Carotenoid Composition in the Fruits of *Capsicum annuum* Cv. Szentesi Kosszarvú during Ripening

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The changes in the carotenoid pigments of *Capsicum annuum* cv. Szentesi Kosszarvú during maturation have been investigated quantitatively by means of a HPLC technique. In all of the chromatograms, 56 peaks were detected; 34 carotenoids were identified. In this study, special attention is paid to the formation of minor carotenoids with 3,6-epoxy-β- (oxabicyclo[2.2.1]) and 3,5,6-trihydroxy-β- end groups. The possible biosynthetic route and the identity of capsolutein with the cucurbitaxanthin A are described.

Keywords: *Capsicum annuum; carotenoids; analysis; biosynthesis*

INTRODUCTION

Paprika, *Capsicum annuum*, is one of the oldest and most important carotenoid food colorants, and it is widely used. The composition of the carotenoid pigments produced by paprika has been investigated for a long time. A detailed pioneer work (Cholnoky et al., 1955) on the qualitative and quantitative distribution of carotenoids in red paprika (*C. annuum lycopersiciforme rubrum*) revealed that the red carotenoids (capsanthin, capsorubin, cryptocapsin) are formed from the appropriate 5,6-epoxycarotenoids (antheraxanthin, violaxanthin, cryptoxanthin 5,6-epoxide). At that time, the carotenoid composition of yellow paprika (*C. annuum lycopersiciforme flavum*) was investigated, too; although the yellow paprika contained a large amount of 5,6-epoxycarotenoids, they were lacking in red carotenoids (Cholnoky et al., 1958). Since then, some of the different varieties of paprika have been investigated. First, the red and green paprikas were studied, using the countercurrent distribution method for the separation of pigments. About 30 carotenoids were found in red pepper, but these compounds were not characterized exactly (Curl, 1962, 1964). At the beginning of the 1970s, the different varietes of paprika were studied by TLC. On the basis of the analytical results, a possible biosynthetic sequence for the formation of the red ketocarotenoids from β-carotene was described (Davies et al., 1970). The biochemical evidence of the formation of capsanthin and capsorubin from antheraxanthin and violaxanthin by pinacol rearrangement was obtained using labeled antheraxanthin and violaxanthin (Camara, 1980, 1985). Recently, the capsanthin−capsorubin synthase (an enzyme catalyzing the conversion of 5,6-epoxycarotenoid into ketocarotenoid) was isolated and characterized (Bouvier et al., 1994).

In our laboratory, a HPLC method was developed (Baranyai et al., 1982). By means of this method, four new carotenoids, karpoxanthin, cucurbitaxanthin A, capsanthin 3,6-epoxide, and capsanthin 5,6-epoxide, were isolated from red paprika (Parkes et al., 1986). The presence of these new compounds containing 3,6-epoxy- and 3,5,6-trihydroxy end groups in the red paprika may indicate new biosynthetic routes.

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In some papers, particular attention was paid to industrial purposes (Mínguez-Mosquera and Hornero-Méndez, 1993, 1994a,b).

Earlier we reinvestigated the carotenoid composition of two different varieties of paprika. First, a yellow variety of paprika was studied, which, in unripe state, is green, and, in ripe state, is yellow, but its color never turns red (*C. annuum lycopersiciforme flavum*) (Matus et al., 1991). Later, a red variety (*C. annuum* var. *longum nigrum*) was investigated (Deli et al., 1992). This variety, in unripe state, is black, because it contains a large amount of chlorophyll, and, during ripening, its color turns red or deep red. The aim of this research was to study the quantitative changes of carotenoids in different varieties of paprika during ripening and to correlate the carotenoid biosynthesis of yellow paprika to that of red paprika. As a result of this work, some minor carotenoids (cucurbitaxanthin B, cycloviolaxanthin, nigroxanthin, and capsanthone) could be isolated from red paprika (Deli et al., 1991, 1994, 1995).

In this paper, carotenoid compositions during the ripening of the fruits of another Hungarian variety, Szentesi Kosszarvú paprika, are studied.

MATERIALS AND METHODS

Materials. The fruits of pepper (*C. annuum* var. *longum ceratoides* cv. Szentesi Kosszarvú paprika) were collected from a research plantation at Szentes and immediately transported to our laboratory. The fruits, which were at different stages of ripening, were divided into six batches according to their color from green to red. To obtain reliable samples, pods (50−300 g, fresh weight; see Table 1), free from their shells and seeds, were used for extraction.

Analytical grade chemicals were used, and authenthic samples were taken from our collection. Reports on characteristic data of the authentic minor carotenoids (cycloviolaxanthin, cucurbitaxanthins A and B, capsanthin 3,6-epoxide, capsanthin 5,6-epoxide, karpoxanthin, nigroxanthin, capsanthone) were published earlier (Deli et al., 1991, 1992, 1994, 1995; Parkes et al., 1986).

Pigment Extraction. Pigments were extracted from a sample, using MeOH three times and finally diethyl ether twice. The extract was saponified in ether with 30% KOH−MeOH at room temperature. The saponified pigments were stored in benzene solution at −20 °C under nitrogen away from light until the preparation of HPLC samples.

General methods, including sample taking, extraction, workup, and quantitative determination of chlorophyll, were

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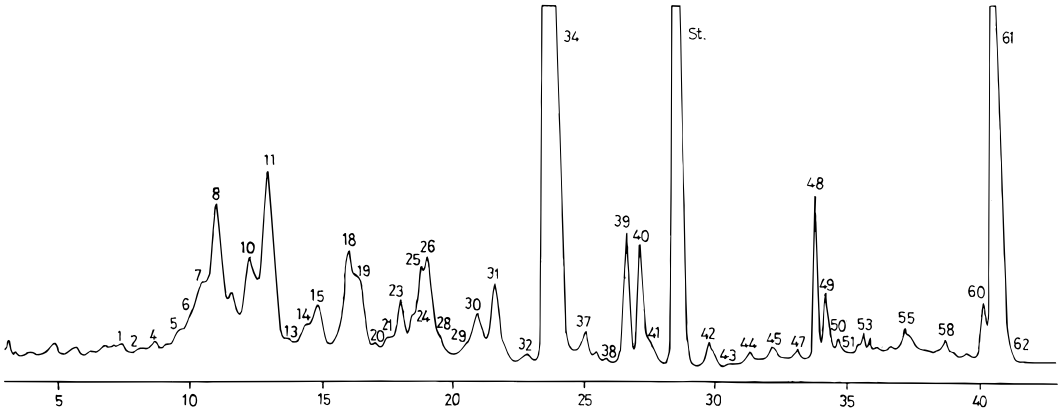


Figure 1. HPLC separation of carotenoids in unripe (green) paprika. Conditions: Chromsil C_{18} 6 μm end-capped, detection at 450 nm, other conditions as in the text. For peak numbers see Table 2. St., canthaxanthin (internal standard).

Table 1. Miscellaneous Properties

property	stage of maturation					
	green	pale yellow	yellow	orange	red	deep red
fresh wt of sample, g	97.00	236.64	199.50	189.60	302.00	73.60
dry wt of sample, g	4.95	11.48	9.84	9.73	18.91	5.24
dry wt/fresh wt, %	5.10	4.85	4.93	5.13	6.26	7.12
chlorophyll content, mg/100 g of dw	19.42	6.99	4.67	1.35	0.0	0.0
total carotenoid, mg/100 g of dw	11.54	16.80	44.75	132.73	610.69	994.71
red component, %	1.99	1.90	35.04	38.00	38.97	39.40

described in detail in a previous study of yellow paprika (Matus et al., 1991).

High-Performance Liquid Chromatography. The chromatographic system consisted of Gynkotek Model 300 B pump with Gynkotek gradient former and a Waters 991 photodiode array detector. Columns were 250 × 4.6 mm i.d. Chromsil C_{18}, 6 μm, end-capped and Chromsil C_{18}, 6 μm, not end-capped. The eluent was 12% (v/v) H_2O in methanol (A), methanol (B), and 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.

Identification of Peaks. The peaks in a chromatogram were identified by means of authentic carotenoid samples, different chemical tests (Baranyai et al., 1982; Matus et al., 1991), and the UV−vis spectra of the individual peaks. Photodiode array measurements of spectral properties for the individual peaks (from 300 to 510 nm) were determined at the upslope, apex, and downslope. The matching of the three spectra indicated the degree of peak purity.

Quantification. The chromatograms were evaluated quantitatively by relating the heights of the individual carotenoids to that of canthaxanthin (Hoffmann-La Roche, mp 205 °C, recrystallized from benzene−hexane), using an internal standard (Matus et al., 1991). The ratios of the 450 nm mole extinctions of the authentic samples in a chromatogram to that of cantaxanthin were used as detector signals to the amount of identified carotenoids in the sample introduced. A mean value of mole extinction was employed for the quantitation of unidentified pigments.

RESULTS AND DISCUSSION

To avoid trans−cis isomerization and epoxide−furanoid oxide rearrangement, great care was taken during the isolation procedures. The individual carotenoid content and total carotenoid and chlorophyll contents were expressed on the basis of the weight and dry weight of fruits. The different stages of ripening were characterized by the total carotenoid content of fruits (Matus et al., 1991).

The concentrations of the chlorophyll and carotenoid pigments were analyzed in six consecutive stages of ripeness: green, pale yellow, yellow, orange, red, and deep red.

During ripening, the changes in total carotenoid content, red carotenoid content, and chlorophyll content are shown in Table 1. The total carotenoid contents were increased ca. 90-fold, while the chlorophyll content was reduced to zero. The ratio of the red and yellow pigments increased from 0.022 to 0.65. Thus, the color of cv. Kosszarvú paprika can range from pale green to deep red, depending on the concentration of chlorophyll relative to those of red and yellow carotenoids. Similar increases in pigment concentration were found by Mínguez-Mosquera and Hornero-Méndez (1994a,b) and Deli et al. (1992).

The changes in the individual carotenoid contents of fruits are given in Table 2. In all of the different stages of maturation, the same 56 peaks were found (Figures 1 and 2), of which 34 were identified. As a result of mixed peaks, 38 carotenoids were identified in the 34 peaks. The pigments were identified by means of cochromatography using authentic samples, various chemical tests (Matus et al., 1981), and UV−vis spectra.

During maturation, the changes of hydrocarbons, xanthophylls, and epoxy- and ketoxanthophylls are demonstrated in Figure 3. The different slopes of the curves show that the rates of accumulation in fruits, in decreasing order, are as follows: ketoxanthophylls, xanthophylls, epoxyxanthophylls, and hydrocarbons.

The percentage distribution of carotenoids is plotted against total carotenoid content in Figures 4 and 5. In the ripened fruits, capsanthin and zeaxanthin accounted for about 29 and 15% of the total, respectively, β-carotene and β-cryptoxanthin for about 9 and 5%, respectively, and cucurbitaxanthin A for about 6%. Numerous minor compounds were detected, such as violaxanthin, antheraxanthin, and capsanthin 5,6-epoxide, all containing a 5,6-epoxy end group, capsanthin 3,6-epoxide, cucurbitaxanthin B, and cycloviolaxanthin, all containing a 3,6-epoxy end group, karpoxanthin and latoxanthin, both containing a 3,5,6-trihydroxy end group, capsanthone, which contains a 3-oxo-κ end group, ni-

Table 2. Relative Carotenoid Content (Percent) of *C. annuum* Fruit at Six Stages of Maturation

peak no.	retention time, min	pigment	stage of maturation					
			green	pale yellow	yellow	orange	red	deep red
1[a]	7.2		0.89	0.94	0.34	0.25	0.12	0.18
2[a]	7.9		0.24	0.27	0.37	0.03	0.07	0.13
3	8.2	trihydroxy-κ	0.34	0.29	0.24	0.24	0.15	0.23
4[a]	8.6		0.0	0.15	0.06	0.06	0.0	0.06
5	9.5	latoxanthin	1.74	0.60	0.91	0.60	0.14	0.28
6[a]	10.0		0.06	0.86	1.11	0.14	0.08	0.11
7[a]	10.8	λ_{max}:[b] 439, 459 nm	4.89	2.06	1.26	0.0	0.45	0.70
8[a]	11.3	λ_{max}:[b] 443, 462 nm	1.41	5.09	0.0	0.0	0.0	0.0
9	11.3	capsorubin	0.0	0.0	2.77	2.72	1.97	2.59
10[a]	12.2	λ_{max}:[b] 443, 462 nm	1.51	4.50	1.34	0.35	0.32	0.44
11	13.1	neoxanthin	3.74	5.46	3.96	0.0	0.0	0.0
12	13.1	capsanthin 5,6-epoxide	0.0	0.0	1.32	2.51	1.46	1.87
13	13.7	karpoxanthin	1.37	0.31	1.38	1.76	1.34	1.53
14[a]	14.3	yellow mixture	1.82	0.81	0.60	0.29	0.58	0.57
15	14.7	violaxanthin	4.76	1.41	6.33	4.23	1.33	2.04
16[a]	15.3		1.22	0.0	0.0	0.0	0.0	0.0
17	15.3	capsanthin 3,6-epoxide	0.0	0.0	2.06	1.43	1.26	1.68
18	16.1	luteoxanthin 2[c]	3.62	3.35	2.05	0.56	0.83	1.11
19	16.5	luteoxanthin 1[c]	1.97	1.73	1.88	1.06	0.71	0.39
20	17.0	auroxanthin 2[c]	0.02	0.22	0.10	0.0	0.0	0.0
21	17.0	cucurbitaxanthin B	0.0	0.0	1.00	0.90	0.90	1.10
22	17.7	cucurbitachrome	0.0	0.0	2.00	0.78	3.50[d]	4.01[d]
23	18.0	capsanthin	0.92	1.26	24.60	28.23	29.25	28.34
24	18.8	auroxanthin 1[c]	0.03	0.59	0.10	0.0	0.0	0.0
25	18.8	capsanthone	0.0	0.0	0.10	0.37	0.40	0.44
26	19.2	λ_{max}:[b] 412, 438, 462 nm	2.94	3.40	1.92	0.0	0.0	0.0
27	19.2	cycloviolaxanthin	0.0	0.0	0.0	0.0	0.60	0.71
28	19.8	antheraxanthin	2.28	0.25	1.43	3.58	1.41	1.64
29	20.9	mutatoxanthin 2[c]	0.52	1.43	1.43	1.89	2.44	2.96
30	21.7	mutatoxanthin 1[c]	0.71	0.0	0.02	0.18	0.66	0.0
31	22.1	cucurbitaxanthin A	0.70	1.88	3.87	4.57	5.34	6.11
32	22.9	9-*cis*-capsanthin	0.50	0.12	1.32	0.96	1.84	1.43
33	23.5	13-*cis*-capsanthin	0.0	0.0	1.36	1.55	2.51	2.07
34	24.1	lutein	31.90	28.78	1.46	0.06	0.0	0.0
35	24.1	zeaxanthin	6.72	6.78	10.48	19.45	16.88	15.33
36[a]	24.7		0.11	0.0	0.03	0.02	0.0	0.0
37	25.1	nigroxanthin	0.13	0.52	0.32	0.34	0.59	0.65
38[a]	26.2		0.06	0.12	0.08	0.02	0.01	0.01
39	27.2	9-*cis*-zeaxanthin	2.94	2.29	0.78	0.45	0.38	0.32
40	27.8	13-*cis*-zeaxanthin	1.90	1.98	0.50	0.60	0.50	0.43
41	28.1	15-*cis*-zeaxanthin	0.33	0.38	0.11	0.0	0.10	0.09
42[a]	29.9		0.33	0.49	0.36	0.37	0.41	0.48
43[a]	30.9		0.0	0.05	0.07	0.24	0.16	0.28
44	31.5	cryptocapsin	0.26	0.26	0.26	0.79	0.53	0.76
45[a]	32.3		0.14	0.39	0.16	0.35	0.35	0.37
46[a]	32.9		0.04	0.07	0.10	0.05	0.10	0.18
47[a]	33.2		0.0	0.16	0.11	0.05	0.03	0.19
48	33.9	α-cryptoxanthin	0.98	1.83	0.59	0.32	0.31	0.26
49	34.3	β-cryptoxanthin	0.70	0.77	3.45	6.49	5.82	5.13
50	34.6	*cis*-cryptoxanthin	0.26	0.27	0.67	1.25	1.19	0.65
51	34.8	*cis*-cryptoxanthin	0.0	0.38	0.43	0.04	0.02	0.21
52[a]	35.0		0.02	0.04	0.39	0.05	0.24	0.26
53[a]	35.8		0.22	0.63	0.29	0.11	0.12	0.15
54[a]	36.4		0.23	0.39	1.24	0.91	0.85	0.70
55[a]	36.9		0.61	0.53	0.40	0.27	0.26	0.19
56[a]	37.6		0.28	0.47	1.13	0.60	0.53	0.48
57[a]	38.2		0.20	0.19	0.19	0.10	0.09	0.05
58[a]	38.9		0.31	0.37	0.29	0.21	0.28	0.19
59[a]	39.2		0.06	0.08	0.26	0.43	0.38	0.23
60	40.4	α-carotene	0.26	0.72	0.38	0.46	0.19	0.20
61	40.8	β-carotene	11.25	12.18	7.11	5.86	9.19	8.89
62	41.2	*cis*-β-carotene	1.39	1.54	0.96	0.87	0.79	0.60
		total carotenoid, mg/100 g of dw	11.54	16.80	44.75	132.73	610.69	994.71

[a] Unidentified. [b] λ_{max} in methanol. [c] The numbers indicate the adsorption affinities, in decreasing order, on a calcium carbonate column. [d] Shoulder, could not be detected exactly.

groxanthin, which contains a γ end group, capsorubin, cryptocapsin, and several furanoid oxides and cis isomers.

An abrupt change was noted in the pigment content, in both qualitative and quantitative terms. In the early stages of maturation, the carotenoids characteristic of yellow paprika are formed. In the unripe fruits, the main carotenoids are lutein and β-carotene. While the ratio of lutein decreases and disappears until the stage of disappearence of chlorophyll, β-carotene reaches a more or less constant value during ripening. Neoxanthin, luteoxanthin, and auroxanthin (originating from violaxanthin) have also been found in unripe states. These pigments could be found in yellow paprika *C. annuum lycopersiciforme flavum*) (Matus et al., 1991) but could not be detected in red paprika (Deli et al.,

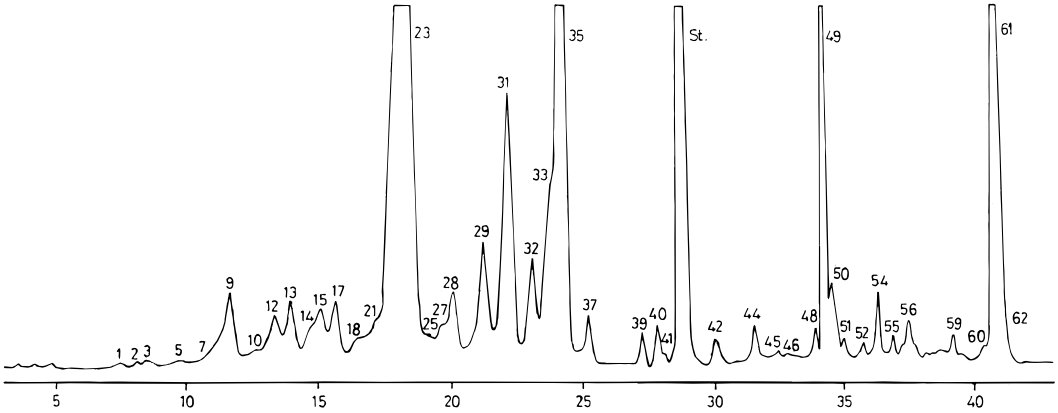
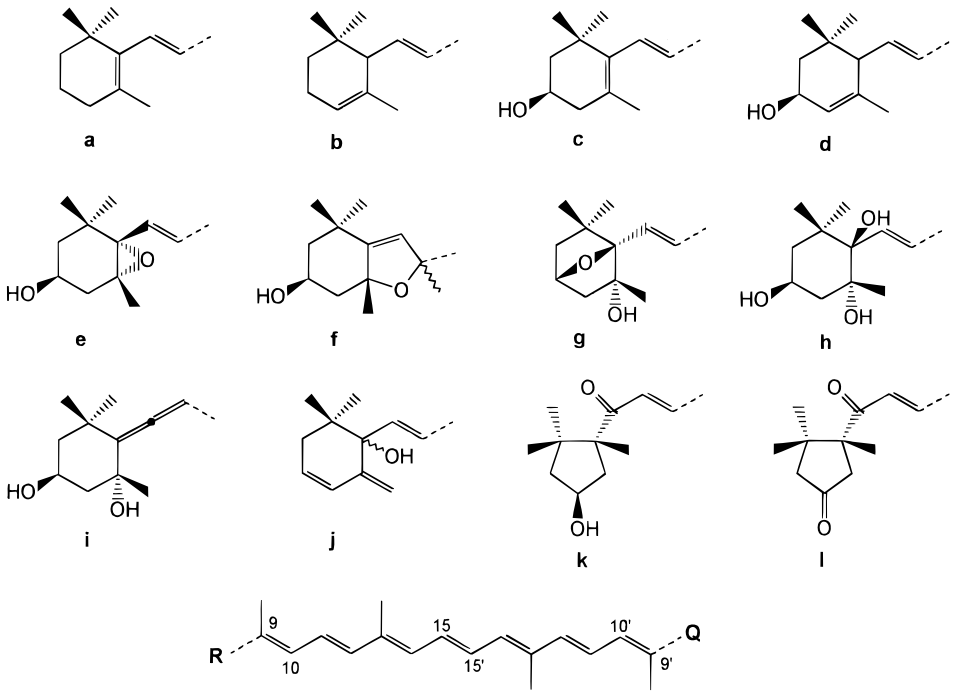


Figure 2. HPLC separation of carotenoids in ripe (deep red) paprika. Conditions: Chromsil C_{18} 6 μm end-capped, detection at 450 nm, other conditions as in the text. For peak numbers see Table 2. St., canthaxanthin (internal standard).

Chart 1[a]



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

1992). In the Kosszarvú variety, neoxanthin and auroxanthin were formed only in early stages, and they disappeared when the lutein disappeared. In the case of yellow paprika (*C. annuum lycopersiciforme flavum*), these pigments showed decreases of their percentage concentration similarly, but they did not disappear, and they could be found in the ripe fruits too.

In the first and second stages, the percentage concentration of α-cryptoxanthin was higher than that of β-cryptoxanthin. While the higher α-cryptoxanthin ratio was characteristic of the yellow paprika, in the red paprika the α-cryptoxanthin was detected only in traces, in all stages of maturation. In fruits of Kosszarvú variety the ratio of α- and β-cryptoxanthin changed, too, at the third stage, and the percentage concentration of α-cryptoxanthin began to decrease and of β-cryptoxanthin to increase as in the case of red paprika. The α-carotene could be detected in traces, in all different stages of maturation. This fact shows a similarity between the red paprika and the beginning of maturation of yellow paprika. The ratio of α-carotene and β-carotene changed from 0.06 to 1.39 during maturation in the yellow paprika (Matus et al., 1991).

When, at the third stage, the amount of lutein decreased considerably, the percentage concentration of capsanthin increased to a great extent. Similarly, from this stage the formation of capsorubin, capsanthin 3,6-epoxide, and capsanthin 5,6-epoxide could be observed. From this stage on, the violaxanthin (precursor of capsanthin 5,6-epoxide and capsorubin) and antheraxanthin (precursor of capsanthin) curve showed a moderate decrease, which was associated with the increase of capsanthin and capsorubin curve. It should be noted that the curves of antheraxanthin, violaxanthin, and capsanthin 5,6-epoxide are parallel to each other within measuring error.

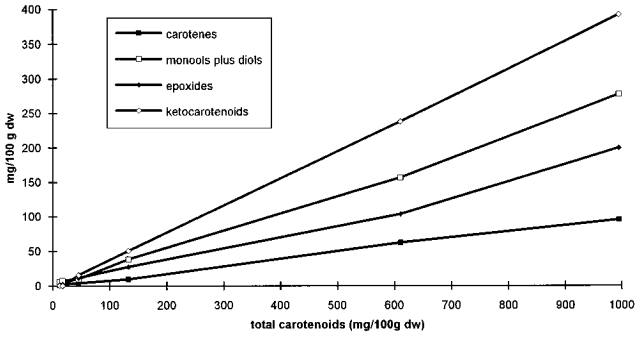


Figure 3. Pigment changes during ripening.

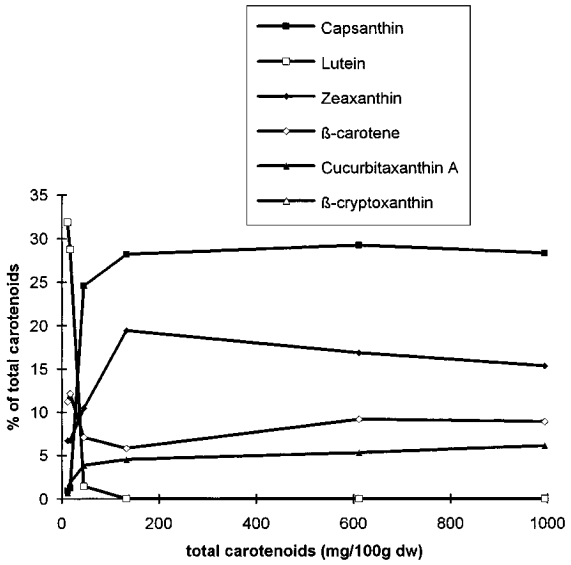


Figure 4. Changes in relative carotenoid content during ripening.

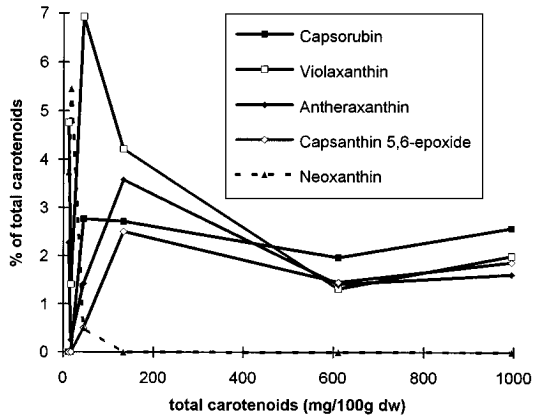


Figure 5. Changes in relative carotenoid content during ripening.

The changes of cis isomers in the fruits of Kosszarvú paprika are similar to those in yellow and black paprika during the process of ripening, so we assume that the cis isomers are likely to be "post-mortem artifacts".

In Table 2, it is demonstrated that furanoid oxides (auroxanthin, luteoxanthin, mutatoxanthin) are always present during the process of ripening too. In the ripe paprika, the epimers only of luteoxanthin and mutatoxanthin were identified. The ratio of mutatoxanthin epimers differs very much from what was found after acid treatment of antheraxanthin under laboratory conditions (Matus et al., 1991). It should be noted that the ratio of mutatoxanthin epimer 2 to mutatoxanthin epimer 1 was constant in yellow pepper during maturation. Therefore, we assume that the mutatoxanthin epimer 1 and some of the mutatoxanthin epimer 2 may have been post-mortem artifacts in this paprika. However, a stereospecific enzymatic action linked to the pinacol rearrangement of antheraxanthin cannot be ruled out in the formation of mutatoxanthin epimer 2. A similar ratio may be observed in the case of epimers of luteoxanthin.

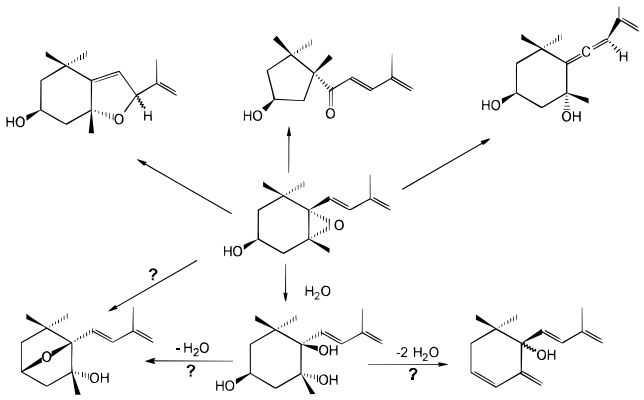


Figure 6. Possible formation of a variety of carotenoid end group from a 3-hydroxy-5,6-epoxy-5,6-dihydro-β-ring.

A number of previous investigations have reported a carotenoid, namely capsolutein. First, Curl (1962) found a diol, which he called capsolutein. Curl used the countercurrent distribution method for the separation of the pigments. He found about 30 carotenoids in red bell pepper, but these compounds were not characterized exactly. Curl used only UV−vis light spectrometry and chemical tests. In his opinion, capsolutein may be derived from capsanthin by replacing the carbonyl group with a methylene group. Other authors have suggested other structures for capsolutein, such as 3,3′-dihydroxy-5,8-dihydro-5,8-epoxy-β,κ-carotene originating from lutein (Mínguez-Mosquera and Hornero-Méndez, 1994a,b). However, to date, nobody has ever isolated capsolutein in crystalline form, and nobody has ever described the structure of capsolutein. In spite of this fact, the occurrence of capsolutein in the paprika has been reported several times (Almela et al., 1990, 1991).

We assume the capsolutein is identical with cucurbitaxanthin A containing 3,6-epoxy- (oxabicyclo[2.2.1]) end group, which have been isolated and its structure has been elucidated (Parkes et al., 1986). This identity is based on the similarity of the polarity, the UV−vis spectrum, and the percentage concentration of these two compouds. In addition, we have performed the systematic investigation of many different kinds of paprika, but we have never succeded in isolating the capsolutein. However, we have isolated and identified some other compounds with 3,6-epoxy end group, such as cucurbitaxanthin B, cycloviolaxanthin, capsanthin 3,6-epoxide (Deli et al., 1991, 1992). The 3,6-epoxy end group is formed from 5,6-epoxy end group via the 3,5,6-trihydroxy end group, in accordance with Figure 6. In this way, cucurbitaxanthin A may be formed from antheraxanthin via karpoxanthin, cucurbitaxanthin B may be formed from violaxanthin via latoxanthin, cycloviolaxanthin may be formed from violaxanthin via latoxanthin and mactraxanthin, and capsanthin 3,6-epoxide may be formed from capsanthin 5,6-epoxide via the trihydroxy-κ pigment (3,5,6,3′-tetrahydroxy-5,6-dihydro-β,κ-caroten-6′-one). We have obtained chemical evidence in support of the occurrence in paprika of some 3,5,6-trihydroxy compounds, such as karpoxanthin (peak

13; Parkes et al., 1986), [λ_{max} (in benzene) 487, 458, 434 nm, no furanoid reaction]; latoxanthin (peak 5; Märki-Fischer et al., 1984) [λ_{max} (in benzene) 483, 453, 428 nm; λ_{max} (in benzene after acid treatment) 460, 433, 409 nm]; and trihydroxy-κ pigment [3,5,6,3′-tetrahydroxy-5,6-dihydro-β,κ-caroten-6′-one, peak 3; λ_{max} (in benzene) 505, 480 nm, λ_{max} (in benzene after $NaBH_4$ reduction) 481, 451, 426 nm]. Full details of the determination of the structure of these minor carotenoids will be published elsewhere.

Although the formation of the 5,6-epoxy group, in the paprika, is well-known, the transformation of the 5,6-epoxy end group is not cleared up completely. We assume, while in the early ripening stages of red paprika, the formations of the 5,8-epoxy end group and the allenic 3,5-dihydroxy end group, characterizing neoxanthin, are operative and, later on, the pinacollic rearrangement resulting in the κ end group and the hydrolytic ring opening resulting in the 3,5,6-trihydroxy end group becomes dominant. Further transformations of the 3,5,6-trihydroxy end group result in the 5-hydroxy-3,6-epoxy and 3,4-didehydro-6-hydroxy-γ end groups. The plausible biosynthetic transformations of the 5,6-epoxy-β-ring are summarized in Figure 6.

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