Carotenoid Composition in the Fruits of Black Paprika (*Capsicum annuum* Variety *longum nigrum*) during Ripening

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The changes in the carotenoid pigments of black paprika (*Capsicum annuum* var. *longum nigrum*) during maturation have been investigated quantitatively by means of a HPLC technique. In the chromatograms 58 peaks were detected, 34 carotenoids (92–95% of the total carotenoid content) were completely or tentatively identified. The total carotenoid content of the ripe fruits was about 3.2 g/100 g of dry weight, of which capsanthin constituted 42%, zeaxanthin 8%, cucurbitaxanthin A (3,6-epoxy-5,6-dihydro-β,β-carotene-5,3′-diol) 6.6%, capsorubin 3.2%, and β-carotene 7%. The remainder was composed of capsanthin 5,6-epoxide, capsanthin 3,6-epoxide (3,6-epoxy-5,3′-dihydroxy-5,6-dihydro-β,κ-caroten-6′-one), karpoxanthin, violaxanthin, antheraxanthin, zeaxanthin, β-cryptoxanthin, lutein, and several cis isomers and furanoid oxides. During ripening, an increase in capsanthin and, to a lesser extent, an increase in carotenoids with κ and oxabicyclo[2.2.1] end groups were observed.

INTRODUCTION

Although red paprika is one of the most extensively investigated natural carotenoid food colors (Klaüi and Bauernfend, 1981; Camara, 1980, 1985; Camara and Bardat, 1983), the black variety, *Capsicum annuum* var. *longum nigrum*, has not yet been analyzed in detail. As a continuation of our work on paprika carotenoids (Baranyai et al., 1982; Baranyai and Szabolcs, 1976; Parkes et al., 1986; Matus et al., 1991), the present paper deals with the distribution of yellow and red carotenoids in ripening black paprika, paying special attention to the formation of minor carotenoids with oxabicyclo-β and 3,5,6-trihydroxy-β end groups.

MATERIALS AND METHODS

The black paprika (*C. annuum* var. *longum nigrum* cv. Szentesi fekete füszer paprika) was collected from a research plantation at Szentes (central Hungary) in September 1988 and immediately transported to our laboratory. The fruits, which were at different stages of ripening, were divided into six batches according to their black to red colors.

General methods, including sample taking, extraction, workup, instrumentation, and quantitative determination of carotenoids and chlorophyll, were described in a parallel study of yellow paprika (Matus et al., 1991). Mass spectra were recorded on a JEOL MS-01SG-2 spectrometer.

The chromatographic system consisted of Models 250B and 300B HPLC pumps (Gynkotek), a Glenco injector, and a Beckman UV–vis variable-wavelength detector (Ohmacht, 1979). Columns were 250 × 4.6 mm i.d. (Labor MIM) packed with Chromsil C_{18} 6 μm endcapped (Labor MIM) and Chromsil C_{18} 6 μm not endcapped (Labor MIM). The eluent was 12% (v/v) H_2O in methanol (A), methanol (B), 50% (v/v) acetone in methanol (C). The gradient program was 100% A 8 min to 80% A/20% B in 8 min, to 50% A/50% B in 8 min, to 100% B in 7 min, 100% B 2 min, to 100% C in 6 min, 100% C 5 min (linear steps). The flow rate was 1.5 mL/min, and detection was at 430, 450, 480, 400, and 340 nm.

Analytical chemicals were used, and authentic samples were taken from our collection. Characteristic data of the authentic minor carotenoids [karpoxanthin, capsanthin 5,6-epoxide, cucurbitaxanthin A (3,6-epoxy-5,6-dihydro-β,β-carotene-5,3′-diol), capsanthin 3,6-epoxide (3,6-epoxy-5,3′-dihydroxy-5,6-dihydro-β,κ-caroten-6′-one)] were published earlier (Parkes et al., 1986).

RESULTS AND DISCUSSION

To avoid pigment decomposition, and epoxide–furanoid oxide and trans–cis rearrangements, the isolation of carotenoids was carried out under nitrogen in darkness using methanol for dehydration at low temperatures (4–23 °C). The different stages of ripening were characterized by the total carotenoid content of fruits (Matus et al., 1991).

During ripening, the changes in total carotenoid content, red carotenoid content, and chlorophyll content are shown in Table I. The total and the red carotenoid contents were increased 66- and 214-fold, respectively, while the chlorophyll content was reduced to zero. The ratio of the red and yellow pigments increased from 0.22 to 1.34. Thus, the color of black paprika can range from greenish black to deep red, depending on the concentration of chlorophyll relative to those of red and yellow carotenoids. The ripe fruits of black paprika had a very high carotenoid content, the red variety (*Capsicum annuum* var. *lycopersiciforme*

Table I. Miscellaneous Properties

property	stage of maturation 1	2	3	4	5	6
fresh wt, g	465.46	279.52	228.48	234.43	225.62	161.57
dry wt, g	27.62	15.01	12.45	11.56	11.50	8.86
dry wt/fresh wt, %	5.93	5.37	5.45	4.93	5.10	5.49
chlorophyll content, mg/100 g of dw	109.35	74.20	44.85	10.02	0	0
total carotenoid, mg/100 g of dw	48.50	162.00	378.90	1753.90	1960.60	3211.00
red component, %	17.71	34.30	43.89	53.28	54.04	57.29
partition coefficient						
before saponification	1.12					0.07
after saponification	1.84					3.69
phytoxanthin, %	84.13					91.94
esterified phytoxanthin, %	37.30					93.30

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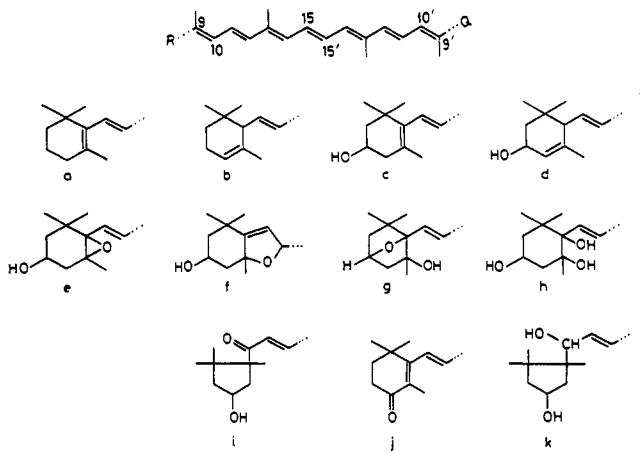
Chart I [a]



[a] Antheraxanthin, R = e, Q = c; canthaxanthin, R = Q = j; capsanthin, R = c, Q = i; capsanthin 5,6-epoxide, R = e, Q = i; capsanthin 3,6-epoxide (oxabicyclo,κ pigment), R = g, Q = i; capsanthol, R = c, Q = k; capsochrome, R = f, Q = i; capsorubin, R = Q = i; capsorubol, R = Q = k; α-carotene, R = a, Q = b; β-carotene, R = Q = a; cryptocapsin, R = a, Q = i; α-cryptoxanthin, R = c, Q = b; β-cryptoxanthin, R = c, Q = a; cucurbitaxanthin A (oxabicyclo,β pigment), R = g, Q = c; cucurbitaxanthin B (oxabicyclo,β-epoxide pigment), R = g, Q = e; cycloviolaxanthin (oxabicyclo,oxabicyclo pigment), R = Q = g; karpoxanthin, R = h, Q = c; latoxanthin (trihydroxy-β,β-epoxide pigment), R = h, Q = e; lutein, R = c, Q = d; luteoxanthin, R = e, Q = f; mactraxanthin (trihydroxy-β,trihydroxy-β pigment), R = Q = h; mutatoxanthin, R = f, Q = c; violaxanthin, R = Q = e; zeaxanthin, R = Q = c; 3,5,6,3′-tetrahydroxy-5,6-dihydro-β,κ-caroten-6′-one (trihydroxy-β,κ pigment), R = h, Q = i; 3,6-epoxy-5,6,5′,6′-tetrahydro-β,β-carotene-5,3′,5′,6′-tetrol (oxabicyclo,trihydroxy-β pigment), R = g, Q = h.

rubrum) possessing (Cholnoky et al., 1955) only 13% of that of the black variety.

The partition coefficients of the extracts measured before and after saponification and the HPLC analysis revealed that the percentages of the esterified phytoxanthins had increased from 37 to 93% (Table I), which is in agreement with the literature (Cholnoky et al., 1955).

The changes in the individual carotenoid contents of fruits are given in Table II; 58 peaks were detected by HPLC at all stages of ripening. The pigments were identified by using authentic carotenoids, various chemical tests, and different wavelengths of detection (Matus et al., 1981) (Figures 1 and 2).

During maturation, the changes [in milligrams per 100 g of dry weight (dw)] of hydrocarbons, xanthophylls, and epoxy- and ketoxanthophylls are demonstrated in Figure 3. The different slopes of the curves show that the rates of accumulation (rate of formation minus rate of transformation) in fruits, in decreasing order, are as follows: ketoxanthophylls, xanthophylls, hydrocarbons, and epoxyxanthophylls. In the case of black paprika, the situation is more complex than that in yellow paprika (Matus et al., 1991); therefore, we limit ourselves to a single conclusion: the rate of pinacol rearrangement exceeds the rate of epoxydation.

The percentage distribution of carotenoids is plotted against total carotenoid content in Figures 4 and 5. From the relative position of the principal capsanthin curve and the antheraxanthin (precursor of capsanthin) curve, it is seen that the sharp increase of capsanthin is accompanied by a moderate decrease of antheraxanthin. Similarly, a moderate increase of the capsorubin curve is associated with a moderate decrease of the violaxanthin (precursor of capsorubin) curve. It is important to recognize that the curves of antheraxanthin and violaxanthin are parallel to each other within measuring errors. β-Carotene increases until the stage of disappearance of chlorophyll, when it reaches a more or less constant value. In contrast, lutein, which makes up the highest percentage (29%) of carotenoids at the very beginning of ripening, plummets to below 0.1%. However, the most important finding is brought out by the curve of cucurbitaxanthin A and capsanthin 3,6-epoxide; the trend of the rate of accumulation of the carotenoids with an oxabicyclo end group resembles that of the carotenoids with a κ end group. The carotenoids with both oxabicyclo and κ end groups are end products in the biosynthetic pathways, so their rates of accumulation are equal to their rates of formation.

During ripening, the changes of pigment concentrations reveal a general increase which is extremely high (470-fold) for capsanthin. The rates of accumulation, in decreasing order, are as follows: capsanthin, zeaxanthin, β-carotene, cucurbitaxanthin A, β-cryptoxanthin, capsorubin, capsanthin 3,6-epoxide, karpoxanthin, antheraxanthin, violaxanthin, capsanthin 5,6-epoxide, and cryptocapsin.

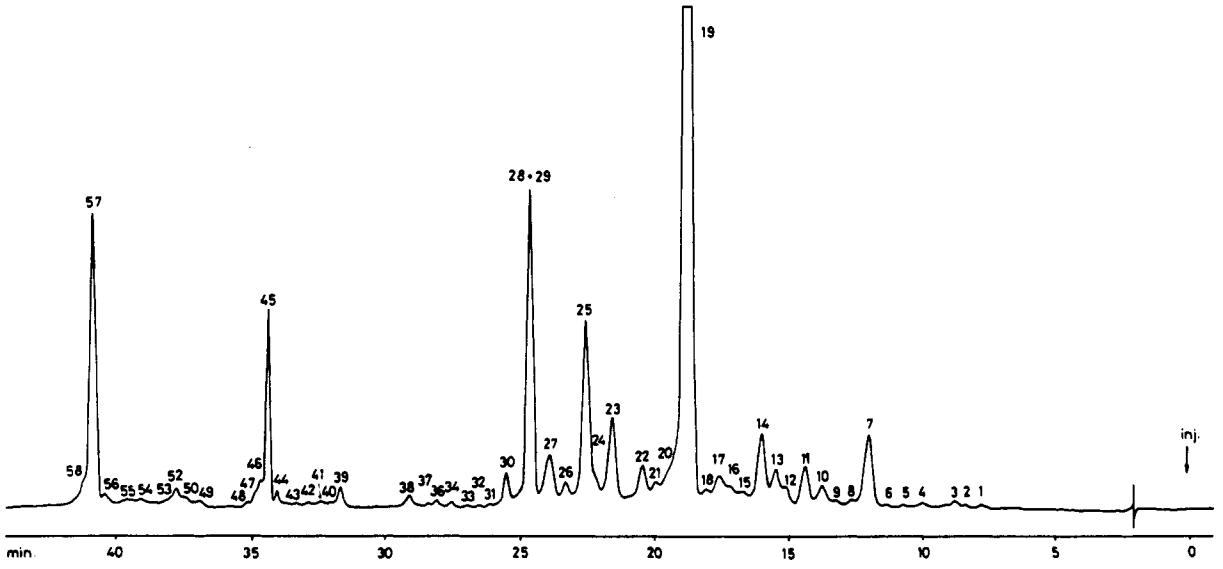


Figure 1. HPLC separation of carotenoids in ripe black pepper. Conditions: Chromsil-C_{18} 6 μm endcapped, detection at 450 nm, other conditions as in the text. For peak numbers see Table II.

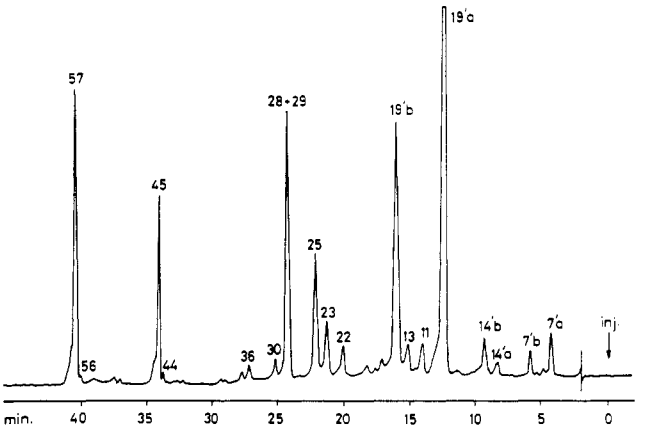


Figure 2. HPLC chromatogram after $NaBH_4$ reduction. Conditions: Chromsil-C_{18} 6 μm endcapped, other conditions as in the text. For peak numbers see Table II. Peaks: 7'a and 7'b (from 7), capsorubol epimers; 14'a and 14'b (from 14), capsanthol 3,6-epoxide epimers; 19'a and 19'b (from 19), capsanthol epimers.

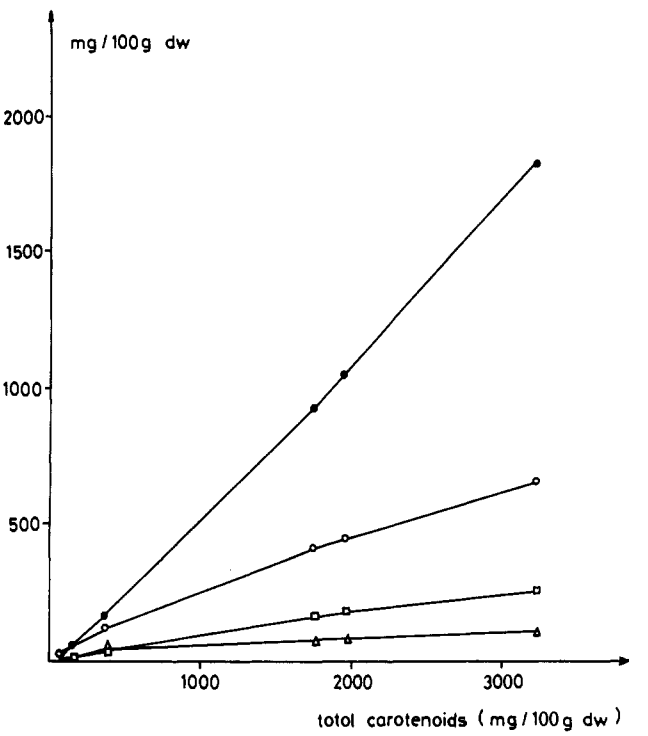


Figure 3. Pigment changes during ripening. (●) Ketocarotenoids; (△) epoxides; (○) monools plus diols; (□) carotenes.

A number of previous investigations have demonstrated that some of the natural carotenoids are isolation artifacts. In this experiment, the question of isolation artifacts emerges in connection with cis isomers and furanoid oxides (5,8-epoxides), which are always present in the fruits of black paprika (Table II).

The changes of cis isomers in black paprika are similar to those in yellow paprika during the process of ripening (Matus et al., 1991); i.e., the related percentage values (cis form/cis form + trans form) decrease with ripening until about the decomposition of chlorophyll, after which they remain at a more or less constant value. Since coexistence of the all-trans, 9-cis, and 13-cis forms was consistently observed and the average total amount of the cis isomers was only 5%, we believe that the cis isomers are likely to be "post-mortem artifacts".

Table II. Relative Carotenoid Content (Percent) of *C. annuum* Fruit at Six Stages of Maturation

peak	pigment	stage of maturation 1	2	3	4	5	6	peak	pigment	stage of maturation 1	2	3	4	5	6
1[a]		0.16	0.14	0.12	0.08	0.06	0.06	31[a]		0.07	0.08	0.05	0.04	0.04	0.05
2[a]		0.07	0.04	0.04	0.05	0.05	0.05	32[a]		0.07	0.14	0.02	0.04	0.03	0.03
3	trihydroxy-β,κ pigment	0.11	0.09	0.16	0.21	0.17	0.21	33	9(9')-*cis*-lutein	0.86	0.15	0.04	0.04	0.04	0.04
4[a]		0.32	0.25	0.22	0.17	0.18	0.17	34	9-*cis*-zeaxanthin	1.77	0.38	0.20	0.12	0.11	0.12
5[a]		0.22	0.16	0.11	0.09	0.08	0.08	35	13(13')-*cis*-lutein	0.47	0.00	0.00	0.00	0.00	0.00
6[a]		0.95	0.31	0.26	0.09	0.11	0.08	36	13-*cis*-zeaxanthin	0.87	1.16	0.72	0.33	0.28	0.25
7	capsorubin	0.57	1.25	1.75	2.35	2.51	3.16	37[a]		0.18	0.28	0.19	0.11	0.11	0.09
8[a]		0.00	0.29	0.22	0.27	0.22	0.18	38[a,b]		0.09	0.36	0.06	0.15	0.15	0.17
9	epikarpoxanthin	0.38	0.32	0.23	0.19	0.16	0.17	39	cryptocapsin	0.06	0.08	0.13	0.44	0.69	0.68
10	capsanthin 5,6-epoxide	4.82	2.70	2.17	1.15	1.06	0.96	40[a]		0.03	0.07	0.04	0.05	0.11	0.07
11	karpoxanthin	0.35	1.07	1.61	1.79	1.70	1.67	41[a,b]		0.28	0.23	0.23	0.06	0.14	0.09
12	capsochrome	0.00	0.36	0.41	0.54	0.62	0.66	42[a]		0.10	0.12	0.03	0.07	0.11	0.08
13	violaxanthin	3.07	3.87	3.75	1.69	1.46	1.13	43[a,b]		0.35	0.43	0.28	0.10	0.09	0.06
14	capsanthin 3,6-epoxide	0.50	1.24	1.75	2.31	2.70	2.85	44	α-cryptoxanthin	0.41	0.57	0.46	0.30	0.25	0.21
15	9-*cis*-capsorubin	1.74	0.74	0.57	0.26	0.27	0.26	45	β-cryptoxanthin	1.41	4.76	5.68	4.83	4.91	3.39
16	13-*cis*-capsorubin	3.08	1.19	0.86	0.56	0.51	0.55	46	*cis*-cryptoxanthins	0.38	0.80	0.80	0.53	0.53	0.43
17	cucurbitaxanthin B	0.42	0.74	0.81	0.78	0.87	0.74	47							
18	luteoxanthin	0.10	0.18	0.25	0.30	0.27	0.32	48[a,b]		0.05	0.08	0.08	0.10	0.09	0.07
19	capsanthin	5.37	22.05	33.46	39.28	40.37	41.58	49[a]		0.12	0.09	0.05	0.09	0.10	0.08
20	cycloviolaxanthin	0.52	0.68	0.86	0.45	0.46	0.81	50[a]		0.16	0.07	0.05	0.11	0.11	0.10
21[a,c]		0.46	0.34	0.32	0.38	0.51	0.59	51[a]		0.15	0.10	0.09	0.16	0.16	0.16
22	antheraxanthin	3.42	3.94	3.43	1.67	1.57	1.32	52[a]		0.29	0.20	0.13	0.19	0.21	0.18
23	mutatoxanthin epimer 2	1.61	2.23	2.40	3.30	3.46	3.84	53[a]		0.18	0.14	0.06	0.06	0.09	0.07
24	mutatoxanthin epimer 1	1.74	0.80	0.57	0.61	0.64	0.75	54[a]		0.27	0.18	0.09	0.11	0.16	0.18
25	cucurbitaxanthin A	1.08	3.79	4.73	6.32	6.88	6.59	55[a]		0.06	0.16	0.07	0.06	0.09	0.10
26	9(9')-*cis*-capsanthin	0.40	1.23	0.40	1.48	1.23	1.61	56	α-carotene	1.90	1.17	0.57	0.30	0.36	0.31
27	13(13')-*cis*-capsanthin	1.17	3.82	2.80	5.45	4.70	5.64	57	β-carotene	13.97	9.73	6.83	8.38	8.36	7.16
28	lutein	28.49	3.38	0.81	0.09	0.07	0.04	58	*cis*-β-carotene	1.95	1.11	0.61	0.73	0.60	0.59
29	zeaxanthin	11.96	19.96	16.66	9.59	8.35	8.12								
30		0.27	0.50	0.54	0.85	0.88	0.91		total carotenoids (mg/100 g of dw)	48.5	162.0	378.9	1753.9	1960.6	3211.0

[a] Unidentified. [b] No reaction with sodium borohydride and dilute acids. [c] Reaction with sodium borohydride and no reaction with dilute acids.

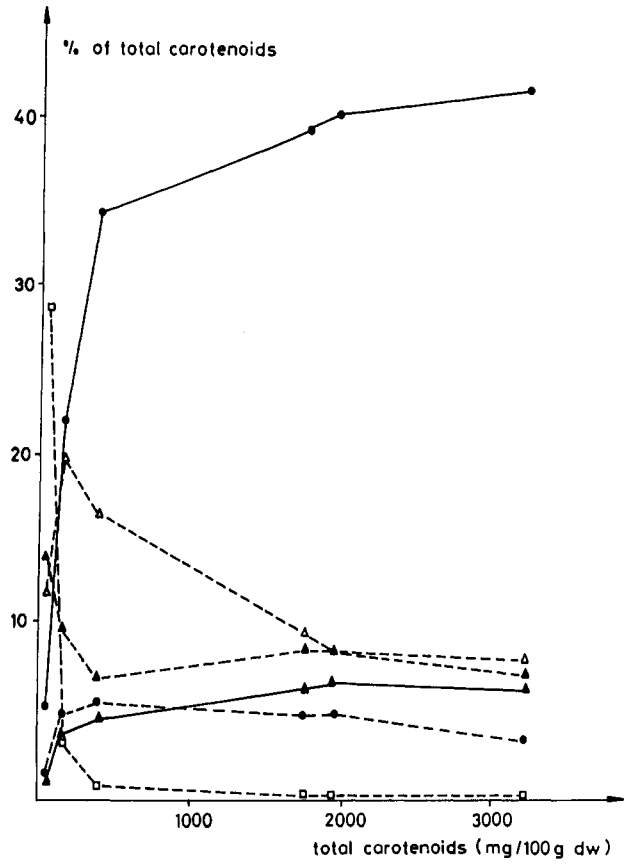


Figure 4. Changes in relative carotenoid content during ripening. (●–●) Capsanthin; (▲–▲) cucurbitaxanthin A; (△- - -△) zeaxanthin; (●- - -●) β-cryptoxanthin; (▲- - -▲) β-carotene; (□- - -□) lutein.

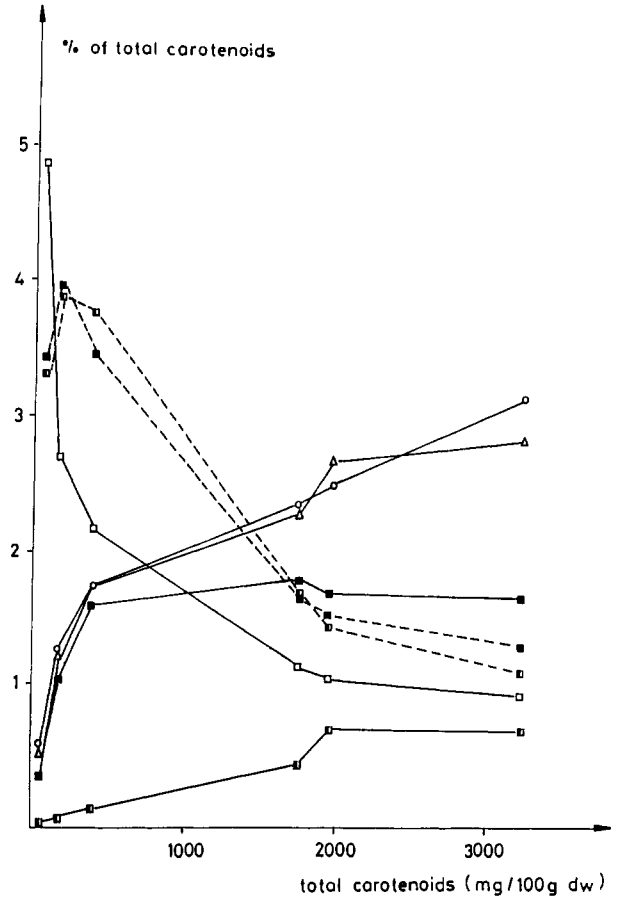


Figure 5. Changes in relative carotenoid content during ripening. (○–○) Capsorubin; (△–△) oxabicyclo,κ pigment; (■–■) karpoxanthin; (□–□) capsanthin 5,6-epoxide; (◧- - -◧) violaxanthin; (■- - -■) antheraxanthin; (◧–◧) cryptocapsin.

In the fruits of black paprika the proportion of furanoid oxides (capsochrome, luteoxanthin, mutatoxanthins) to the corresponding 5,6-epoxides (capsanthin epoxide, violaxanthin, antheraxanthin) increases with maturation from 0, 3, and 97 to 69, 28, and 333%, respectively. Although these figures decrease in the fruits of yellow pepper (Matus et al., 1991), the milligrams of furanoid oxide per 100 g of dw values exhibit a linear increase with maturation in both black and yellow paprika. Why is this so? Capsanthin 5,6-epoxide, violaxanthin, and antheraxanthin are converted via pinacolone rearrangement, respectively, into capsorubin, capsanthin 5,6-epoxide, and capsanthin in black paprika, while in yellow paprika violaxanthin (end product) and antheraxanthin do not undergo pinacol rearrangement; this results in a high concentration of violaxanthin and antheraxanthin, i.e., in a proportion of furanoid oxides to 5,6-epoxides which decreases with maturation. In black paprika the epimers of only mutatoxanthin were identified, showing epimer 2/epimer 1 ratios (increasing from 1:1 to 5:1 during maturation) that differed very much from what was (1.7:1) found after acid treatment of antheraxanthin under laboratory conditions (Matus et al., 1991). In view of the unexpectedly high values of the ratios of the (mutatoxanthin epimer 1 + mutatoxanthin epimer 2)/antheraxanthin and mutatoxanthin epimer 2/mutatoxanthin epimer 1, we confirmed the presence of mutatoxanthin epimer 1 and 2 in black paprika by UV–vis and MS spectroscopy (Baldas et al., 1966) [Mutatoxanthin epimer 1: λ_{max} (in benzene) 466, 439, and 417 nm; λ_{max} (in hexane) 454, 427, and 406 nm; λ_{max} (in Et_2O) 454 and 428 nm. Mutatoxanthin epimer 2: λ_{max} (in benzene) 466, 439, and 417 nm; λ_{max} (in hexane) 454, 428, and 406 nm; λ_{max} (in Et_2O) 454 and 428 nm. MS *m/z* (relative intensity): 584 $[M]^+$ (100), 566 $[M - 18]^+$ (14), 548 $[M - 36]^+$ (19), 504 $[M - 80]^+$ (95), 492 $[M - 92]^+$ (48), 221 (76), 181 (26)].

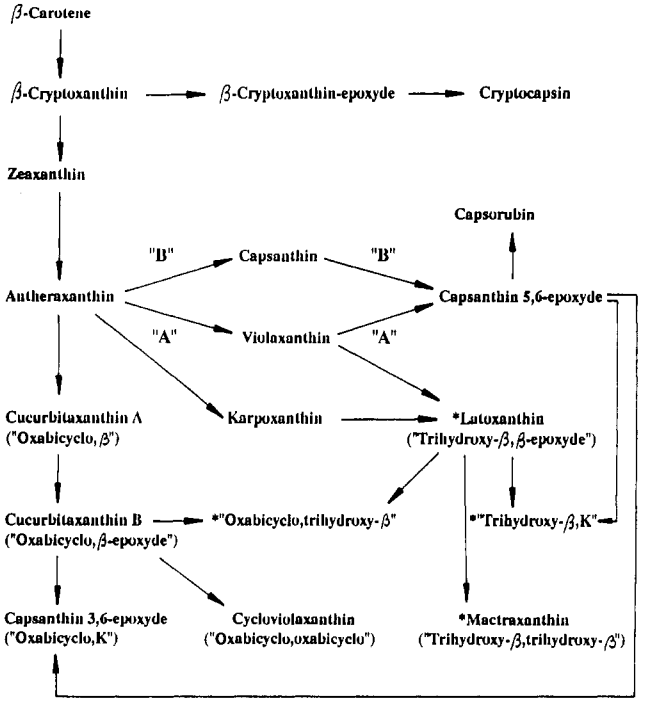
It should be noted that the ratio of mutatoxanthin epimer 2 to mutatoxanthin epimer 1 was constant (1.2:1) in yellow pepper during maturation. Therefore, we believe that the mutatoxanthin epimer 1 and some of the mutatoxanthin epimer 2 may have been post-mortem artifacts in black paprika. However, a stereospecific enzymatic action linked to the pinacol rearrangement of antheraxanthin cannot be ruled out in the formation of mutatoxanthin epimer 2.

According to our analytical data the biosynthesis of capsorubin from antheraxanthin can take place in two ways: (A) via epoxidation and two successive pinacol rearrangements and (B) via pinacol rearrangement, epoxidation, and a further pinacol rearrangement (Scheme I). It is difficult to comment on the two pathways until their enzymology has been worked out in detail. However, we believe that mainly route A is operative.

As is seen from Scheme I, four different biosynthetic routes exist for antheraxanthin. Of these, pinacol rearrangement into capsanthin is the most important. Furthermore, antheraxanthin undergoes epoxidation, epoxide ring opening, and "endo epoxide" rearrangement resulting in violaxanthin, karpoxanthin, and a carotenoid with an oxabicyclo end group, respectively.

Apart from the already known carotenoids just discussed, chemical evidence was obtained in support of the occurrence in black paprika of 3,5,6,3′-tetrahydroxy-5,6-dihydro-β,κ-caroten-6′-one (trihydroxy-β,κ pigment, peak 3) [λ_{max} (in MeOH containing 10% H_2O) 472 nm; λ_{max} (in MeOH containing 10% H_2O after $NaBH_4$ reduction) 468,

Scheme I. Probable Biosynthesis of Carotenoids in Black Paprika[a]



[a] An asterisk indicates carotenoids not or only tentatively identified.

438, and 416 nm], 3,6,5′,6′-diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-5,3′-diol [oxabicyclo,β-epoxide pigment, cucurbitaxanthin B (Matsuno et al., 1986) peak 17] [mp 155–56 °C; λ_{max} (in benzene) 483, 453, 428 nm; λ_{max} (in benzene after acid treatment) 460, 433, 409 nm; MS *m/z* (relative intensity) 600 $[M]^+$ (100), 582 $[M-18]^+$ (7), 564 $[M-36]^+$ (3), 520 $[M-80]^+$ (30), 508 $[M-92]^+$ (26), 287 (28), 221 (100)], and 3,6,3′,6′-diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-5,5′-diol (oxabicyclo,oxabicyclo pigment, cycloviolaxanthin peak 20) [λ_{max} (in benzene) 483, 453, 428 nm; no reaction with acid or $NaBH_4$] (Deli et al., 1991).

3,5,6,3′-Tetrahydroxy-5,6-dihydro-β,κ-caroten-6′-one (trihydroxy-β,κ pigment) and cycloviolaxanthin (oxabicyclo, oxabicyclo pigment) represent end products, while 3,6,5′,6′-diepoxy-5,6,5′,6′-tetrahydro-β,β-carotene-5,3′-diol (oxabicyclo,β-epoxide pigment) is likely to be the precursor of both the oxabicyclo,oxabicyclo pigment (cycloviolaxanthin) and the oxabicyclo,trihydroxy pigment. These relationships are summarized in Scheme I. Characterization and determination of the structures of some minor carotenoids have been published elsewhere.

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