Influence of the Industrial Drying Processes of Pepper Fruits (*Capsicum annuum* Cv. *Bola*) for Paprika on the Carotenoid Content

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The effects of drying pepper fruits of the *Bola* variety during paprika elaboration on their initial carotenoid content have been studied by comparing two industrial drying processes, slow drying by wood combustion and fast drying using hot air. The main carotenoids in the fruits were quantified before and after both industrial drying processes. The drying system with wood combustion provokes an increase in the concentration of some pigments, which could be interpreted as reflecting synthesis. During fast drying there was no increase in the concentration of any pigment so that only the degradative losses were measurable. The importance of the drying stage is evident since, depending on the temperature and time employed, either an increase in the concentration of some pigments or a decrease due to degradation will be favored.

INTRODUCTION

The pepper (*Capsicum annuum* L.) is an annual herbaceous plant belonging to the Solanacea family. The fruit is a rounded or elongated berry, depending on the variety. The ripe, fleshy pericarp matures together with the fruit, until it loses its entire content of chlorophyll and develops a high concentration of carotenoids with different levels of esterification (Camara and Monéger, 1978; Philip and Chen, 1988). The uniqueness of the carotenoids present in this fruit provoked considerable interest during the 1960s and 1970s in the carotenogenic pathways (Curl, 1962; De la Mar and Francis, 1969; Philip and Francis, 1971). As a result, the pathways studied were elucidated, at least in general terms (Davies et al., 1970; Isler, 1971; Davies, 1976). The carotenoid content in some varieties of peppers reaches exceptionally high concentrations, making profitable its use as a colorant only. The number of varieties that can be used for this purpose have gradually increased by a process of genetic improvement aimed at achieving the ideal variety for each type of cultivation and for each particular desired end.

The products manufactured from the paprika pepper can be separated into two large groups, paprika and oleoresins. A great diversity of types of paprika exists depending on the variety of the fruit and the manufacturing process used.

The drying step is the most important stage, determining the final quality of the product. Depending on the industrial process employed, the product develops particular characteristics. Those products obtained from oven-dried fruits and those obtained by drying with wood smoke are worthy of mention. With the first process, the characteristics of the product are similar to those of the fresh fruit and have a residual toasted flavor. With the second one, a slow drying provoked by a weak but constant flame heats the fruits to no more than 30 °C while impregnating them with their characteristic smoked smell and flavor. The paprika imparts its characteristic flavor, along with its color, to the product on which it is used; hence, it is known as smoked paprika (Zapata et al., 1992).

The paprika market is, at present, satisfied by paprika produced by these two types of manufacturing processes, although the oven-dried variety dominates. The process probably affects more than just the organoleptic characteristics. Each of the manufacturing processes has its a priori advantages and disadvantages that inevitably have an important effect on the stability of the quality of the final product. Thus, one disadvantage of rapid oven drying is the high temperatures reached (Ramakrishama and Francis, 1973). Slow drying using wood smoke can present the disadvantage of producing degradative processes associated with the postharvesting physiology as well as rotting arising from breakage, infection, etc. The possible color stability produced by drying at low temperatures can be diminished by the presence of highly reactive chemicals formed during the smoking process, but these can provide an efficient protection against infections.

During milling, it is usual to add a certain amount of inert matter, usually pepper seeds, corn, etc. (Zapata et al., 1992). This industrial practice, far from being fraudulent, is the normal procedure to enhance the characteristics of the product. The high degree of dehydration reached, the rheology of the product, and the high concentrations of existing pigments give pure paprika a dark earthy appearance, not at all like the attractive red color of the parent fruit. It is therefore normal to resort to dilution with seeds with a certain proportion of oil so that, as well as reducing and standardizing the color content, part of the pigment is extracted, giving the product more brightness and color. All of these factors should be taken into account if the maximum benefit is to be achieved from each variety and each process.

A previous study on the evolution of the principal esterified carotenoids of peppers during the manufacture of paprika has shown the losses that occur in the pigment content during the process and, only in peppers from the *Bola* variety, the increase in the concentration of diesterified capsanthin and capsorubin (Mínguez-Mosquera et al., 1993). The aim of the present work was to evaluate the effects of the different steps of paprika processing on pigment degradation and to elucidate the possible biosynthesis of carotenoids during drying. For this purpose the concentrations of the principal carotenoid pigments have been measured in fruits subjected to two distinct types of drying and in their respective paprikas.

MATERIALS AND METHODS

Raw Material Used. Fresh fruits of the *Bola* variety in the red mature stage, cultivated in the Vera zone (Cáceres, Spain), were used. From these same fresh fruits, samples of the oven-

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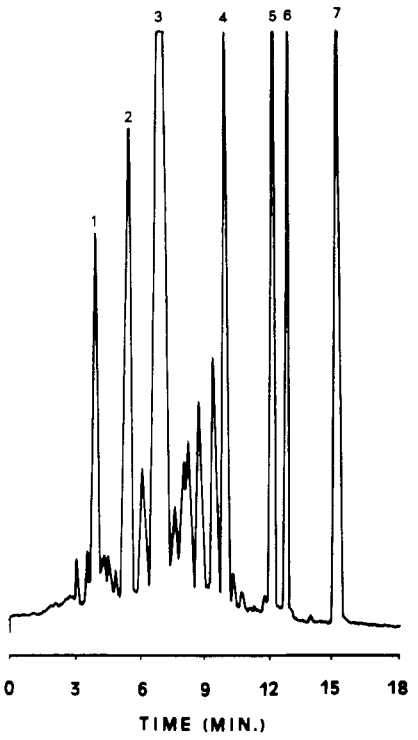

Figure 1. Chromatogram of the pigment extract from fresh pepper fruits of the *Bola* variety. Peaks: 1, capsorubin; 2, violaxanthin; 3, capsanthin; 4, zeaxanthin; 5, internal standard; 6, cryptoxanthin; 7, β-carotene.

dried and smoke-dried peppers, as well as their corresponding paprikas, were provided by the factory Netasa.

Sampling. Sampling was performed on lots of approximately 10 kg of fresh fruit and on 1 kg of dried fruit and paprika from each batch. Random subsamples of 200 g of the fresh fruit were homogenized, and from these homogenates, quadruplicate samples of some 10.000 g were used for pigment analysis. In the case of the dehydrated samples—dried peppers and paprika—a similar procedure was followed, except that samples of some 1.500 g were taken so as to approximate their dry matter content to that of the fresh fruit. In all samples the dry matter content was determined.

Pigment Extraction. Extraction was performed with acetone until the complete disappearance of color. In the case of the dehydrated samples, 10 mL of water was added prior to extraction so as to maintain conditions similar to those of the fresh fruit. The combined acetone extracts were transferred into ethyl ether for saponification with an equal volume of 20% KOH–methanol (w/v). After 2 h, the carotenoids were washed and transferred into diethyl ether with a 10% aqueous solution of NaCl. After evaporation of the solvent, the pigments were recovered in 25 mL of acetone. An aliquot of this was filtered using a 0.45-μm Millipore filter for subsequent chromatographic separation.

Identification, Separation, and Quantification of Carotenoid Pigments. The identification of the pigments was performed by the usual techniques: localization of absorption maxima in the spectra in different solvents and peak ratios, functional group tests (conversion of the 5,6-epoxide group into 5,8-furanoid in acid medium, acetylation of free hydroxyl groups, and reduction with borohydride of ketone groups), and infrared spectrum (Curl, 1962; Foppen, 1974; Moss and Weedon, 1976).

The carotenoid pigment analysis was carried out by high-performance liquid chromatography, using a Perkin-Elmer system with a Series 4 quaternary pump, fitted with an injection valve (Rheodyne Model 7125) with a 5-μL sample loop. Separation was realized on a reversed-phase C_{18} column (Spherisorb ODS2, 5 μm, 250 × 4 mm Hewlett-Packard), protected by a precolumn of the same material (50 × 4 mm), eluting the sample using a binary gradient (acetone–water). Detection was performed at 450 nm with a UV–vis detector, Perkin-Elmer Model LC-85B, and a Hewlett-Packard Model A-3396 integrator. Quantification was realized using β-apo-8′-carotenal as internal standard. The

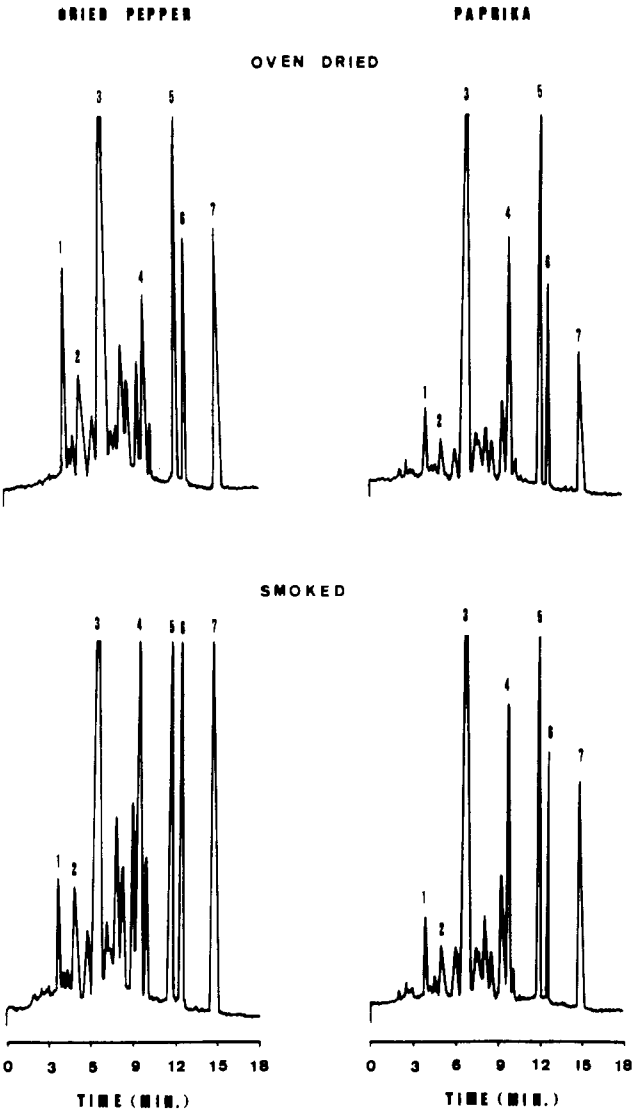

Figure 2. Chromatogram of the pigment extract from peppers of the *Bola* variety dried by two different processes and their respective paprika. Peaks: 1, capsorubin; 2, violaxanthin; 3, capsanthin; 4, zeaxanthin; 5, internal standard; 6, cryptoxanthin; 7, β-carotene.

different moisture contents in the samples studied make it necessary to refer the pigment concentration to the dry matter.

More details about the identification process and system of separation and quantification of pepper pigments by HPLC are included in a previous publication (Mínguez-Mosquera and Hornero-Méndez, 1993).

Reagents. All of the reagents used in the development and application of the chromatographic method were of HPLC grade, and the rest were of analysis grade (ACS). The solvents used in the HPLC were acetone and deionized water, both being vacuum filtered through 0.45-μm nylon filtration membranes (Micron Separations, Westboro, MA) and degassed before analysis.

RESULTS AND DISCUSSION

Only the major pigments present were identified in the samples. In all of the samples, these pigments were β-carotene, cryptoxanthin, zeaxanthin, capsanthin, violaxanthin, and capsorubin. The study of the changes in pigment concentrations was carried out on these pigments. In Figure 1 is shown the chromatogram corresponding to the fresh fruit and in Figure 2 that corresponding to the samples from the different drying systems and their respective paprikas. The pigment contents of the fresh and dried fruits and of their corresponding paprika are

Table 1. Evolution of the Pigment Content in the Paprika Pepper Subjected to Different Processes of Paprika Manufacture

sample	pigment concentration (mg/kg of dry wt)						dry wt (%)
	β-carotene	cryptoxanthin	zeaxanthin	capsanthin	violaxanthin	capsorubin	
fresh fruit	336.7 ± 91.7	199.1 ± 58.1	262.9 ± 145.8	2190.3 ± 396.7	354.6 ± 67.2	344.5 ± 129.3	13.0
				Oven-Dried System			
dried pepper	281.6 ± 64.6	154.9 ± 22.4	195.1 ± 36.1	1554.0 ± 214.4	239.5 ± 33.6	350.6 ± 40.7	97.4
paprika	163.0 ± 9.2	126.0 ± 22.1	213.8 ± 22.5	972.3 ± 63.8	93.1 ± 11.7	139.2 ± 18.8	96.0
				Smoke-Dried System			
dried pepper	465.8 ± 98.2	278.2 ± 77.0	412.7 ± 126.0	1961.5 ± 164.8	228.2 ± 51.7	240.6 ± 54.0	92.7
paprika	217.1 ± 32.0	147.3 ± 21.4	256.0 ± 41.1	1182.6 ± 34.7	99.9 ± 21.3	135.1 ± 30.8	96.6

detailed in Table 1 and are expressed as milligrams per kilogram with respect to the dry matter content. The variation found in the pigment concentration of fresh fruit could be due to the asynchronic maturation of peppers; although they are harvested for processing in the red stage, not all of the peppers are completely ripe and their pigment concentration can change during the period between harvesting and analysis. Zeaxanthin is the pigment whose concentration shows the highest variability in the fresh fruit, probably due to intense metabolic activity of the carotenogenic pathways, particularly those involved in its formation and transformation.

Oven-Drying Process. During drying, except for capsorubin, a statistically significant ($p < 0.05$) fall in the carotenoid content was observed, oscillating between 17% for β-carotene and 32% for violaxanthin. Capsorubin is the only one of the carotenoid compounds measured that did not show a fall in concentration, its mean concentration increasing by 1%, although this increase was not statistically significant. In the resulting paprika the losses were even more acute, the concentrations of β-carotene and capsanthin being reduced by about 40% while those of violaxanthin and capsorubin decreased by 60%. Cryptoxanthin seemed to be the most stable, and zeaxanthin even increased in concentration by 9%. Thus, a total loss of 54% in carotenoid content occurred between the fresh fruit stage and the paprika stage, 25% being lost in the drying phase.

Smoking and Drying Process. The evolution of the pigment content in the same fruits submitted to smoke drying showed a different pattern. During dehydration and smoking, β-carotene, cryptoxanthin, and zeaxanthin increased in concentration by about 40%, although the increase in zeaxanthin came close to 60%. The mean concentration of capsanthin decreased by 11%, although analysis of variance showed this to be insignificant at the 5% level. Violaxanthin and capsorubin diminished in concentration by 35 and 30%, respectively. The drying process led to a net loss of 3% with respect to the initial pigment content.

The results obtained show again that the most acute losses of pigments occurred during the final stage leading to paprika production. The carotenoid that was least affected at this stage was zeaxanthin, which showed a loss of 38% compared with the dry fruit, while the concentration of violaxanthin decreased by 57%. The total pigment content showed, in the final stage, a 43.2% loss of pigment, this being almost identical to the losses incurred during the whole process (45%).

It is worth noting that β-carotene, cryptoxanthin, and zeaxanthin all showed statistically significant ($p < 0.05$) increases in concentration during the smoke-drying phase. This fact can only be explained by there being either complete or partial synthesis of these pigments. In the case of complete synthesis an overall net increase in the carotenoid content would be seen, and this is not what

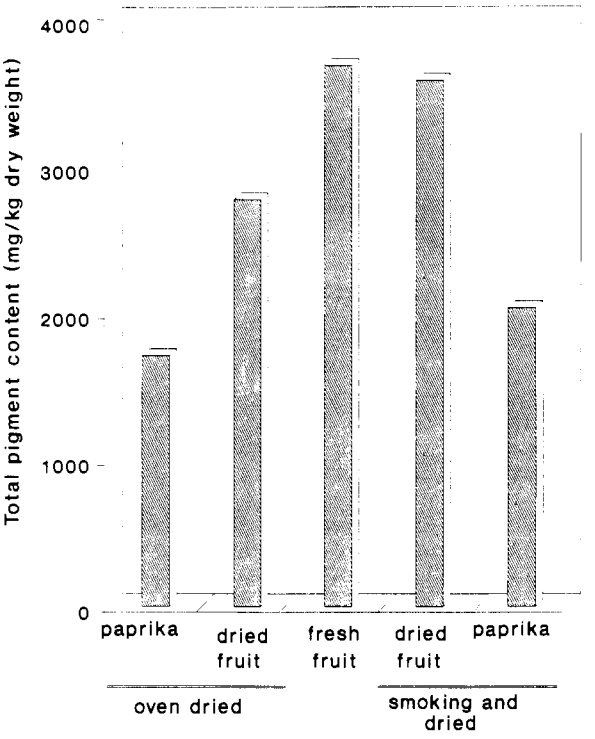

Figure 3. Evolution of the carotenoid content during the industrial processing of paprika and influence of the drying step.

seems to have occurred, since the balance of pigmentary material between the fresh fruit and the dry fruit shows a loss during drying of 1.27×10^{-4} mol/kg. The second hypothesis would not necessarily mean that there was an increase in the balance of material but that, by activation or reversal of biosynthetic pathways, synthesis occurs from existing pigments that would thus act as precursors. It is not possible from the existing data to deduce which of these two hypotheses is correct. The slight fall in the total concentration of pigments obviously demonstrates that losses occurred but does not permit evaluation of the extent of degradation since it is possible that loss and synthesis were coexistent. If the degradation of pigments had been greater than 3%, this would indicate a real and complete synthesis, while if the loss were precisely 3%, this would indicate synthesis by interconversion. It is significant that in the last stage of the process—milling and standardization—the individual loss of each pigment is very similar to the overall loss.

Comparison of Processes. From a comparison of the two drying systems, it can be seen in Figures 2 and 3 that the final products obtained from each have similar quantitative and qualitative characteristics, which contrasts with the differences found in the behavior of the pigments during these two processes. Using the fresh fruit for reference, the percentage losses are similar for both types of paprika. On the other hand, if the dried fruit is

used for reference, then the differences in the two types of paprika are much greater. In the paprika obtained from smoke-dried fruits, the losses that occurred (43%) were very uniform for all pigments. When oven drying is used, individually the losses are less uniform, varying between 19 and 62%. This different behavior can be seen in the chromatograms corresponding to dried fruits and paprikas from both drying systems (Figure 2). The only common change observed in the pigments in fruits dried by both methods is the statistically similar decrease in the violaxanthin concentration.

The fact that, to a greater or lesser extent, all of the pigments decrease between the dried fruit and the paprika stages, but that they do so within narrow margins which vary between 38 and 57%, is noteworthy. The constant nature of these losses would seem to indicate that they do not arise from oxidative degradations, since each of the pigments has a different stability from the others and here they all behave in much the same manner. It could be that there was no loss as such and that the effect mentioned was due to dilution of these compounds by inert material, a practice which is common in the paprika industry to standardize the quality of all of the processed material. Taking as reference the pigment showing the least loss during the whole process, it would be possible to calculate the percentage of inert material added. It is necessary to assume that the pigment selected is the most stable and that it has not undergone any alteration in the last stage. In all of the other pigments, the losses would include the effects of dilution and degradation. According to the results obtained, zeaxanthin is the most stable pigment followed by capsanthin. The evolution of both being very similar in the final stage, it is better to choose capsanthin, which, being specific to peppers, ensures that no dilution occurs using totally unrelated pigment materials. Using the previously mentioned premises, the paprika obtained from smoke-dried fruits was found to be diluted by approximately 40% with inert material and the losses, even in the case of violaxanthin, the worst case, did not reach 17%.

In oven drying, using the same criterion, it was surprising to find that one pigment, zeaxanthin, increased in concentration in the final product compared to that in the dried fruit, a fact which has to be associated with the addition of some inert material with a certain content in pigment. As in the previous case, capsanthin was chosen to calculate the percentage of inert material, this pigment being exclusive to peppers and showing the smallest losses. In this case the percentage of inert material added was 38% and the maximum loss due to oxidative processes was again for violaxanthin with a fall of 24%. With respect to the increase in the concentration of zeaxanthin, the only reasonable explanation is that the paprika was diluted with a product containing 240 mg of zeaxanthin/kg, giving the levels found in the final mixture. On the basis of this reasoning, the added product must also have contained 80 mg of cryptoxanthin/kg. All of this supposes that during the manufacture of this paprika no degradative losses occur. In the case of zeaxanthin, the results obtained in the paprika derived from smoke-dried fruits may be acceptable, but this is not the case for cryptoxanthin, the degradation of which reaches 12% during milling.

As can be seen, samples that show different changes in the pigment content during drying finally give products with similar characteristics. Starting with the same fruit and using two different processes, it is possible to obtain two dried products with very different organoleptic and analytical characteristics. For commercial purposes almost the only important parameter is the coloring capacity, and the industry must offer a uniform quality in all of the products. The smoked fruits will maintain their characteristic flavor, but in order for them to have a coloring capacity similar to that of paprika produced by oven drying, it is necessary to dilute their paprika to a greater extent.

ACKNOWLEDGMENT

We express our sincere gratitude to CICYT (Spanish government, ALI-91-1166-C03-02) for financial support of this research.

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Received for review July 6, 1993. Revised manuscript received February 8, 1994. Accepted February 25, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1994.