Effects of Ripening, Cultivar Differences, and Processing on the Carotenoid Composition of Mango

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The carotenoid composition of mangoes produced in Brazil was determined by HPLC to appraise the effects of some influencing factors. Total carotenoid rose from 12.3 to 38.0 μg/g in the cultivar Keitt and from 17.0 to 51.2 μg/g in the cultivar Tommy Atkins from the mature-green to the ripe stage. Ripening alterations occurred principally in the major carotenoids, violaxanthin and β-carotene. In the Keitt mangoes, *all-trans*-β-carotene, *all-trans*-violaxanthin, and 9-*cis*-violaxanthin (location of cis double bond tentative) increased from 1.7, 5.4, and 1.7 μg/g in the mature-green fruits to 6.7, 18.0, and 7.2 μg/g, respectively, in the ripe fruits. In the Tommy Atkins cultivar, these carotenoids went from 2.0, 6.9, and 3.3 μg/g to 5.8, 22.4, and 14.5 μg/g, respectively, on ripening. In both cultivars, the small amount of 13-*cis*-violaxanthin practically disappeared on ripening. Geographic effects appeared to be substantial. In commercially processed mango juice, violaxanthin was not detected, auroxanthin appeared at an appreciable level, and β-carotene became the principal carotenoid.

Keywords: *Carotenoids; mango; HPLC; ripening; cultivar differences; processing effects*

INTRODUCTION

Mango (*Mangifera indica* L.) is one of the better studied tropical fruits in terms of carotenoids. However, earlier studies have dealt with only the total carotenoid, total carotene, or β-carotene content. In the few papers investigating the carotenoid composition (Jungawala and Cama, 1963; John et al., 1970; Godoy and Rodriguez-Amaya, 1987, 1989; Cano and Ancos, 1994), some inconsistencies can be discerned. Inherent variations are to be expected because of such factors as stage of maturity, cultivar/varietal differences, geographic or climatic effects, and processing and storage conditions. On the other hand, part of this discrepancy is due to the analytical procedures employed, and greater agreement of results should ensue as the methods are improved and refined.

To overcome analytical problems, Mercadante et al. (1997) developed a quantitative method of high-performance liquid chromatography (HPLC) with a diode array detector, and confirmation of carotenoid identity was carried out by mass spectrometry.

More quantitative data are needed to appraise the natural variation of the carotenoid composition of mango samples and the magnitude of the effects of different factors. In the present work, quantitative changes during ripening and cultivar differences in the carotenoid composition of mangoes produced in Brazil were studied by HPLC. To detect gross differences between fresh and processed fruit juices offered to consumers, different brands of commercial fruit juice were also analyzed.

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MATERIALS AND METHODS

Materials. Samples of mango cultivars Keitt and Tommy Atkins were purchased from the Central Distribution Center of Campinas, São Paulo, Brazil. These mangoes were produced in the Araraquara region of the state of São Paulo. Three lots, consisting of 24 fruits each, were acquired for each cultivar at different times during the season. For each lot, the mangoes were separated into mature-green, partially ripe, and ripe fruits. Each lot came from the same plantation so that the fruits were presumably subjected to the same conditions at the plantation and during transport to the distribution center and were collected on the same day. Thus, this paper represents the ripening process under commercial conditions, rather than strict physiological conditions (i.e. fruits harvested at the mature-green stage and followed periodically over the ripening process). Maturity stage was judged by means of visual color and texture. The Keitt mangoes change from green to yellow with slight specks of pink when ripe. On the other hand, the Tommy Atkins mangoes turn from green to varying but predominantly red against a yellow-orange background.

For each stage of maturity three fruits were chosen at random, peeled, and, after removal of seed, homogenized. Samples of 15 g (ripe fruit) to 40 g (mature-green fruit) were taken for immediate analysis.

Three brands of processed mango juice from supermarkets and grocery stores in Campinas were also examined. For each brand, three lots collected at different times, each consisting of three bottles of juice taken at random, were analyzed. The contents of the three bottles were homogenized, and 30−35 g was taken for analysis.

Carotenoid Determination. The carotenoid composition was determined by using HPLC as described previously (Mercadante et al., 1997). Briefly, this involved extraction with acetone, transfer to diethyl ether/petroleum ether, overnight saponification with 10% KOH in methanol, washing, and concentration prior to HPLC. Identification of the carotenoids was based on retention time, co-injection with carotenoid standards, UV−visible absorption spectrum, chemical reactions monitored by HPLC, and electron impact mass spec-

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Table 1. Carotenoid Composition and Vitamin A Value of Ripening Mango Cv. Keitt

carotenoid	concentration (μg/g) mature-green[a]	partially ripe[a]	ripe[a]	ripe (Bahia)[b]
all-trans-β-carotene	1.7 ± 0.3	4.2 ± 0.4	6.7 ± 1.6	15.1 ± 1.5
unidentified	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
cis-β-cryptoxanthin	tr	ND−tr	tr−0.1	tr−0.1
all-trans-β-cryptoxanthin	ND−tr	ND−0.1	0.2 ± 0.0	0.3 ± 0.0
all-trans-zeaxanthin	0.3 ± 0.0	0.3 ± 0.0	0.8 ± 0.3	0.8 ± 0.2
luteoxanthin isomers	1.0 ± 0.2	1.6 ± 0.4	2.7 ± 0.2	3.8 ± 0.6
all-trans-violaxanthin	5.4 ± 1.7	11.2 ± 1.5	18.0 ± 4.0	21.1 ± 2.9
9-*cis*-violaxanthin[c]	1.7 ± 0.4	3.9 ± 0.5	7.2 ± 1.4	10.1 ± 1.0
13-*cis*-violaxanthin[c]	0.3 ± 0.1	0.2 ± 0.3	ND−tr	1.4 ± 0.1
cis-neoxanthin	0.1 ± 0.0	0.2 ± 0.1	0.3 ± 0.2	tr−0.2
all-trans-neoxanthin	1.6 ± 0.6	1.9 ± 0.5	1.9 ± 0.9	2.1 ± 1.3
total	12.3 ± 3.2	23.6 ± 1.8	38.0 ± 7.7	55.0 ± 5.0
vitamin A value (RE[d]/100 g)	28 ± 5	70 ± 7	112 ± 27	251 ± 26

[a] Mean and standard deviation of three sample lots from São Paulo for each maturity stage. ND, not detected; tr, trace. [b] Taken from Mercadante et al. (1997) for comparison. [c] Location of cis double bond tentative. [d] RE, retinol equivalent.

Table 2. Carotenoid Composition and Vitamin A Value of Ripening Mango Cv. Tommy Atkins

carotenoid	concentration (μg/g)[a] mature-green[a]	partially ripe[a]	ripe[a]
all-trans-β-carotene	2.0 ± 0.8	4.0 ± 0.8	5.8 ± 2.5
unidentified	ND−tr	ND−tr	ND
cis-β-cryptoxanthin	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.1
all-trans-β-cryptoxanthin	0.1 ± 0.0	0.1 ± 0.0	0.3 ± 0.1
all-trans-zeaxanthin	0.3 ± 0.1	0.5 ± 0.1	0.4 ± 0.2
luteoxanthin isomers	1.3 ± 0.7	2.7 ± 1.1	2.0 ± 0.6
all-trans-violaxanthin	6.9 ± 3.0	17.5 ± 6.7	22.4 ± 9.1
9-*cis*-violaxanthin[b]	3.3 ± 1.3	9.0 ± 3.2	14.5 ± 4.7
13-*cis*-violaxanthin[b]	0.5 ± 0.2	0.7 ± 0.7	tr
cis-neoxanthin	ND−tr	0.4 ± 0.5	1.0 ± 1.0
all-trans-neoxanthin	2.6 ± 1.8	6.6 ± 5.1	4.9 ± 4.5
total	17.0 ± 7.8	45.1 ± 20.7	51.2 ± 16.8
vitamin A value (RE[c]/100 g)	32 ± 13	68 ± 14	96 ± 42

[a] Mean and standard deviation of three sample lots from São Paulo for each maturity stage. ND, not detected; tr, trace. [b] Location of cis double bond tentative. [c] RE, retinol equivalent.

trometry. Quantification was done by internal calibration, using Sudan I as internal standard.

The separation was carried out on a nitrile column with a multilinear gradient of acetone in hexane from 0 to 15% in 10 min, to 20% in 20 min, to 30% in 10 min, and to 40% in 2 min as mobile phase. The flow rate was 1 mL/min and re-equilibration to the initial condition took 8 min (Mercadante et al., 1997).

RESULTS AND DISCUSSION

Changes during Ripening. Mangoes are usually picked at the mature-green or partially ripe stage to allow sufficient time for transport and commercialization before they turn ripe. No qualitative change was seen in the carotenoid composition of the two mango cultivars studied from the mature-green to the ripe stage (Tables 1 and 2). On the other hand, pronounced quantitative changes took place on ripening. The mean total carotenoid content rose from 12.3 to 38.0 μg/g in cv. Keitt and from 17.0 to 51.2 μg/g in cv. Tommy Atkins from the mature-green to the ripe stage. Alterations of the individual carotenoids were similar in both cultivars, the major change occurring in β-carotene and violaxanthin. In the Keitt mangoes, *all-trans*-β-carotene, *all-trans*-violaxanthin, and 9-*cis*-violaxanthin increased from 1.7, 5.4, and 1.7 μg/g in the mature-green fruits to 6.7, 18.0, and 7.2 μg/g in the ripe fruits, respectively. In cv. Tommy Atkins, these carotenoids rose from 2.0, 6.9, and 3.3 μg/g to 5.8, 22.4, and 14.5 μg/g, respectively. In both cultivars, the small amount of 13-*cis*-violaxanthin found in the mature-green fruits practically disappeared on ripening. Location of the *cis* double bonds is tentative.

β-Carotene was practically the sole contributor to the vitamin A value since the other provitamin A, β-cryptoxanthin, was present at very low level. Thus, the β-carotene trend was reflected in the vitamin A value, which increased from 28 to 112 retinol equivalent (RE)/100 g in cv. Keitt and from 32 to 96 RE/100 g in the Tommy Atkins mangoes during ripening (Tables 1 and 2).

Cultivar Differences and Geographic Effects. Both ripe mangoes showed similar patterns, with *all-trans*-violaxanthin, 9-*cis*-violaxanthin, and β-carotene as the principal carotenoids. However, the Keitt mango had a slightly higher mean *all-trans*-β-carotene concentration (6.7 vs 5.8 μg/g), while the Tommy Atkins mango presented higher *all-trans*-violaxanthin (22.4 vs 18.0 μg/g) and 9-*cis*-violaxanthin (14.5 vs 7.2 μg/g) contents. Neoxanthin was also present at higher level in the Tommy Atkins mango. Consequently, the total carotenoid content of cv. Tommy Atkins surpassed that of the Keitt mango by 35%, but the vitamin A value was lower (Tables 1 and 2).

Comparing the carotenoid composition of the ripe Keitt mango from São Paulo (moderate climate) analyzed in the present study with that of ripe Keitt mango from Bahia (hot climate) analyzed in a previous study (Mercadante et al., 1997), the fruits from the latter state had more than twice as much β-carotene as the fruits from São Paulo. *all-trans*-Violaxanthin and 9-*cis*-violaxanthin were also higher in the Keitt mango from Bahia, approaching the values encountered in the Tommy Atkins mango from São Paulo. These results indicated that climatic effects could have the same or even greater influence on the carotenoid composition than cultivar differences, with fruits from hot regions having generally higher carotenoid contents. This tendency was also observed when the Tommy Atkins mango from São Paulo, analyzed in this study, was compared with mango of the same cultivar from Mato Grosso, analyzed earlier by Godoy and Rodriguez-Amaya (1989), the β-carotene content of the latter mango being twice as much as that of the former.

Similar results were obtained with cv. Solo papaya (Kimura et al., 1991). Papaya from the hot Bahia region contained distinctly greater amounts of β-carotene,

Table 3. Carotenoid Composition and Vitamin A Value of Commercial Mango Juice

carotenoid	concentration (μg/g) brand A[a]	brand B[a]	brand C[b]
β-carotene	7.8 ± 0.9	11.7 ± 1.3	6.3 ± 1.3
unidentified	0.1 ± 0.0	ND	ND
β-cryptoxanthin	0.1 ± 0.0	0.3 ± 0.0	0.2 ± 0.1
auroxanthin	3.8 ± 1.1	5.8 ± 0.2	6.4 ± 4.3
total	11.9 ± 1.3	17.9 ± 1.5	13.5 ± 6.3
vitamin A value (RE[c]/100 g)	130 ± 16	196 ± 23	105 ± 21

[a] Mean and standard deviation of three sample lots. ND, not detected. [b] Mean and standard deviation of two sample lots. [c] RE, retinol equivalent.

β-cryptoxanthin, and lycopene than papaya from São Paulo. The difference, especially in relation to β-carotene, surpassed that seen among four cultivars from the same state.

Carotenoid Composition of Processed Mango Juice. In Brazil, mango juice is manufactured from different cultivars or even a mixture of cultivars, including Keitt and Tommy Atkins. Thus, comparison between commercial fresh fruit and commercially processed juice is not straightforward. Nonetheless, the effect of processing appeared to be so marked that the composition of the juice is dramatically different. Violaxanthin, the principal carotenoid of fresh mango, was not detected in the three brands of mango juice analyzed. Instead, auroxanthin, not present in the fruits, appeared at an appreciable level (Table 3). This change in pattern could be explained by the conversion of the 5,6-epoxide groups of violaxanthin to the 5,8-furanoxide groups of auroxanthin. The liberation of organic acids during disintegration of the mango fruits could create the conditions necessary for the transformation of violaxanthin to auroxanthin. With the disappearance of violaxanthin, β-carotene became the major carotenoid, followed by auroxanthin in the commercial juices analyzed.

In canned Alphonso mango, the predominance of β-carotene could be easily noted from the chromatogram, although quantification was not done (Cano and Ancos, 1994). It was followed at a great distance by *cis*- and *trans*-mutatochrome, a 5,8-furanoxide derivative of β-carotene.

In a study in which the same lots of mangoes were analyzed before and after processing of mango slices and puree, thus directly appraising the effects of processing, epoxide−furanoxide transformations were also the most apparent changes (Godoy and Rodriguez-Amaya, 1987).

The above transformation can also occur during analysis, and the results obtained with processed mango reinforce the supposition raised previously (Mercadante et al., 1997) that violaxanthin may have been underestimated in previous studies, most of which cited β-carotene as the principal carotenoid, because of violaxanthin's facile transformation and/or degradation.

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