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Evaluation of volatiles from ripening papaya (*Carica papaya* L., var. Maradol roja)

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Abstract

The effect of ripening on the chemical composition of papaya (*Carica papaya* L., var. Maradol roja), especially regarding volatile components, was investigated in four ripening stages. Ripening was characterized sensorily, as well as through physical and chemical analyses. Volatile compounds were isolated by a simultaneous distillation/solvent extraction method. Butanol, 3-methylbutanol, benzyl alcohol and α-terpineol showed maximum concentrations in the third maturation stage, in correspondence with fruit ripeness. Other ripeness indicators could be hardness and soluble solids.

Keywords: Papaya; var. Maradol roja; Ripening; Volatile compounds

1. Introduction

Papaya (*Carica papaya* L.) is native of tropical America, but is currently disseminated throughout the tropics. The Maradol roja variety is well known in Cuba, Mexico, Colombia and neighbouring countries. This variety has a high sugar content and its pulp maintains a firm texture and high resistance to oxidation during ripening.

Several studies have identified fruit maturity indicators for many commercial varieties. These indicators have been used to determine harvest times of fruits (Wills, McGlasson, Graham, Lee, & Hall, 1989; Meredith, Robertson, & Horvat, 1989; Robertson et al., 1990) and include skin colour, hardness, as well as concentration of soluble solids, acid, volatile compounds and other constituents (Ben Arie & Lurie, 1986; Chapman, Horvat, Cavaletto, Nakayama, & Brekke, 1990).

One author (Flath, Light, Tang, Mon, & John, 1990) has extensively investigated the aroma composition of papaya fruits at different ripening stages, but Maradol roja variety has never been studied.

Papaya, like many climacteric fruits, undergoes a variety of physical and chemical changes after harvest (Shiota, 1991). The ripeness stage determines the fruit's final quality, which explains why many studies have attempted to define the ripening parameters for commercial fruit (Peterson, 1990; Wills et al., 1989).

This study examines the relationship between volatile flavour development in four ripening stages and changes in sensory, physical and chemical properties. The parameters were evaluated as to their usefulness as maturity indicators of papaya var. Maradol roja.

2. Materials and methods

2.1. Papaya samples

The study was made with papaya var. Maradol roja, grown in Havana. The fruits were collected at harvest time in the "rayona" phase (appearance of the first yellow stripe). They were ripened at room temperature (mean value: 25.9 °C, with a standard deviation of

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1.0 °C and 87.5% relatively humidity, standard deviation of 3.0%), for a period of four days.

Skin colour was determined in all samples. Experienced judges, for each of four ripening categories, selected three fruits at 0 (10–15% orange–yellow colour of the peel), 48 (60–70% orange–yellow colour of the peel), 72 (100% orange–yellow colour of the peel) and 120 h (more intensity of orange–yellow colour of the peel).

2.2. Physical and chemical analyses

Soluble solids, acid content (citric acid%) and pH were determined according to the AOAC (1980).

Fruit samples were analyzed for hardness using an Instron 1140 testing machine, equipped with a 50 kg load cell, depending on fruit softness. Across head speed was 50 mm/min and a 12 mm diameter cylindrical probe was used. Samples were punctured to 1 cm depth. Three fruits, at each ripening stage, were evaluated for hardness in the central part of the fruit.

2.3. Sensory analyses

Analyses were conducted in the sensory analysis laboratory. Eight assessors were recruited for each panel session. Training procedures followed those described by Stone (1992). Prior to sample testing, panellists were familiarized with attribute descriptions. Panellists were seated in individual booths. They were presented with a tray of 3-digit randomly coded papaya samples and a descriptive-quantitative analysis ballot consisting of an unmarked 10-point linear scale for each attribute. Panellists were asked to evaluate each sample for overall fruity aroma: fruity, resinous, balsamic and seedy; test profile: fruity character, sweetness, hardness, juiciness and internal colour.

2.4. Volatile analyses

200 g of papaya puree (from three fruits at each ripening stage) and 800 ml of distilled water were simultaneously distilled and extracted in 25 ml of diethyl ether for 90 min in a Likens and Nickerson apparatus (Likens & Nickerson, 1964). The condenser was kept at 0–10 °C during this operation. The extracts obtained were dried over anhydrous sodium sulfate, concentrated to 0.1 ml and 2 mg of standard (methyl undecanoate) were added before GC analysis.

The concentrated extracts at four ripening stages were analyzed using capillary column gas chromatography (GC) for quantification of compounds. Capillary GC separation of volatile compounds was achieved by injecting 1 μl of each sample into a KONIK 4000A gas chromatograph operated with a DB-1 (Chrompack) capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as carrier gas at a flow rate of 1 ml/min. Injector temperature was 250 °C, detector temperature, 250 °C and the oven temperature programme featured an initial temperature of 65 °C (2 min hold), rising to 250 °C at 4 °C/min and held isothermal for 20 min. Quantitative data were calculated as area ratios of each compound/standard, from the areas measured electronically.

Mass spectra were obtained using a Hewlett–Packard 5972 gas chromatograph-mass spectrometer. Identification of peaks was achieved by matching electron impact spectra (70 eV) to those of library spectra. The retention indices were determined using a series of n-paraffins (Maljat, Erdos, & Takacs, 1974). The identification of compounds was carried out by comparison of retention indices and mass spectra of standard compounds and also of mass spectra reported in the literature (McLafferty & Stauffer, 1989; Adams, 1995).

Results for each ripening stage were processed by two-way ANOVA and Duncan's multiple range test.

3. Results and discussion

3.1. Volatile changes

Major volatile components typically present in the extract obtained by simultaneous distillation/solvent extraction from a puree of papaya var. Maradol roja, at four ripening stages, are listed in Table 1. Alcohols, such as butanol, 3-methylbutanol, benzyl alcohol and α-terpineol, showed an increase in area ratios at 72 h and diminished thereafter. Other alcohols (linalool and terpinen-4-ol) and dodecanoic acid also increased their ratios at this time and this is maintained up to 120 h. At 72 h the fruit is ready for consumption. These changes could be used as maturity criteria for this fruit.

Benzyl isothiocyanate concentration decreased during ripening, which is in agreement with data reported by Tang (1971). On the other hand, no significant tendency was observed in linalool oxides during ripening.

Esters (e.g., methyl butanoate, ethyl hexanoate and ethyl dodecanoate) increased their concentrations in the fruit during the five days of analysis.

3.2. Sensory changes

The results of sensory analysis are shown in Table 2. Almost all sensory attributes changed during ripening; internal colour, fruity and balsamic odours, fruity taste, juiciness and sweetness increased, while seedy and resinous odours and hardness decreased. Only fruity odour showed significant changes at all ripening stages (linear correlation coefficient: 0.95 for odour vs. time). This fruity odour should be associated with the increase in concentration of esters, which have fruity notes (Arctander, 1969). On the other hand, the increase in balsa-

Table 1
Area ratios of some volatile compounds typically present in papaya var. Maradol roja

Compounds	Area ratios (compound×100/standard)			
	0 (h)	48 (h)	72 (h)	120 (h)
Butanol	0.1 (0.1)a	0.2 (0.1)a	5.0 (1.0)b	1.1 (0.1)c
Methyl butanoate	1.1 (1.2)a	3.9 (0.8)b	1.8 (0.1)a	6.9 (1.6)c
3-Methylbutanol	0.3 (0.5)a	5.3 (1.4)a	23.4 (11.6)b	4.9 (1.8)a
Ethyl hexanoate	0.0 (0.0)a	0.0 (0.0)a	1.5 (0.1)b	3.9 (0.2)c
Benzyl alcohol	0.0 (0.0)a	0.6 (0.1)b	1.9 (0.3)c	1.0 (0.3)b
(Z)-Linalool oxide	0.0 (0.0)a	0.4 (0.2)b	0.2 (0.1)c	0.3 (0.1)bc
(E)-Linalool oxide	0.0 (0.0)a	0.1 (0.1)a	0.4 (0.3)a	0.2 (0.1)a
Linalool	0.0 (0.0)a	0.0 (0.0)a	0.1 (0.1)b	0.2 (0.1)c
Terpinen-4-ol	0.0 (0.0)a	0.1 (0.1)a	0.7 (0.1)b	0.6 (0.2)b
α-Terpineol	0.0 (0.0)a	0.0 (0.0)a	2.4 (1.6)b	0.4 (0.1)a
Benzyl isothiocyanate	6.1 (0.7)a	2.9 (0.3)b	0.9 (0.1)c	0.3 (0.0)c
Ethyl dodecanoate	0.0 (0.0)a	2.9 (1.6)bc	3.9 (2.3)c	0.9 (0.1)b
Dodecanoic acid	0.1 (0.1)a	0.3 (0.1)a	2.9 (0.9)b	2.9 (0.7)b

Different letters in the same row indicate significant differences at $p < 0.05$.
( ): standard deviation of three replicates.

Table 2
Sensory results for papaya var. Maradol roja ($n = 3$)

Attributes	0 (h)	48 (h)	72 (h)	120 (h)
Colour	1.8 (0.1)a	3.7 (0.1)b	5.1 (0.0)c	7.2 (0.2)d
Fruity odour	0.0 (0.0)a	4.6 (0.3)b	6.1 (0.1)c	7.1 (0.0)d
Resinous odour	6.4 (0.4)a	3.6 (0.3)bc	2.2 (0.6)cd	0.8 (0.1)d
Balsamic odour	0.0 (0.0)a	3.8 (0.1)bc	4.9 (0.6)cd	6.6 (0.3)d
Seedy odour	4.1 (0.1)a	3.3 (0.2)ab	2.9 (0.1)ab	0.4 (0.4)c
Fruity taste	0.0 (0.0)a	4.2 (0.3)b	6.5 (0.3)c	8.6 (0.1)d
Sweetness	0.0 (0.0)a	2.3 (0.3)a	4.3 (0.4)b	6.5 (0.4)b
Juiciness	0.0 (0.0)a	3.7 (0.4)b	5.8 (0.1)c	7.6 (0.1)d
Hardness	10.0 (0.0)a	6.4 (0.3)b	5.5 (0.3)c	5.0 (0.1)c

Different letters in the same row indicate significant differences at $p < 0.05$.
( ): standard deviation.

mic odour could be attributed to benzyl alcohol and α-terpineol concentrations during ripening.

3.3. Physical and chemical changes

Table 3 shows the variations of physical and chemical indicators during the four ripening stages. No significant differences were found in pH and acid contents during maturation.

Table 3
Physical and chemical indicators for papaya var. Maradol roja

Mean value	0 (h)	48 (h)	72 (h)	120 (h)
Acid content (%)	0.14 (0.01)a	0.08 (0.02)a	0.07 (0.01)a	0.07 (0.01)a
Soluble solids (Brix)	4.3 (0.8)a	7.9 (0.2)b	8.9 (0.2)c	9.6 (0.01)d
pH	5.5 (0.03)a	5.5 (0.03)a	5.4 (0.02)a	5.5 (0.03)a
Hardness (kg)	16.6 (1.5)a	2.3 (0.4)b	1.9 (0.2)c	1.2 (0.3)c

Different letters in the same row indicate significant differences at $p < 0.05$.
( ): standard deviation.

Soluble solids content varied during maturation, due to starch degradation to mono- and disaccharides, which contribute sweetness to the fruit.

Hardness of the fruit falls substantially and then declines slowly after 72 h, which coincides with the results of sensory analysis. During the ripening process, hydrolytic enzymes are activated, resulting in the breakdown of cell walls and loss of hardness.

In summary, the results of this study suggest that maxima in area ratios of butanol, 3-methylbutanol, benzyl alcohol and α-terpineol at 72 h would be used as ripeness indicators of papaya var. Maradol roja. Other ripeness indicators could be hardness and soluble solids.

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