Comparative Study of the Effect of Paprika Processing on the Carotenoids in Peppers (*Capsicum annuum*) of the *Bola* and *Agridulce* Varieties

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Reversed-phase HPLC has been applied to monitor changes in individual carotenoids during the industrial processing of paprika from two pepper varieties, *Bola* and *Agridulce*. The ripe fruit, dry fruit, and paprika from the *Agridulce* variety always show higher carotenoid content than those from the *Bola* variety. The different stabilities associated with each carotenoid in the industrial processing of paprika are mainly due to intrinsic factors of the variety rather than to processing factors. Whereas in the *Agridulce* variety the drying and milling stages propitiate a global carotenoid degradation, in the *Bola* variety carotenoid biosynthesis is detected during the drying step. This biosynthesis is associated with an incomplete maturation of fruit, in such a way that in the *Bola* variety the drying step induces the synthesis of red pigments from their yellow precursors already present in the fruit. This synthesis is not *de novo* but a transformation. Irrespective of the variety, red pigments always show greater stability than yellow pigments. The *Agridulce* variety is more suitable for paprika production since, as well as giving rise to a final product with a greater carotenoid pigment concentration and, therefore, with a more intense color, the final product also has a higher provitamin A content.

Keywords: *Paprika processing, dry peppers, peppers, carotenoid, xanthophyll, provitamin A, pigment stability, pigment degradation*

INTRODUCTION

The red color of ripe peppers (*Capsicum annuum* L.) is mainly due to the *de novo* synthesis of ketocarotenoids, principally capsanthin and capsorubin, which are peculiar to this genus (Curl, 1962; Davies et al., 1970; Camara and Moneger, 1978). At the same time, these fruits are also rich in other xanthophylls, such as zeaxanthin, β-cryptoxanthin, violaxanthin, and antheraxanthin, and in carotenes, principally β-carotene. Another characteristic feature of the fruit ripening is that, as the color changes, the carotenoid pigments responsible for the change undergo distinct degrees of esterification with different fatty acids (Curl, 1962; Baranyai et al., 1982). This process seems to confer on them a greater stability. As a result of this, any xanthophyll acquires a whole range of related products of esterification with the different fatty acids present in the pepper, different degrees of esterification of each one taking place at the same time.

In their natural environment the carotenoid pigments are fairly stable, but when the foodstuff is triturated or heated or when the carotenoids are extracted with oil or organic solvents, they become much more labile. Furthermore, while heat in general increases the rate of all reactions, the thermo-oxidative reactions are highly effective in thermal degradation of carotenoids.

The extent of color destruction, in large part, depends on the presence of oxidants (fundamentally molecular oxygen) and on there being a sufficient supply of energy for the degradation reaction to take place. The energy is supplied in the form of light or heat. The principal cause of the deterioration of the carotenoids is oxygenation, this being more severe once cellular integrity has been lost. The high degree of unsaturation of the carotenoids makes them particularly sensitive to light, heat, and oxygen (De la Mar and Francis, 1969; Kanner and Mendel, 1976; Carnevale et al., 1980; Malchev et al., 1982). During storage and processing of foodstuffs, the type of pretreatment and the temperatures to which they are subjected are particularly significant in determining the stability of the final product.

The combination of all the industrial operations involved in the production of paprika can provoke destruction of some of the components initially present in the fruit, affecting especially that fraction containing the carotenoids, these being the compounds which are wholly responsible for the final quality of the paprika (Lease and Lease, 1956, 1962; Salmerón, 1973).

A previous study (Mínguez-Mosquera et al., 1992) showed that in varieties of peppers from Murcia, Spain, the relative proportions of the principal pigment fractions, irrespective of the variety used, remained constant within the limits of variability expected for a natural product. This was also true for laboratory-produced paprika. However, when the pigment fractions were measured in commercial paprika, it was found that in some cases the aforementioned relationships varied, as a result of the degradation of pigments during the process of paprika production or the subsequent storage.

A subsequent study on the *Bola* and *Agridulce* varieties from the Vera zone (Cáceres, Spain), which examined only the carotenes and the esterified xanthophylls (Mínguez-Mosquera et al., 1993), showed that the stability of the paprika color depended to a great extent on the variety of pepper used, the yellow fraction being more unstable than the red fraction.

In the present study similar determinations have been performed using the same varieties but examining all of the carotenoid pigments individually, using a previously developed HPLC method (Mínguez-Mosquera and Hornero-Méndez, 1993).

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MATERIALS AND METHODS

Samples. The study was performed on peppers (*C.annuum* L.) of the *Bola* (*grossum*) and *Agridulce* (*longum*) varieties, harvested in Comarca de La Vera (Cáceres, Spain) and processed by the Spanish companies Netasa (Plasencia) and Tiburcio Pérez Trancón (Cuacos de Yuste). Fruits of the *Bola* variety are more or less spherical with a diameter between 4 and 6 cm and weight between 15 and 30 g. Fruits of the *Agridulce* variety are long, being between 15 and 25 cm long with a diameter of some 3 cm, and weigh between 15 and 25 g. Three different types of samples were taken of each variety, according to the processing stage: ripe red pepper, red pepper which had been dried, and the corresponding paprika obtained by milling the previously dried fruits. From the fresh and dried fruit 1-kg samples free of seeds and peduncles were taken, while 250-g samples were obtained from the paprika.

High-Performance Liquid Chromatography. For HPLC analysis a computerized Perkin-Elmer system was used with a Series 4 quaternary pump. This was equipped with a Perkin-Elmer Model LC-85B UV–vis detector and a Hewlett-Packard Model 3396-A integrator. The chromatograph was fitted with a Model 7125 Rheodyne injection valve and a 5-μL injection loop. A reversed-phase C_{18} column packed with Spherisorb ODS 2 (5 μm, 25 cm × 4 mm i.d.), supplied by Hewlett-Packard, was used. A precolumn (1 cm × 4 mm i.d.) of the same material protected the main column. Detection was performed at 450 nm.

Pigment Extraction. The process has already been described in previous publications (Mínguez-Mosquera and Hornero-Méndez, 1993). Ten grams was taken from representative samples of pepper that had been minced and homogenized. In the case of dried samples and paprika 1.5 g was used. Each sample was subjected to extraction in a homogenizer (Ultra-Turrax) with 50 mL of acetone. This treatment was repeated several times until no more color was extracted. All extracts from the same sample were pooled in a separating funnel and treated with 100 mL of ethyl ether. The funnel was then shaken and left to stand. Subsequently, a sufficient amount of 10% (w/v) NaCl solution was added to effect the separation of the phases. The ether phase containing the pigments was treated several times with a 2% (w/v) solution of anhydrous Na_2SO_4 to remove all of the water that remained. The ether phase containing the carotenoid pigments in different stages of esterification with fatty acids was saponified by adding 100 mL of 20% (w/v) KOH–MeOH. The mixture was allowed to stand for 1 h with occasional shaking. Once the aqueous phase had been removed, the organic layer was washed with distilled water. Washing was repeated several times until the washings were neutral. When this point had been reached, the organic layer was filtered through a bed of anhydrous Na_2SO_4 and then evaporated to dryness at 35 °C in a rotary evaporator. The residue was taken up in 25 mL of acetone and stored in the refrigerator until its subsequent analysis by HPLC.

Pigment Identification. Identification of pigments has been described in detail in a previous publication (Mínguez-Mosquera and Hornero-Méndez, 1993) and consists of separation of pigment by TLC and cochromatography with purified pigments; observation of the pigment color on TLC plates under white, UV_{254nm}, and UV_{360nm} lights with a Desaga UV–vis lamp; recording of UV–visible spectra in different solvents with a Hewlett-Packard UV–vis diode array spectrophotometer Model 8452A; and comparison with the values reported in the literature (Foppen, 1971; Davies, 1976; Davies and Köst, 1988). 5,6-Epoxide groups were investigated by addition of 2% (v/v) HCl in EtOH; carbonyl and hydroxyl groups were investigated by FT-IR spectroscopy using a Bio-Rad FTS-7 IR spectrophotometer and also by acetylation with Ac_2O/Py to test for hydroxyl groups and by reduction with $NaBH_4$ in EtOH to test for carbonyl groups.

Separation and Quantification of Pigments by HPLC. The separation and quantification of carotenoid pigments by HPLC was realized according to the method of Mínguez-Mosquera and Hornero-Méndez (1993), using a reversed-phase C_{18} column and binary gradient elution with water and acetone as eluents at a flow rate of 1.5 mL/min. Detection was carried out at 450 nm. Quantification was realized using the internal standard method with β-apo-8′-carotenal as the standard, this pigment being absent from the pepper. The response factors as a function of the standard for each pigment have been given in a previous publication (Mínguez-Mosquera and Hornero-Méndez, 1993).

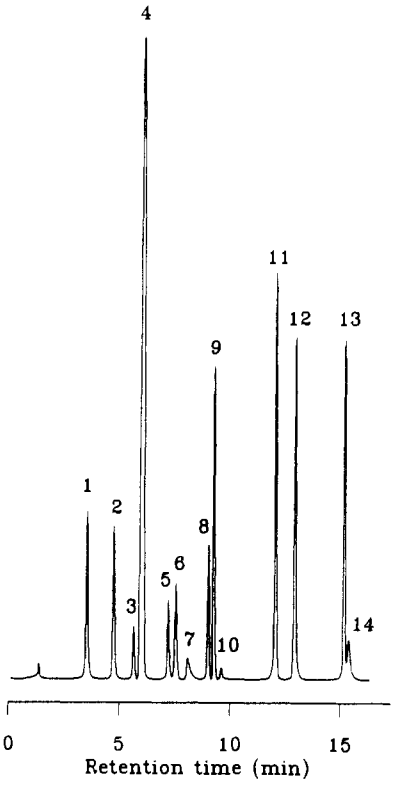

Figure 1. Reversed-phase HPLC of saponified extract of carotenoid pigments from ripe fruit peppers of *Bola* variety. Peak identity: 1, capsorubin; 2, violaxanthin; 3, capsanthin 5,6-epoxide; 4, capsanthin; 5, antheraxanthin; 6, *cis*-capsanthin; 7, mutatoxanthin; 8, capsolutein; 9, zeaxanthin; 10, *cis*-zeaxanthin; 11, β-apo-8′-carotenal (internal standard); 12, β-cryptoxanthin; 13, β-carotene; 14, *cis*-β-carotene.

Reagents. All of the reagents used in the development and application of the HPLC method were of HPLC grade. For all other purposes analytical grade (ACS) reagents were employed. The solvents used for HPLC were Me_2CO and deionized water, both of which were filtered through a 0.45-μm membrane and degassed prior to being used.

RESULTS AND DISCUSSION

Pigments Present in the Ripe Fresh Fruit, Dry Fruit, and Paprika. Figure 1 shows the HPLC chromatogram of a saponified extract of pigments from fresh fruit. Similar chromatograms were obtained from carotenoid extracts of dry pepper and paprika, being in agreement with a previous work (Mínguez-Mosquera and Hornero-Méndez, 1993). The carotenoids monitored were β-carotene, zeaxanthin, β-cryptoxanthin, capsanthin, capsanthin 5,6-epoxide, capsorubin, capsolutein, antheraxanthin, and violaxanthin. Those pigments are normally present in the greatest quantities in the fresh fruit and are, therefore, chiefly responsible for the color.

Quantitative Changes in the Carotenoid Composition during Industrial Processing of Paprika. Table 1 shows the changes in the red and yellow pigment fractions and in the total carotenoids as well as the moisture content during the different processing stages. All results are expressed on a dry matter basis, allowing direct comparisons to be made. In this way, the effects of the different processing stages on the initial carotenoid content could be determined.

The *Agridulce* variety always showed a higher pigment content than the *Bola* variety. This observation is in

Table 1. Changes in the Red Pigments Fraction, Yellow Pigments Fraction and Total Carotenoid Content during Prapika Processing (Comparison between *Bola* and *Agridulce* Varieties)

	concentration						percentage of loss during		
	fresh fruit		dry fruit		paprika				
pigment	mg/kg[a]	%[b]	mg/kg	%	mg/kg	%	drying	milling	total
			Bola Variety						
red pigments	2627.93 ± 222.01[c]	56.58	3748.19 ± 225.75	74.70	2109.71 ● 125.08	77.93	−40.23	43.71	21.07
yellow pigments	2051.22 ± 184.09	43.42	1262.47 ± 125.67	25.30	597.48 ± 60.27	22.07	38.45	52.67	70.87
total carotenoids	4724.15 ± 406.10		5017.66 ± 351.42		2707.19 ± 185.35		−6.21	46.05	42.69
moisture (%)		86		9		3			
			Agridulce Variety						
red pigments	4565.38 ± 220.80	63.74	4266.59 ± 254.32	63.80	2130.21 ± 90.91	67.14	6.54	50.07	53.34
yellow pigments	2597.12 ± 172.92	36.26	2420.86 ± 167.78	36.20	1042.57 ± 53.70	32.86	6.78	56.93	59.86
total carotenoids	7162.50 ± 393.72		6687.45 ± 422.10		3172.78 ± 144.61		6.63	52.55	55.70
moisture (%)		88		10		3			

[a] Expressed on the basis of dry matter. [b] Percentage composition. [c] Average ± standard deviation of eight determinations.

accordance with that made during a previous study on the changes in the photosynthetic pigments during ripening of fruits of both of these varieties (Mínguez-Mosquera and Hornero-Méndez, 1994) as well as with the observations made on the changes in the concentrations of β-carotene and the major esterified xanthophylls during paprika processing (Mínguez-Mosquera et al., 1993). In the latter work a clear difference was observed between the two varieties during the drying step, an increase of the pigment concentration being observed in the *Bola* variety. The authors suggested that this increase could be due to either esterification during drying of the nonesterified pigment, which was not measured, leading to an increase in the total concentration, or *de novo* synthesis.

In the present study, in which the individual carotenoid pigments were monitored, synthesis of pigments was observed in the *Bola* variety during the drying phase. This synthesis of pigments should not be attributed completely to *de novo* synthesis, since the net content of pigments increases from 4724.15 to 5017.66 mg/kg (an increase of 6.21%), but rather to a conversion of the existing yellow pigments into red pigments by the same metabolic pathways as those operating during normal biosynthesis. This would explain the increase in the red pigment fraction (1120 mg/kg) at the expense of the yellow fraction (decreasing 789 mg/kg), indicating that the fruits were not completely ripe and that, consequently, they underwent further ripening during the drying process to which they were submitted. In contrast, in the *Agridulce* variety the pigment content falls from 7162.50 to 6687.45 mg/kg, which may be usual in mild conditions of drying. This would seem to indicate that in these fruits no net synthesis of pigments has occurred during this step.

To elucidate the differences in the carotenoid composition of the two varieties studied arising from the processing, each pigment was monitored. The individual concentrations of the major pigments present in the *Bola* and *Agridulce* varieties, as well as the percentage losses during each stage (drying and milling) and during the process as a whole, are shown in Tables 2 and 3, respectively. In both varieties capsanthin was the pigment present in the greatest concentration in all stages of the process. In the fresh fruit this pigment is followed in order of decreasing concentration by β-carotene, zeaxanthin, β-cryptoxanthin, and capsorubin, irrespective of the variety.

The concentrations of β-carotene, β-cryptoxanthin, and zeaxanthin can be seen to decrease by 40% (this loss taking in the total degradative losses due to drying), while at the same time antheraxanthin, the 5,6-monoepoxy derivative of zeaxanthin and precursor of capsanthin, increases in concentration together with capsanthin and capsanthin 5,6-epoxide. Similarly, violaxanthin (precursor of capsorubin) decreases while capsorubin increases (Davies et al., 1970).

Capsolutein also shows a great increase, which could indicate that its synthesis is related to that of capsanthin and capsorubin. It has also been shown in a previous publication (Mínguez-Mosquera and Hornero-Méndez, 1994) that there is a striking difference between varieties of peppers with respect to their capsolutein contents. Thus, in the *Bola* variety this pigment is present in concentrations similar to, or even greater than, those of zeaxanthin, while in the *Agridulce* variety the concentration of zeaxanthin is invariably higher. This fact also demonstrates that in the *Bola* variety synthesis of pigments takes place, since in the fruits which are considered to be mature the concentration of capsolutein is lower than that of zeaxanthin. This difference, however, disappears during drying. In the present study the percentage of red pigments in the fresh fruit (56.68%, Table 1) is somewhat lower than the corresponding value (69.42%) reported for fully ripe fruit in other studies (Mínguez-Mosquera and Hornero-Méndez, 1994). This difference supports the suggestion that the fruits used in this study were not completely ripe. Furthermore, the value of 74.70% for the total red pigments in the dry fruit demonstrates that the synthesis of these pigments occurred at the expense of the yellow pigments. Since there was no synthesis of the latter, the equilibrium between the red and yellow pigments existing in the normal fruit breaks down.

With respect to the *Agridulce* variety (Table 3), during drying some pigments show an increase in concentration—β-cryptoxanthin, zeaxanthin, antheraxanthin, and, above all, capsolutein—which would again seem to suggest that their synthesis is more complicated than that of capsanthin or capsorubin and, therefore, that it occurs later. In this variety the percentages of total red and yellow pigments did not change as a result of drying, indicating that the peppers were ripe prior to undergoing drying. The reason fruits of the *Bola* variety are harvested before they are completely ripe is due, in part, to the farmers' worries that adverse weather conditions could destroy the harvest. The thickness of the flesh of the *Bola* variety (5–8 mm) in comparison to that of the *Agridulce* variety (2–3 mm) means that in the former the fruit does not ripen uniformly, although externally it may appear to do so. This does not occur in the *Agridulce* variety since, as well as having a thinner flesh, it has a larger surface area, which facilitates rapid and uniform ripening.

The fact that there is an interconversion of pigments in the *Bola* variety means that it is impossible for us to draw many conclusions as to the influence of the drying process

Table 2. Quantitative Changes in the Carotenoid Composition and Provitamin A Content during the Processing of Paprika from Fruits of the *Bola* Variety

	concentration						percentage of loss during		
	fresh fruit		dry fruit		paprika				
pigment	mg/kg[a]	%[b]	mg/kg	%	mg/kg	%	drying	milling	total
capsorubin	313.07 ± 8.90[c]	6.63	362.48 ± 31.22	7.27	176.64 ± 20.58	6.53	−15.78	51.27	43.58
violaxanthin	295.43 ± 36.49	6.25	189.13 ± 26.81	3.77	112.20 ± 12.71	4.15	35.98	40.68	62.02
capsanthin 5,6-epoxide	233.07 ± 23.68	4.93	238.10 ± 18.37	4.75	123.35 ± 10.08	4.56	−2.16	48.19	47.08
capsanthin	1885.73 ± 167.89	39.92	2796.61 ± 158.10	55.79	1602.36 ± 83.22	59.20	−48.30	42.70	15.03
antheraxanthin	129.64 ± 13.11	2.74	141.60 ± 11.19	2.82	98.75 ± 7.16	3.65	−9.23	30.26	23.83
capsolutein	241.21 ± 21.54	5.11	351.05 ± 18.01	7.00	207.27 ± 11.20	7.65	−45.54	40.96	14.07
zeaxanthin	528.29 ± 58.38	11.18	312.39 ± 33.69	6.23	178.03 ± 14.21	6.58	40.87	43.02	66.31
β-cryptoxanthin	382.71 ± 34.61	8.10	239.18 ± 16.88	4.76	80.80 ± 4.79	2.98	37.50	66.22	78.89
β-carotene	715.00 ± 41.50	15.13	387.11 ± 37.10	7.71	127.15 ± 6.44	4.70	45.86	67.15	82.22
provitamin A[d]	1529.84 ± 99.74		856.51 ± 76.75		283.31 ± 14.96		44.01	66.92	81.48

[a] Expressed on the basis of dry matter. [b] Percentage composition. [c] Average ± standard deviation of eight determinations. [d] Expressed as IU of provitamin A/kg dry of weight × 10^3 = 1667 (mg of β-carotene) + 883 (mg of β-cryptoxanthin)/kg dry of weight × 10^3.

Table 3. Quantitative Changes in the Carotenoid Composition and Provitamin A Content during the Processing of Paprika from Fruits of the *Agridulce* Variety

	concentration						percentage of loss during		
	fresh fruit		dry fruit		paprika				
pigment	mg/kg[a]	%[b]	mg/kg	%	mg/kg	%	drying	milling	total
capsorubin	455.25 ± 4.78[c]	6.36	381.16 ± 16.87	5.70	217.44 ± 11.33	6.85	16.27	42.95	52.24
violaxanthin	227.33 ± 30.24	3.17	200.61 ± 22.84	3.00	123.96 ± 4.14	3.91	11.75	38.21	45.47
capsanthin 5,6-epoxide	311.58 ± 25.11	4.35	223.45 ± 15.96	3.34	117.02 ± 6.61	3.69	28.28	47.63	62.44
capsanthin	3444.67 ± 178.30	48.09	3242.16 ± 198.26	48.48	1590.20 ● 60.60	50.12	5.88	50.95	53.84
antheraxanthin	145.08 ± 20.76	2.03	147.67 ± 25.46	2.21	97.80 ± 8.93	3.08	−1.79	33.77	32.59
capsolutein	353.83 ± 12.61	4.94	420.02 ± 23.23	6.28	205.40 ± 12.37	6.47	−18.71	51.10	41.95
zeaxanthin	721.84 ± 56.14	10.08	730.43 ± 51.63	10.92	318.54 ± 15.51	10.04	−1.19	56.39	55.87
β-cryptoxanthin	578.83 ± 28.97	8.08	629.40 ± 40.82	9.42	199.95 ± 13.71	6.30	−8.74	68.23	65.46
β-carotene	924.08 ± 36.81	12.90	712.54 ± 27.12	10.65	302.47 ± 11.41	9.54	22.89	57.55	67.27
provitamin A[d]	2051.55 ± 86.94		1743.56 ± 36.04		680.77 ± 31.12		15.01	60.96	66.82

[a] Expressed on the basis of dry matter. [b] Percentage composition. [c] Average ± standard deviation of eight determinations. [d] Expressed as IU of provitamin A/kg dry of weight × 10^3 = 1667 (mg of β-carotene) ± 883 (mg of β-cryptoxanthin)/kg dry of weight × 10^3.

on pigment stability in this variety. However, it is possible that what occurs in the *Agridulce* variety can be extrapolated to the *Bola* variety at an optimum stage of ripeness. In this variety during drying there is a decrease in the concentration of every pigment. Nevertheless, approximately the same percentage composition is maintained, which indicates that no one pigment is affected by the process more than others.

During the milling stage, in both varieties there is a sharp decrease in the pigment concentration. This is undoubtedly due to two causes. On the one hand, the dilution may be due to the addition of a high proportion of seeds (between 45 and 50% of weight), which is a normal practice at this stage of the industrial process. The extent of this addition is estimated, taking capsanthin as the reference (Mínguez-Mosquera et al., 1993). Capsanthin, being the more stable pigment, is least affected by the process, and so any decrease in its concentration is taken to be due to dilution by the seeds. Using these premises it can be deduced that there is a 51% addition of seeds to the *Agridulce* variety and a 43% addition to the *Bola* variety. On the other hand, the decrease in the carotenoid pigment concentration will be in part due to the effect of the milling process on the stability of each pigment. Examining the percentage composition in the dry and milled states, especially in the *Agridulce* variety, shows that it is principally the yellow pigments which exhibit a decrease, while there is a corresponding increase in the percentage of red pigments. This leads one to believe that the yellow pigments are less stable than the red pigments and so are affected to a greater extent by the milling process.

Effect of Paprika Processing on the Pigment Stability. An examination of the overall process also shows that the yellow pigments are degraded to a greater extent than the red pigments and that, among the former, β-carotene is the most unstable followed by β-cryptoxanthin and finally zeaxanthin. As other authors (Biacs et al., 1989) have observed, the esterified pigments have a greater degree of stability in comparison with the free forms. This fact accounts for the observed order of stability, since β-carotene cannot occur in an esterified form, β-cryptoxanthin can occur in the free form or in the monoesterified form, and zeaxanthin can occur in the free, the monoesterified, or even the diesterified forms. Among the red pigments capsanthin and capsorubin appear to be the most stable, these also occurring in the free, monoesterified, and, more often, diesterified forms. These conclusions can easily be drawn from the results from the *Agridulce* variety. Fruits of the *Bola* variety, however, not being completely ripe at the start of the process, do not provide a suitable reference for assessing the overall process, since, as well as pigments being synthesized during the drying stage, there was probably also esterification of the pigments thus formed.

Table 4 shows the principal relationships among the pigments as a function of the stage of processing. By examining the data, it is possible to deduce the stability of some pigments in comparison to others as a function of the stages of the process and independently of the possible dilutions occurring as a result of the addition of seeds. In previous studies (Mínguez-Mosquera et al., 1993), this has been done by overall quantification of the red and yellow fractions as well as by examining the relationships between these two. In the present study, due to the fact that the individual pigments have been measured, it is possible to study the relationships among each of them and, therefore, their comparative stabilities.

Table 4. Changes in the Carotenoid Pigment Ratios during Paprika Processing (Comparative Stability of Pigments According to Variety)

	Bola variety			*Agridulce* variety		
pigment ratio	fresh	dry	paprika	fresh	dry	paprika
β-carotene/						
β-cryptoxanthin	1.87	1.62	1.57	1.60	1.13	1.51
zeaxanthin	1.37	1.24	0.71	1.28	0.98	0.95
violaxanthin	2.42	2.05	1.13	4.06	3.55	2.44
capsanthin	0.38	0.14	0.08	0.27	0.22	0.19
capsorubin	2.28	1.07	0.72	2.03	1.87	1.39
capsolutein	2.96	1.10	0.61	2.61	1.70	1.47
β-cryptoxanthin/						
zeaxanthin	0.72	0.77	0.45	0.80	0.86	0.63
violaxanthin	1.30	1.26	0.72	2.55	3.14	1.61
capsanthin	0.20	0.09	0.05	0.17	0.19	0.13
capsorubin	1.22	0.66	0.46	1.27	1.65	0.92
capsolutein	1.59	0.68	0.39	1.64	1.50	0.97
xeaxanthin/						
violaxanthin	1.79	1.65	1.59	3.18	3.64	2.57
capsanthin	0.28	0.11	0.11	0.21	0.23	0.20
capsorubin	1.69	0.86	1.01	1.59	1.92	1.46
capsolutein	2.19	0.89	0.86	4.98	4.95	3.26
violaxanthin/						
capsanthin	0.07	0.06	0.08	0.16	0.07	0.07
capsorubin	0.50	0.53	0.57	0.94	0.52	0.64
capsolutein	0.64	0.48	0.60	1.22	0.54	0.54
capsanthin/						
capsorubin	6.02	7.72	9.07	7.57	8.51	7.31
capsolutein	7.82	7.97	7.73	9.74	7.72	7.74
capsorubin/						
capsolutein	1.30	1.03	0.85	1.29	0.91	1.06
total yellow/						
β-carotene	2.87	3.28	4.69	2.81	3.39	3.44
β-cryptoxanthin	5.36	5.31	7.39	4.49	3.85	5.21
zeaxanthin	3.88	4.06	3.35	3.60	3.31	3.27
violaxanthin	6.94	6.71	5.32	11.42	12.07	8.41
capsanthin	1.09	0.45	0.37	0.75	0.75	0.66
capsorubin	6.55	3.50	3.38	5.70	6.35	4.80
capsolutein	8.50	3.62	2.88	7.34	5.76	5.08
total red/						
β-carotene	3.74	9.68	16.59	4.94	5.99	7.04
β-cryptoxanthin	6.98	15.67	26.11	7.89	6.78	10.66
zeaxanthin	5.06	12.00	11.85	6.32	5.84	6.69
violaxanthin	9.05	19.82	18.80	20.08	21.27	17.19
capsanthin	1.42	1.34	1.32	1.33	1.32	1.34
capsorubin	8.54	10.34	11.94	10.03	11.19	9.80
capsolutein	11.08	10.68	10.18	12.90	10.16	10.37
total red/total yellow	1.30	2.95	3.53	1.76	1.76	2.04

The yellow pigments can be seen to decrease more than the red pigments during the whole process. While in the *Agridulce* variety the red:yellow ratio increases gradually, in the *Bola* variety this increase is very sharp. This difference is in part due to the greater stability of the red pigments and in part due to the fact that, as the synthesis of red pigments takes place at the expense of the yellow pigments during the drying stage, the ratio increases more. The fact that the ratio of β-carotene to the other pigments decreases again demonstrates that it is the least stable of the yellow pigments, followed by β-cryptoxanthin and zeaxanthin in order of increasing stability. Capsanthin and capsorubin appear to have similar degrees of stability. Capsolutein is somewhat more stable than the latter two pigments, although this observation is influenced by the fact that, in both varieties, capsolutein is synthesized during the drying process. In summary, it can be concluded that the red pigments are more stable than the yellow pigments.

Effect of the Processing of Paprika on the Provitamin A Content. As ripe red peppers have high concentrations of β-carotene and β-cryptoxanthin, both of which have provitamin A activity, this fruit can be considered to be rich in this provitamin. In the present work the observations of a previous publication (Mínguez-Mosquera and Hornero-Méndez, 1994) are confirmed; i.e., the *Agridulce* variety has a higher provitamin A content than the *Bola* variety.

Since during the manufacture of paprika the carotenoid pigments, especially the yellow pigments which include β-carotene and β-cryptoxanthin, are degraded, the provitamin A value will also decrease during processing. As can be seen in Tables 2 and 3, during the drying stage the *Agridulce* variety suffers a 15.01% loss of provitamin A activity, whereas the *Bola* variety shows a 44.01% loss. This enormous difference is due to the synthesis of red pigments in the *Bola* variety at the expense of their yellow precursors. This process leads to a sharp decrease in the concentrations of both β-cryptoxanthin and, especially, β-carotene. As a result, the provitamin A content also decreases. During the milling stage the decreases in the provitamin A values are similar in both varieties—60.96% in *Agridulce* and 66.92% in *Bola*. This is explained by the fact that there are similar losses of those carotenoids having provitamin A activity in both varieties during this stage. As a result of both stages in the overall process, *Agridulce* loses 66.82% of its initial provitamin A content and *Bola* loses 81.48%.

It can be concluded that fruits of the *Agridulce* variety are more suitable for paprika production since, as well as giving rise to a final product with a greater carotenoid pigment concentration and, therefore, with a more intense color, the final product also has a higher provitamin A content.

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