded glass screw-cap vials (3  $\times$  1.5 in.) and equilibrated to room temperature ( $21 \pm 2^\circ\text{C}$ ) until presentation to panelists.

Sensory analysis testing was conducted in the sensory analysis testing laboratory. Thirty-five panelists were recruited for the 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, 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 lx). Once seated, 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, cut grass aroma, sweet aroma, melon-like aroma, and fermented aroma intensities. The attributes



**Figure 1.** Gas chromatograms of headspace volatiles from unripe (top), semiripe (middle), and ripe (bottom) tree-ripened pawpaw fruit (*A. triloba*) using a fused silica 25-m HP-5 capillary column. The identities of selected peaks are listed in Table 1.

used in the sensory panels to describe pawpaw aroma were determined by a group familiar with pawpaw aroma characteristics. 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

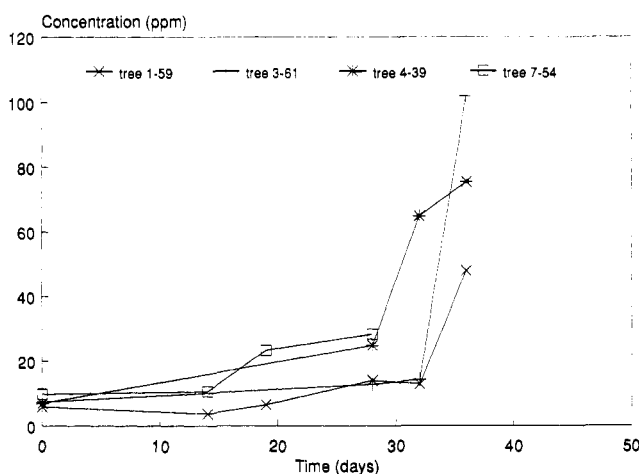
**Concentration of Volatile Headspace Compounds as an Indicator of Ripeness.** Volatile headspace compounds that contribute to the sweet fruity character of

ripe pawpaws develop as a part of the maturation process. Capillary gas chromatograms of volatile headspace compounds isolated from tree-ripened mature unripe, semiripe, and ripe pawpaws are shown in Figure 1. Peak identification and concentrations of selected volatile compounds contributing to the intense fruity character of pawpaw fruits are reported in Table 1. Compounds identified from the headspace of pawpaws in the current study were previously identified by Shiota (1991) when a simultaneous distillation-extraction method was employed. The majority of volatile compounds that contribute to highly intense fruity flavor character are the short-chain methyl and ethyl esters listed in Table 1. Many of these esters are formed through enzymic degradation of fatty acids during the ripening process (Eriksson, 1975; Buttery, 1981;

**Table 1. Concentrations of Selected Headspace Volatiles of Typical Tree-Ripened Pawpaw (*A. triloba*) Fruit<sup>a</sup>**

compound	peak no.	HP-5 $I_R^b$	concn <sup>e</sup> (ppb)				ID <sup>c</sup>	odor descriptor <sup>d</sup>
			0 days from fruit maturity (DFM)	28 DFM	32 DFM	36 DFM		
ethyl acetate	1	2.00	— <sup>f</sup>	72	1265	246	a, b, c	ethereal, fruity, banana-like
acetoin	2	3.00	—	—	36	310	a, b, c	creamy, butter-like
methyl butanoate	3	3.14	—	—	—	207	a, b, c	pungent, acrid
ethyl butanoate	4	4.00	—	9	39	11136	a, b, c	banana, pineapple
ethyl 2-butenate	6	4.42	—	—	5	3013	a, b, c	sour, caramellic, fruity
methyl hexanoate	9	5.24	—	—	91	3900	a, b, c	ether-like, reminiscent of pineapple
ethyl 3-hydroxybutanoate	10	5.35	—	—	—	13	a, b	pleasant tropical fruit-like
ethyl hexanoate	14	6.00	39	42	423	67056	a, b, c	powerful, fruity pineapple, banana
$\gamma$ -hexalactone	19	6.62	—	—	11	82	a, b	warm, herbaceous, sweet
ethyl heptanoate	21	7.00	internal standard					
methyl octanoate	22	7.28	—	68	323	1907	a, b, c	powerful, fruity orange-like
ethyl octanoate	26	8.00	—	7	368	3715	a, b, c	pleasant, fruity, floral
methyl decanoate	29	9.30	—	138	221	750	a, b, c	pleasant, fruity, floral
methyl geranate	30	9.37	—	—	—	16	a, b	fresh, green, leafy
ethyl decanoate	31	10.00	—	—	—	13	a, b	sweet, brandy-like

<sup>a</sup> Samples taken from cultivar 3-61. Values reflect the mean of three extractions from each sampling interval and are within 20% variance of the mean. <sup>b</sup> Retention indices (Van den Dool and Kratz, 1963); HP-5 capillary column. <sup>c</sup> a, retention index; b, mass spectrometry; c, odor assessment. <sup>d</sup> Odors described by Fenaroli (1975). <sup>e</sup> Concentration calculated using ethyl heptanoate as the internal standard and assuming a one-to-one recovery of measured compounds compared to the internal standard. <sup>f</sup> None detected.



**Figure 2.** Changes in total headspace volatile concentrations during tree ripening of pawpaw fruit (*A. triloba*) from four selected pawpaw cultivars.

Tressl et al., 1981). Increasing concentrations of volatile compounds during tree ripening of pawpaw fruit (Table 1) follow the same pattern as that observed for other climacteric fruit such as peaches (Do et al., 1969), papayas (Flath et al., 1990), apples (DePooter and Schamp, 1989), lulo fruit (Suarez and Duque, 1992), pineapples (Umano et al., 1992), and guava (Chyau et al., 1992).

When concentrations of total volatile headspace compounds were monitored for tree-ripened pawpaws over time, it was observed that a slow increase occurred through the preripe stage of fruit maturity for all trees sampled (up to about 28 days of ripening, Figure 2) followed by a burst in the production of headspace volatiles when fruit were fully ripe (between days 32 and 36; Figure 2). The same trend in the production of headspace volatiles was observed when mature unripe pawpaw fruit underwent postharvest ripening in the laboratory. Low concentrations of total headspace volatiles were observed during the mature preripe stage, followed by a substantial increase when fruit were fully ripe. However, compared to tree-ripened fruit, postharvest-ripened fruit showed substantial concentration increases of the same magnitude after only 8–12 days of ripening (data not shown). Therefore, these findings indicate that accelerated ripening, as measured

by the production of total headspace volatiles, occurred in pawpaws after mature unripe fruit were harvested.

The increased volatile concentration in ripe pawpaws was primarily responsible for the differences observed in the aroma properties of unripe, semiripe, and ripe pawpaws when evaluated by a descriptive sensory panel. Ripe samples of pawpaws were observed to be significantly more fruity, sweet, melon-like, and fermented as compared to either the unripe or semiripe samples tested (Table 2).

**Color as an Indicator of Ripeness.** Pawpaws, like other climacteric fruits, undergo a variety of chemical and physical changes during ripening (Marin and Cano, 1992; Chyau et al., 1992; Chapman et al., 1990; Do et al., 1969). The external skin color of pawpaw fruits at various stages of ripeness is reported in Tables 3 and 4 as Hunter  $L, a, b$  values and hue angle,  $\theta$ . In general, all color values as measured by hue angles decreased as ripening progressed, with a faster rate of decline being observed for fruit allowed to ripen after being harvested from the tree (Tables 3 and 4).

Hue angle,  $\theta$  ( $\theta = \tan^{-1} b/a$ ), which is an indicator of color change from green to yellow to red (Little, 1975), has been used to assess fruit ripeness of other climacteric fruits (Flath et al., 1990; Robertson et al., 1990a,b). This value parallels the color change associated with the enzymic degradation of chlorophyll that occurs during ripening (Brady, 1987). At the initial mature green stage of ripeness (day 0), values for hue angle were observed to be at their highest level (109.1–112.1; Tables 3 and 4). As ripening progressed, a decrease in hue angle was observed for fruit from all trees sampled (Tables 3 and 4), with the greatest rate of hue angle change being observed for mature green fruits that were ripened after harvesting (Table 3). Although fruit from each tree ripened at slightly different rates, it was observed that fruit having hue angle values of around 100 or lower typically had high total headspace volatile contents which were indicative of ripe fruit (day 12, Table 3; day 28, Table 4; Figure 2).

Meredith et al. (1989) and Robertson et al. (1990a,b) used Hunter  $L, a, b$  values and hue angle to follow changes in physical and chemical parameters of ripening peaches. Results of those studies indicated that as the fruit ripened, hue angle decreased significantly to a point where the fruit was considered to be ripe. Flath et al. (1990) used Hunter  $b$  values to determine the stage of ripeness of papayas in

**Table 2. Mean Scores ( $n = 35$ ) for the Descriptive Sensory Analysis of Typical Tree-Ripened Unripe, Semiripe, and Ripe Pawpaw (*A. triloba*) Fruit<sup>a</sup>**

stage of ripeness	sensory attributes of pawpaws <sup>b</sup>				
	fruity aroma intensity <sup>c</sup>	cut grass aroma intensity <sup>c</sup>	sweet aroma intensity <sup>d</sup>	melon-like aroma intensity <sup>c</sup>	fermented aroma intensity <sup>c</sup>
unripe	2.53 <sup>a</sup>	3.53 <sup>a</sup>	2.49 <sup>a</sup>	2.64 <sup>a</sup>	2.53 <sup>a</sup>
semiripe	3.15 <sup>b</sup>	3.13 <sup>a</sup>	3.15 <sup>b</sup>	3.25 <sup>a</sup>	2.90 <sup>a</sup>
ripe	5.57 <sup>c</sup>	2.14 <sup>b</sup>	5.12 <sup>c</sup>	4.44 <sup>b</sup>	3.86 <sup>b</sup>
lsd <sup>e</sup>	0.40	0.65	0.55	0.71	0.70

<sup>a</sup> Fruit taken from cultivar 2-47. <sup>b</sup> Mean scores in the same column with different superscripts are significantly different ( $P < 0.05$ ). <sup>c</sup> Scale: 1 = imperceptible; 7 = very pronounced. <sup>d</sup> Scale: 1 = not sweet; 7 = very sweet. <sup>e</sup> lsd, least significant difference.

**Table 3. Mean Hunter  $L, a, b$  Values<sup>a</sup> and Hue Angle ( $\theta$ )<sup>b</sup> for Fruit Skin Color of Laboratory-Ripened Pawpaws (*A. triloba*) from Selected Cultivars Grown at the Wye Research and Education Center during the 1990 Growing Season**

days of storage <sup>c</sup>	cultivar ID	cultivar ID			
		1-59	3-61	4-39	7-54
0	<i>L</i>	60.74	53.69	55.30	53.48
	<i>a</i>	-8.11	-7.80	-7.73	-7.01
	<i>b</i>	23.41	19.43	19.22	20.17
	$\theta$	109.1	111.9	111.9	109.2
4	<i>L</i>	54.46	52.57	55.54	51.17
	<i>a</i>	-6.69	-7.77	-7.10	-4.02
	<i>b</i>	20.43	19.56	19.86	20.17
	$\theta$	108.1	111.7	109.7	101.3
8	<i>L</i>	52.02	55.23	56.43	35.96
	<i>a</i>	0.13	-6.10	-6.56	3.99
	<i>b</i>	20.92	20.04	19.93	8.18
	$\theta$	89.6	106.9	108.2	64.0
12	<i>L</i>	33.23	55.10	48.65	30.02
	<i>a</i>	3.14	-2.96	0.57	2.23
	<i>b</i>	8.09	20.62	17.61	2.09
	$\theta$	68.8	98.2	88.1	43.1
16	<i>L</i>	- <sup>d</sup>	47.21	33.68	-
	<i>a</i>		0.74	2.60	
	<i>b</i>		10.95	3.13	
	$\theta$		86.1	50.3	

<sup>a</sup> Values reflect the mean of three measurements per fruit from at least three fruit at each sampling interval. Values were within 15% variance of the mean. <sup>b</sup> Hue angle ( $\theta$ ) =  $\tan^{-1}(b/a)$ . <sup>c</sup> Initial sample date was Aug 27, 1990. <sup>d</sup> Fruit were not sampled on this day.

a study in which headspace volatiles of ripening fruit were evaluated. Stages of ripeness for experimental papaya samples were determined using colorimetric standards developed by Couey and co-workers (Couey et al., 1984; Couey and Hayes, 1986) for classifying fruit ripeness. It should be noted that the Hunter *b* values reported for ripening papayas increased as ripening progressed, thus indicating a color change from green to yellow. In the current study, Hunter *b* values for ripening pawpaws showed a declining trend as fruits ripened (Tables 3 and 4). This observation may be attributed to the visual color change from green to brownish black as the fruit ripened instead of a yellow color character observed for many other ripening fruits. Therefore, hue angle, which measures more of the overall color character of fruit by taking into account both the green and yellow/red components, appears to be a more useful measure of color change in ripening pawpaws.

**Hardness as an Indicator of Ripeness.** Flesh hardness values for ripening pawpaws are reported in Table 5. Slight variations in initial fruit hardness were reflective of the differences in fruit development from each tree at the beginning of the study. Softening trends were observed for all fruit from all trees ripened either in the laboratory or on the tree (Table 5). The softening rate for laboratory-ripened fruit from all trees occurred within 12 days of harvest. Fruit allowed to ripen on the tree took up to 28

**Table 4. Mean Hunter  $L, a, b$  Values<sup>a</sup> and Hue Angle ( $\theta$ )<sup>b</sup> for Fruit Skin Color of Tree-Ripened Pawpaws (*A. triloba*) from Selected Cultivars Grown at the Wye Research and Education Center during the 1991 Growing Season**

day of sampling <sup>c</sup>	cultivar ID	cultivar ID			
		1-59	3-61	4-39	7-54
0	<i>L</i>	57.36	54.10	55.39	48.76
	<i>a</i>	-8.30	-6.65	-7.13	-6.95
	<i>b</i>	21.80	18.19	17.92	17.14
	$\theta$	110.4	110.1	111.7	112.1
14	<i>L</i>	60.60	- <sup>d</sup>	-	60.42
	<i>a</i>	-8.08			-7.20
	<i>b</i>	22.96			24.23
	$\theta$	109.4			106.5
19	<i>L</i>	59.77	-	-	55.24
	<i>a</i>	-7.09			-4.68
	<i>b</i>	23.92			23.71
	$\theta$	106.5			105.2
28	<i>L</i>	56.61	54.11	58.70	53.32
	<i>a</i>	-0.30	-2.51	-5.03	0.91
	<i>b</i>	24.96	24.32	22.78	22.75
	$\theta$	90.7	95.9	102.6	87.8
32	<i>L</i>	58.48	54.60	50.87	-
	<i>a</i>	-3.42	-3.06	-0.44	
	<i>b</i>	24.56	22.53	19.66	
	$\theta$	97.9	97.7	91.0	
36	<i>L</i>	40.44	52.13	47.86	-
	<i>a</i>	3.83	0.73	3.18	
	<i>b</i>	14.81	20.89	17.96	
	$\theta$	75.5	87.3	79.9	

<sup>a</sup> Values reflect the mean of three measurements per fruit from at least three fruit at each sampling interval. Values were within 10% variance from the mean. <sup>b</sup> Hue angle ( $\theta$ ) =  $\tan^{-1}(b/a)$ . <sup>c</sup> Initial sample date was Aug 2, 1991. <sup>d</sup> Fruit were not sampled on this day.

days to reach the same hardness level (Table 5). Hardness values of fruit ranging from 1 to 3 kg were indicative of preripe fruit, whereas fruit having a hardness value around 0.5 kg were considered to be ripe on the bases of the increased volatile headspace compounds observed in fruit at this hardness stage. It should be noted that decreases in hardness values paralleled declines in hue angle values for each treatment group (Tables 3-5).

Softening of fruit flesh is an integral part of fruit ripening. Activation of hydrolytic enzymes during the ripening process is responsible for breaking down cell walls that result in softening (Brady, 1987). The increased rate of softening of harvested fruit would indicate that the activation of hydrolytic enzymes is related to fruit harvest (Ben Arie and Lurie, 1986). Maturation studies of several other climacteric fruits such as mangoes, peaches, and papayas have utilized hardness and skin color as indices of maturity and ripeness (Marin and Cano, 1992; Robertson et al., 1990a,b; Meredith et al., 1989).

**Soluble Solids Content as an Indicator of Ripeness.** Mean values of soluble solids content from tree-ripened pawpaws are shown in Table 6. Degrees Brix values for

**Table 5. Mean Hardness Values at Various Stages of Pawpaw (*A. triloba*) Ripeness from Selected Cultivars Grown at the Wye Research and Education Center**

day of sampling <sup>a</sup>	fruit hardness <sup>b</sup> (kg)							
	cv. 1-59		cv. 3-61		cv. 4-39		cv. 7-54	
	lab	tree	lab	tree	lab	tree	lab	tree
0	9.7	12.8	22.1	27.0	16.0	21.6	20.9	20.9
4	5.1	— <sup>c</sup>	17.3	—	16.5	—	4.5	—
8	1.0	—	5.5	—	0.3	—	2.7	—
12	0.1	—	2.9	—	0.4	—	0.4	—
14	—	10.9	—	—	—	—	—	4.5
19	—	1.5	—	—	—	—	—	2.7
28	—	0.4	—	0.7	—	0.5	—	0.4
32	—	0.6	—	0.7	—	0.2	—	—
36	—	0.2	—	0.2	—	0.3	—	—
44	—	—	—	—	—	0.5	—	—

<sup>a</sup> Number of days after first sampling of mature unripe fruit for each treatment group (lab, laboratory-ripened fruit; tree, tree-ripened fruit). <sup>b</sup> Values reflect the mean of three measurements per fruit from at least three fruit at each sampling interval. Values were within 10% variance from the mean. <sup>c</sup> Fruit were not sampled on this day.

**Table 6. Mean Values of Percent Soluble Sugars Extracted from Tree-Ripened Pawpaws (*A. triloba*) at Various Stages of Ripeness from Selected Cultivars Grown at the Wye Research and Education Center during the 1991 Growing Season**

day of sampling <sup>a</sup>	°Brix <sup>b</sup>			
	cv. 1-59	cv. 3-61	cv. 4-39	cv. 7-54
0	8.1 <sup>a</sup>	8.4 <sup>a</sup>	7.4 <sup>a</sup>	8.6 <sup>a</sup>
14	7.7 <sup>a</sup>	— <sup>c</sup>	—	13.6 <sup>b</sup>
19	13.4 <sup>b</sup>	—	—	19.8 <sup>c</sup>
28	22.9 <sup>c</sup>	22.5 <sup>b</sup>	20.3 <sup>b</sup>	21.7 <sup>c</sup>
32	20.1 <sup>d</sup>	24.9 <sup>c</sup>	19.0 <sup>c</sup>	—
36	21.9 <sup>c,d</sup>	25.9 <sup>c</sup>	21.2 <sup>b</sup>	—
44	—	—	20.6 <sup>b</sup>	—

<sup>a</sup> Initial sample date Aug 2, 1991. <sup>b</sup> Values reflect the mean of two extractions per fruit from three fruit at each sampling interval. Values were within 10% variance of the mean. Mean values in the same column with different superscripts are significantly different at  $P < 0.05$ . <sup>c</sup> Fruit were not sampled on this day.

ripe pawpaws from all tree cultivars tested (days 28 and above; 20.1–25.9; Table 6) were significantly greater than values observed for unripe fruit (day 0; 7.4–8.6; Table 6). Increases in soluble solids content coincided with the observed increase in volatile headspace compounds and decrease in hardness and hue angle in ripe fruit (Tables 1 and 3–5; Figure 2).

An increase in soluble solids content is typically found in ripening fruit. The degradation of starch during the ripening process to mono- and disaccharides not only provides precursors for the formation of flavor compounds but adds to the sweetness of the edible fruit. Although glucose and fructose are the soluble sugars that are generally present in many ripe fruits, tropical fruits such as bananas, carambolas, and mangoes are known to contain 8–10% sucrose (Wills et al., 1989). Peterson et al. (1982) reported that the soluble sugar content of pawpaws consisted of 6% sucrose, 1.3% fructose, and 1.8% glucose.

Sugar to acid ratios are often used to assess the sweet/tart character of fruit. As this ratio increases, fruit become less tart and more sweet (Potter, 1978). Because most fruit contain substantial acid contents (pH 3.1–4.6; Lakshminarayana, 1980; Bueso, 1980; Sistrunk, 1985), this ratio has been considered as an important index of fruit maturity. Chapman et al. (1990, 1991) evaluated nonvolatile acids and sugars as possible indicators of peach maturity. They concluded that these compounds either singly or in combination could be useful as maturity indicators in peaches.

**Table 7. Proximate Analysis of Tree-Ripened Pawpaws (*A. triloba*)**

stage of ripeness	% composition (as is) <sup>a</sup>				
	moisture <sup>b</sup>	lipid <sup>c</sup>	ash <sup>d</sup>	protein <sup>e</sup>	carbohydrate by difference
unripe	72.7 <sup>a</sup>	0.50 <sup>a</sup>	1.02 <sup>a</sup>	1.21 <sup>a</sup>	24.6
semiripe	76.4 <sup>b</sup>	0.37 <sup>a</sup>	0.93 <sup>a</sup>	0.97 <sup>b</sup>	21.3
ripe	77.0 <sup>b</sup>	0.47 <sup>a</sup>	0.74 <sup>a</sup>	0.81 <sup>b</sup>	20.8

<sup>a</sup> Values reflect the mean of at least three analyses from three cultivars at each stage of ripeness. Mean values in the same column with different superscripts are significantly different at  $P < 0.05$ . <sup>b</sup> Coefficient of variation is 3.4. <sup>c</sup> Coefficient of variation is 17.8. <sup>d</sup> Coefficient of variation is 39.6. <sup>e</sup> Coefficient of variation is 20.6.

In comparison to other fruit, pawpaws exhibit pH values ranging from 5.9 to 6.4. It is likely that low acid contents in ripe pawpaws contribute to their intense sweet aroma and flavor character (Table 2). Since the increase in soluble solids content of pawpaws appears to directly parallel other indices of maturity such as concentration of total volatile headspace compounds, hardness, and hue angle, it appears that this index could also be used to monitor ripeness. The data indicate that degrees Brix values greater than 19–20 would be required to categorize pawpaws as ripe.

Sensory evaluation of pawpaws at various stages of ripeness illustrates the importance of fruit maturity in relationship to aroma and flavor impact (Table 2). Although total volatiles concentration would be the most accurate indicator of flavor and aroma intensity of pawpaws, hardness, color, and soluble solids content could be used as indicators of ripeness for production purposes because of their direct relationship to fruit maturity.

**Changes in Other Chemical Properties.** Proximate compositions of mature unripe, semiripe, and ripe pawpaws are given in Table 7. No significant differences were observed in moisture, lipid, or ash contents for the samples tested. However, the protein content of unripe fruit was seen to be significantly greater than that for either semiripe or ripe fruit (Table 7). Changes in protein content have been observed for other fruits, but these changes have not been shown to be a dependable index of maturity for several fruits including avocados (Biale and Young, 1971) and tomatoes (Sacher, 1973). Although significantly lower protein contents were observed in ripening pawpaws in the current study, conclusive evidence that associates protein content with pawpaw ripening is lacking. Since macronutrients of pawpaw fruits are precursors to flavor compounds, soluble sugars, and acid production, it is likely that some decrease would occur in the overall concentration during ripening. However, the magnitude of the decrease does not appear to be great enough to make a noticeable difference in these parameters.

In summary, the results of this study suggest that changes in hardness, color, soluble solids content, and volatile flavor compounds can be used as indices of pawpaw fruit maturity. Hardness values of less than 1.0 kg, soluble solids content of greater than 20 °Brix, and hue angle values of less than 100 are parameters that typically define a ripe pawpaw containing elevated concentrations of volatile flavor and aroma compounds. Changes in these chemical and physical parameters are consistent with those of other climacteric fruit and can be monitored to assess the maturity of ripening pawpaws.

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