



Carotenoid and Anthocyanin Contents of Papaya and Pineapple: Influence of Blanching and Predrying Treatments

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ABSTRACT

Effects of blanching and predrying treatments on the stability of carotenoids and anthocyanins in papaya (Carica papaya var Subang) and pineapple (Ananas comosus var Mauritius) were investigated. Carotenoids which are relatively heat-stable showed higher retention than anthocyanins after blanching and drying in both of the fruits. Carotenoids and anthocyanins decreased progressively in pineapple and papaya as the blanching temperature and time increased. Pretreatment with sodium metabisulphite prevented carotenoids from oxidation but caused bleaching of anthocyanins. Orthophosphoric acid, which changed the colour intensity of anthocyanins, showed no effect on carotenoids. Carotenoids were more protected in a system with higher moisture retained by glycerol and sugar. Anthocyanins, however, were stable only within a certain range of moisture contents.

INTRODUCTION

Conventional drying of tropical fruits has not proven successful mainly because retention of their pleasant colour and delicate flavour is rather difficult. The distinctive colour of fruits is due to the natural pigments present such as chlorophylls, carotenoids, anthocyanins and betalaines (Von Elbe, 1987). Therefore, in order to achieve the desirable colour and acceptability of product, an understanding of such pigment stability is essential.

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The stability of pigments in dried fruits is influenced by several predrying treatments. Depending upon the pigment class under study, stability during processing can be a function of blanching temperature, water activity, pH and the presence of pro- or anti-oxidants (Von Elbe, 1987).

Carotenoids have received the most attention because of their nutritional importance (Speck *et al.*, 1988). Both enzymatic and nonenzymatic oxidation of carotenoids with concurrent colour lost is a major problem in dehydrated food (Goldman *et al.*, 1983; Edwards & Lee, 1986). Rhee and Watts (1966) found that bleaching of carotenoids was associated with activity of lipoxygenase enzyme. Carotenoids were found to be most stable at a_w of 0.33 in freeze-dried papaya, and their rate of destruction was higher both below or above this level (Arya *et al.*, 1983).

Anthocyanins are the largest group of water-soluble pigments in fruits. According to Mazza and Brouillard (1987), the colour of anthocyanins is highly pH-dependent due to structural changes. These unstable compounds also change colour during drying and if sulphuring is not employed they become greyish (McBean *et al.*, 1971). Although little information relating a_w and anthocyanin stability is available, relative values reported by Kearsley and Rodriguez (1981) showed that the colour of anthocyanin in a glycerol-water mixture increased as the a_w became lower.

The literature dealing with the effect of blanching and predrying treatments on pigment stability is very limited, partly because the degradation reactions of pigments are poorly understood. The objective of this study was to assess the stability of carotenoid and anthocyanin in papaya and pineapple under various conditions of blanching temperature and time. Effects of sodium metabisulphite, orthophosphoric acid, glycerol and sugar during predrying treatments and after drying were also studied.

MATERIALS AND METHODS

Fruits

Good quality Mauritius pineapple (>8 yellow eyes) and red flesh Subang papaya (skin 50% yellow) were purchased from a local market. The fruits were hand-peeled, trimmed and cut into 0.8 × 0.8 × 0.8 cm cubes. Triplicate samples of 100 g papaya and pineapple cubes were used separately for each of the treatments described below.

Blanching

Papaya and pineapple cubes were blanched for five different durations of time at 70°C, 85°C and 100°C. The blanching times were 4, 6, 8, 10 and

12 min at 70°C, 2, 4, 6, 8 and 10 min at 85°C and 1, 2, 4, 6 and 8 min for 100°C. After blanching, pineapple and papaya cubes were drained and then dried in an oven (Memmert, FRG) at 65°C for 5 and 6 h, respectively. The weights of the fruits were recorded and samples were taken for carotenoid and anthocyanin determination before and after drying.

Predrying treatments

The suitable blanching temperatures (100°C) and times (1 min for pineapple and 4 min for papaya) were chosen from the above experiment. After blanching 100 g of triplicate samples, the fruit cubes were soaked for 20 h in the solutions each containing different types of additives; namely, sugar (20%, 40% and 60%), orthophosphoric acid (pH 2.5, pH 3.5 and pH 4.5), glycerol (10%, 20% and 30%) and sodium metabisulphite (0.2%, 0.4% and 0.6%). Fruit cubes were then drained, weighed, dried and sampled for pigment determination. Duplicate readings of pigment content were obtained from each of the triplicate samples.

Estimation of carotenoids

Total carotenoids from raw, blanched and dried papaya and pineapple were extracted with acetone-hexane (40:60) mixture according to AOAC (1984). Crushed samples (5–10 g) were soaked overnight in the extracting solvent (20 ml). Extraction was performed by successive washing and filtration of the samples until the solvent coming out was clear. Acetone in the extract was washed with saturated NaCl solution. The volume of the hexane layer was made up to 100 ml and the absorbance was measured at 450 nm using a spectrophotometer (Bausch & Lomb, Spectronic 20). Total carotenoids are expressed as β -carotene using $E_{1\text{cm}}^{1\%} 450 = 2500$ (Arya *et al.*, 1979).

Estimation of anthocyanins

Total anthocyanins from raw, blanched and dried papaya and pineapple (5–10 g) were determined by soaking (overnight) the crushed samples in 20 ml of extracting solvent (1% HCl/methanol). Extraction was done by successive washing and filtration of the samples until the solvent coming out was clear (Roggero *et al.*, 1986). The extracts were then made up to 100 ml with extracting solvent and the absorbance was measured at 535 nm using a spectrophotometer (Bausch & Lomb, Spectronic 20). Total anthocyanins are expressed as cyanidin-3-galactoside using $E_{1\text{cm}}^{1\%} 535 = 920$ (Clydesdale & Francis, 1976).

RESULTS AND DISCUSSION

Total carotenoid contents of fresh papaya and pineapple pulps were 106.7 $\mu\text{g/g}$ and 25.2 $\mu\text{g/g}$ dry weight, respectively, and their concentrations decreased progressively with the increase in blanching temperature and duration (Table 1). Several investigations reported changes in carotenoid content during blanching, cooking or heat sterilization. However, according to Singleton *et al.* (1961), the total carotenoid content is unchanged and the colour changes that occur during these processes can be attributed to the isomerization of *trans*-carotenoids to the less intensely coloured *cis*-form. Besides that, the decrease could also be due to the leaching of pigments into the blanching solution (Table 2). Higher blanching temperature and longer duration caused more carotenoids to leach and isomerize, thus reducing the carotenoid retention.

Fresh papaya and pineapple pulps contained 49.8 $\mu\text{g/g}$ and 10.8 $\mu\text{g/g}$ dry weight of anthocyanins, respectively. Anthocyanin retention was found to

TABLE 1
Carotenoid Content of Papaya and Pineapple after Blanching and after Drying

Blanching temperature (°C)	Duration (min)	Carotenoid content ($\mu\text{g/g}$ dry weight)			
		After blanching		After drying	
		Papaya	Pineapple	Papaya	Pineapple
—	0	106.7 ^a	25.2 ^{a1}	99.4 ^{a2}	22.6 ^{a3}
70	4	98.8 ^b	22.7 ^{b1c1}	92.4 ^{b2}	20.9 ^{b3}
	6	95.0 ^c	22.3 ^{b1c1}	90.2 ^{c2}	20.2 ^{c3}
	8	92.8 ^d	21.4 ^{d1}	88.5 ^{e2}	19.4 ^{e3f3}
	10	91.3 ^e	21.2 ^{d1}	87.0 ^{f2}	18.9 ^{g3}
	12	88.5 ^f	20.4 ^{f1}	85.1 ^{h2}	18.5 ^{h3}
85	2	97.4 ^b	22.8 ^{b1}	92.2 ^{b2}	20.9 ^{b3}
	4	95.0 ^c	22.4 ^{b1c1}	91.6 ^{b2}	20.0 ^{b3}
	6	92.8 ^d	21.9 ^{d1}	89.3 ^{d2}	19.9 ^{d3}
	8	91.3 ^e	21.0 ^{d1e1}	87.1 ^{f2}	19.1 ^{g3}
	10	89.6 ^f	20.6 ^{f1}	85.8 ^{h2}	18.7 ^{h3}
100	1	97.2 ^b	22.9 ^{b1}	91.8 ^{b2}	20.9 ^{b3}
	2	96.2 ^{bc}	22.6 ^{b1c1}	91.1 ^{b2c2}	20.4 ^{c3}
	4	95.3 ^c	22.2 ^{c1}	90.7 ^{c2}	20.2 ^{c3}
	6	92.8 ^d	21.6 ^{d1}	88.0 ^{e2}	19.6 ^{e3}
	8	89.5 ^f	20.8 ^{e1f1}	86.2 ^{g2}	19.2 ^{f3g3}

Means in the same column with unlike superscripts indicate significant difference ($p < 0.001$).

TABLE 2
Weight Changes from 100 g of Papaya and Pineapple after Blanching and after Drying

Blanching temperature (°C)	Duration (min)	Weight (g)			
		After blanching		After drying	
		Papaya	Pineapple	Papaya	Pineapple
Control	—	Without blanching		28.9 ^{f2}	25.1 ^{g3}
70	4	84.8 ^c	75.9 ^{b1}	32.8 ^{b2}	30.4 ^{b3}
	6	84.1 ^{cd}	74.5 ^{c1d1}	30.4 ^{d2}	29.1 ^{c3}
	8	83.5 ^d	73.2 ^{e1}	29.9 ^{e2}	27.8 ^{e3}
	10	81.1 ^e	72.9 ^{f1}	28.2 ^{f2}	26.2 ^{f3}
	12	80.3 ^f	70.4 ^{g1}	27.1 ^{g2}	24.7 ^{h3}
85	2	87.8 ^a	76.5 ^{a1}	33.7 ^{b2}	30.8 ^{b3}
	4	84.9 ^c	74.8 ^{c1d1}	32.4 ^{c2}	30.1 ^{c3}
	6	83.8 ^d	73.4 ^{e1}	30.6 ^{d2}	28.5 ^{d3}
	8	83.5 ^d	71.5 ^{f1g1}	29.1 ^{e2}	25.4 ^{g3}
	10	81.2 ^e	70.0 ^{h1}	27.6 ^{g2}	25.3 ^{g3}
100	1	87.6 ^b	76.8 ^{a1}	34.6 ^{a2}	31.5 ^{a3}
	2	87.1 ^b	75.4 ^{b1c1}	33.5 ^{b2}	30.3 ^{b3c3}
	4	84.7 ^c	74.1 ^{d1}	32.9 ^{b2}	29.4 ^{c3}
	6	83.6 ^d	72.2 ^{f1}	30.1 ^{d2}	26.8 ^{f3}
	8	82.2 ^{de}	70.6 ^{g1}	28.3 ^{f2}	24.2 ^{h3}

Means in the same column with unlike superscripts indicate significant difference ($p < 0.001$).

decrease gradually with the increase in blanching temperature and time (Table 3). This could be due to the heat-lability of anthocyanin (Markakis, 1974), as well as the water-soluble anthocyanins which could leach and dissolve into blanching water (Table 2).

After drying, the unblanched papaya and pineapple retained the highest carotenoid and anthocyanin contents (Table 1 and 3) for there were no pigment losses due to blanching. Although blanching period (a few minutes) was very much shorter compared with drying time (a few hours), the amount of pigment lost during blanching was higher than the amount lost during drying (Tables 1 and 3). This indicates that pigment loss due to leaching, where the pigments were liberated from ruptured cells caused by blanching, was greater than the prolonged heating effect of drying.

Pigment retentions of both carotenoids and anthocyanins after blanching or drying were lower in pineapple than papaya, most probably due to its higher weight loss during blanching (Table 2) which could be due to the loss

TABLE 3
Anthocyanin Content of Papaya and Pineapple after Blanching and after Drying

Blanching temperature (°C)	Duration (min)	Anthocyanin content (µg/g dry weight)			
		After blanching		After drying	
		Papaya	Pineapple	Papaya	Pineapple
—	—	49.8 ^a	10.8 ^{a1}	44.2 ^{a2}	9.2 ^{a3}
70	4	39.8 ^b	8.2 ^{b1}	36.8 ^{b2}	7.6 ^{b3}
	6	38.2 ^{bc}	8.1 ^{c1}	35.8 ^{b2c2}	7.4 ^{c3d3}
	8	37.9 ^c	7.8 ^{d1}	34.8 ^{c2}	7.3 ^{c3d3}
	10	37.3 ^c	7.7 ^{d1e1}	34.2 ^{c2d2}	7.1 ^{d3}
	12	36.2 ^{de}	7.5 ^{f1}	33.0 ^{e2}	6.9 ^{e3}
85	2	39.4 ^b	8.1 ^{c1}	37.1 ^{b2}	7.7 ^{b3}
	4	38.7 ^b	8.0 ^{c1}	36.2 ^{b2c2}	7.4 ^{c3d3}
	6	37.3 ^c	7.7 ^{d1e1}	35.6 ^{c2}	7.2 ^{d3}
	8	36.0 ^e	7.5 ^{f1}	34.2 ^{c2d2}	7.0 ^{e3}
	10	35.0 ^f	7.3 ^{g1}	33.7 ^{e2}	6.8 ^{f3}
100	1	39.7 ^b	8.1 ^{c1}	37.2 ^{b2}	7.7 ^{b3}
	2	38.8 ^b	7.9 ^{c1}	36.2 ^{b2c2}	7.5 ^{c3}
	4	37.1 ^c	7.7 ^{d1e1}	35.5 ^{c2}	7.3 ^{c3d3}
	6	36.3 ^d	7.5 ^{f1}	34.1 ^{c2d2}	7.1 ^{d3}
	8	35.2 ^f	7.3 ^{g1}	32.8 ^{e2f2}	6.7 ^{f3}

Means in the same column with unlike superscripts indicate significant difference ($p < 0.001$).

of turgor where cells contract and express some of the cell contents (Selman & Rolfe, 1979). The porous structure of pineapple tissues allows greater diffusion of solutes and pigments out of the damaged cell membranes, compared with the compact tissue structure of papaya.

Blanching temperature and time chosen for pineapple and papaya were 100°C for 1 and 4 min, respectively. These are the blanching times suggested by Soleha *et al.* (1988) for sufficient enzyme inactivation. Although the pigment retention for papaya was not the highest at 4 min, it was still acceptable because there was no appreciable difference from the highest value. Carotenoid and anthocyanin contents varied with predrying treatments given to the fruits (Tables 4 and 5). Sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) imparted some stability to carotenoids but not to anthocyanins. Retention of carotenoids increased slightly as the percentage of $\text{Na}_2\text{S}_2\text{O}_5$ increased. Sulphur dioxide has long been used for its action in inhibiting nonenzymatic and enzymatic browning and some other enzyme-catalyzed

TABLE 4
Carotenoid Content of Papaya and Pineapple after Predrying Treatments and after Drying

Additives	Carotenoid content ($\mu\text{g/g}$ dry weight)			
	After pretreatment		After drying	
	Papaya	Pineapple	Papaya	Pineapple
Distilled water (control)	94.2 ^g	22.4 ^{c1}	87.9 ^{f2}	20.2 ^{f3}
Metabisulphite				
0.2%	96.2 ^d	22.3 ^{c1d1}	92.8 ^{d2}	21.4 ^{b3}
0.4%	97.9 ^b	22.6 ^{b1c1}	93.3 ^{c2}	21.6 ^{a3}
0.6%	98.2 ^a	22.8 ^{b1}	84.3 ^{b2}	21.8 ^{a3}
Orthophosphoric acid				
pH 2.5	95.4 ^f	22.4 ^{c1}	89.7 ^{e2f2}	20.8 ^{d3}
pH 3.5	95.3 ^f	22.4 ^{c1}	89.8 ^{e2f2}	20.8 ^{d3}
pH 4.5	95.4 ^f	22.4 ^{c1}	89.9 ^{e2f2}	20.8 ^{d3}
Sugar				
20%	96.2 ^d	22.8 ^{b1}	90.4 ^{e2}	20.9 ^{c3d1}
40%	96.0 ^e	22.6 ^{b1c1}	89.8 ^{e2f2}	20.7 ^{d3}
60%	96.6 ^c	22.5 ^{b1c1}	98.6 ^{a2}	20.6 ^{e3}
Glycerol				
10%	95.2 ^f	22.4 ^{c1}	88.5 ^{f2}	20.5 ^{e3}
20%	96.6 ^c	22.6 ^{b1c1}	89.7 ^{e2f2}	20.8 ^{d3}
30%	97.7 ^b	23.0 ^{a1}	90.8 ^{d2e2}	21.0 ^{c3}

Means in the same column with unlike superscripts indicate significant difference ($p < 0.001$).

reactions (Rahman & Buckle, 1981). Sulphur dioxide in this experiment prevented carotenoids from oxidation. This effect was more pronounced during drying after which higher contents of carotenoid were retained compared with the other treatments. However, addition of SO_2 resulted in rapid bleaching of anthocyanins. The process was a simple sulfite addition reaction at positions 2 or 4 of the anthocyanin structure, producing compounds which are colourless but quite stable (Clydesdale & Francis, 1976).

Carotenoids were stable to changes in pH for there were no differences in carotenoid contents of pineapple and papaya even though pH changed from 2.5 to 4.5 (Table 4). It has been reported by Kearsley and Rodriguez (1981) that β -carotene was stable in foods over the range pH 2.3–8.0. On the other hand, anthocyanins were sensitive to changes in pH as the amounts of anthocyanin were found to decrease as the pH increased (Table 5). Similar findings were well documented by Kearsley and Rodriguez (1981). According to Chichester (1972), at pH 0.71 anthocyanin is intense red and

TABLE 5
Anthocyanin Content of Papaya and Pineapple after Predrying Treatments and after Drying

Additives	Anthocyanin content ($\mu\text{g/g}$ dry weight)			
	After treatment		After drying	
	Papaya	Pineapple	Papaya	Pineapple
Distilled water (control)	39.2 ^c	8.8 ^{c1}	38.7 ^{b2}	8.1 ^{a3}
Metabisulphite				
0.2%	39.7 ^c	8.5 ^{c1d1}	37.5 ^{d2}	5.8 ^{d3}
0.4%	39.1 ^d	8.2 ^{d1}	37.1 ^{d2e2}	5.5 ^{d3e3}
0.6%	38.9 ^d	7.9 ^{d1}	36.8 ^{e2}	5.0 ^{e3}
Orthophosphoric acid				
pH 2.5	39.5 ^{cd}	8.7 ^{c1}	36.6 ^{e2}	7.3 ^{b3}
pH 3.5	38.7 ^e	8.5 ^{c1d1}	36.4 ^{e2f2}	7.0 ^{c3}
pH 4.5	32.0 ^f	6.3 ^{f1}	30.9 ^{f2}	5.8 ^{d3}
Sugar				
20%	40.3 ^b	8.9 ^{b1}	38.9 ^{a2}	7.1 ^{c3}
40%	40.6 ^a	9.0 ^{b1}	38.5 ^{b2}	7.5 ^{b3}
60%	39.2 ^d	8.6 ^{c1d1}	38.2 ^{c2}	7.2 ^{c3}
Glycerol				
10%	40.1 ^{bc}	9.0 ^{b1}	38.9 ^{a2}	8.1 ^{a3}
20%	40.5 ^a	9.4 ^{a1}	38.5 ^{b2}	7.4 ^{b3}
30%	39.0 ^d	8.1 ^{d1}	37.0 ^{d2e2}	6.0 ^{d3}

Means in the same column with unlike superscripts indicate significant difference ($p < 0.001$).

the pigment is primarily in flavylium cation form. As the pH value rises, the pigment changes to the anhydro-base and then to the carbinol which is a colourless compound.

Both glycerol and sugar are humectants which have been used widely in food to retain their moisture content. It has been reported that the water content of a food exerts a protective effect on the oxidation mode of the carotenoids (Martinez & Labuza, 1968). Higher percentage of glycerol and sugar could have retained more water with lower weight loss (Table 6); thus more carotenoids were protected. In the present study, soaking of pineapple and papaya in glycerol and sugar solution prior to drying significantly reduced the degradation rate of carotenoids.

The concentration of anthocyanins increased slightly as the percentage of glycerol increased from 10% to 20% but dropped again when 30% of glycerol was added (Table 5). Anthocyanin tends to hydrolyze and release its sugar at too high a water content such as in a system with 30% glycerol. According to von Elbe (1987), glycosylation contributed to the stability and

TABLE 6
Weight Changes from 100 g of Papaya and Pineapple after Predrying Treatments and after Drying

<i>Additives</i>	<i>Weight (g)</i>			
	<i>After treatment</i>		<i>After drying</i>	
	<i>Papaya</i>	<i>Pineapple</i>	<i>Papaya</i>	<i>Pineapple</i>
Distilled water (control)	75.6 ^{cd}	73.8 ^{d1}	24.8 ^{h2}	21.2 ^{h3}
Metabisulphite				
0.2%	74.1 ^e	73.0 ^{e1}	25.1 ^{g2}	22.0 ^{g3}
0.4%	74.0 ^e	73.2 ^{e1}	25.0 ^{g2}	22.0 ^{g3}
0.6%	74.2 ^e	73.1 ^{e1}	25.0 ^{g2}	22.3 ^{g3}
Orthophosphoric acid				
pH 2.5	75.2 ^d	75.2 ^{b1}	25.3 ^{f2g2}	22.7 ^{f3}
pH 3.5	75.8 ^{bc}	78.8 ^{a1}	25.2 ^{f2g2}	22.6 ^{f3}
pH 4.5	75.9 ^{bc}	76.0 ^{a1}	25.4 ^{f2}	22.2 ^{g3}
Sugar				
20%	73.2 ^f	72.5 ^{f1}	37.5 ^{b2}	31.3 ^{c3}
40%	72.6 ^g	71.8 ^{g1}	37.8 ^{b2}	32.0 ^{b3}
60%	71.4 ^h	70.3 ^{h1}	39.1 ^{a2}	36.4 ^{a3}
Glycerol				
10%	76.4 ^{ab}	74.4 ^{c1}	32.4 ^{e2}	29.8 ^{e3}
20%	76.6 ^a	74.6 ^{c1}	33.6 ^{d2}	30.2 ^{d3}
30%	76.9 ^a	74.5 ^{c1}	35.7 ^{c2}	32.0 ^{b3}

Means in the same column with unlike superscripts indicate significant difference ($p < 0.001$).

solubility of anthocyanin. Therefore, retention of anthocyanins was higher as the percentage of sugar increased from 20% to 40%. Anthocyanin retention at 60% sugar became lower most probably due to the higher osmotic effect where there were higher weight losses (Table 6) with more pigments leached into the soaking solution.

CONCLUSIONS

Anthocyanins in papaya and pineapple were found to be heat-labile and sensitive to changes in pH while carotenoids were relatively stable under both conditions. Sulphuring and moisture-retaining of fruits could protect carotenoids from oxidation but caused bleaching and hydrolysis of anthocyanins. If certain processing modifications are made to meet the

conditions where the pigments are stable, then the natural colour can be retained with a reasonable degree of success.

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