Fatty Acid Composition of Two New Pepper Varieties (*Capsicum annuum* L. cv. Jaranda and Jariza). Effect of Drying Process and Nutritional Aspects

Antonio Pérez-Gálvez[a], Juan Garrido-Fernández[a], Mª Isabel Mínguez-Mosquera[a,*], Mercedes Lozano-Ruiz[b], and Vicente Montero-de-Espinosa[b]

[a]Instituto de la Grasa (CSIC), Departamento de Biotecnología de Alimentos, 41012 Sevilla, Spain, and [b]Instituto de Tecnología Agroalimentaria, Consejería de Agricultura y Comercio, 06080 Badajoz, Spain

ABSTRACT: Composition in fatty acids of the pericarp and seeds of two new pepper fruits (*Capsicum annuum* L. cv. Jaranda and Jariza) and the effects of different processing stages on the fatty acid composition of these tissues and of paprika are shown. In the pericarp the polyunsaturated fatty acids (PUFA), linoleic and linolenic, both in the same proportion, are the major acids; in the seed, linoleic is in a very high concentration as compared to in the pericarp. In the pericarp, a storage zone of carotenoid pigments, linolenic acid does not participate in the carotenoid esterification process. From the different lipid patterns, nutritional aspects are deduced. In the drying step the concentrations of constituent fatty acids are constant in the seed, while in the pericarp there is a net increase in the total content of fatty acids.

Paper no. J8983 in *JAOCS 76*, 205–208 (February 1999).

KEY WORDS: *Capsicum*, drying process, esterification, fatty acids, oil, seed.

In plant tissues, the most abundant saturated fatty acids are palmitic and stearic, and the most common unsaturated fatty acids are oleic, linoleic, and linolenic (1). These fatty acids are synthesized in aerobic sequential desaturation, from stearic (18:0) to oleic, then to linoleic, and finally, to linolenic (2). Such reactions can take place in both the plastid and the endoplasmic reticulum (3,4) by the action of the desaturase enzymes. However, due to the different substrate specificity of the plastid acyltransferases, the glycerolipids synthesized in the plastids have an *sn*-1 C_{18} and *sn*-2 C_{16} distribution, while those synthesized outside the plastids have a C_{16} or C_{18} combination at position *sn*-1 but only C_{18} at *sn*-2.

In the ripe fruit of the pepper (*Capsicum annuum* L.), the major lipids are mono- and diacylgalactolipids, while in the endoplasmic reticulum, the major lipid is phosphatidylcholine (5). Fatty acids are accumulated in both the pericarp and the seeds (6,7). Those found in the pericarp, besides fulfilling their structural function as basic components of the cell membrane, are important for the proper incorporation of other membrane compounds. During ripening of the pepper, besides a series of structural changes, disappearance of chloroplasts, and formation of chromoplasts (8), new pigments are biosynthesized that are exclusively carotenoid, esterified to a greater or lesser degree (9,10). The fatty acids esterified to the xanthophylls are mainly lauric, myristic, palmitic, oleic, and linoleic, forming mono- or diesters (11). The pigments are thus more liposoluble and at the same time more stable to photo- and thermoxidative reactions and other processes involving the enzyme lipoxygenase. This greater stability results in longer conservation of the color (a quality used to evaluate both the fruit and its commercial derivatives paprika and oleoresin).

To obtain paprika, the pepper must be dehydrated by heating and then ground. The dehydration stage is not the end of the metabolic life of the fruits, since, as has been demonstrated in previous works (12,13), pigments may continue to be synthesized or transformed into others, altering the initial carotenoid composition. Hence, not only the carotenogenic pathways but all the other biosynthetic pathways of the fruit may be viable. The effect of the drying step on the fatty acid composition has not been studied, and it is not known whether biosynthetic or, conversely, oxidation reactions are possible. The latter would favor the oxidation of fatty acids such as linoleic or linolenic, with the consequent chain of oxidations involving the pigments. In this step, the presence of antioxidants such as α-tocopherol could be important.

The present work reports the fatty acid composition of two new pepper varieties, *Jaranda* and *Jariza*, in the fresh fruit (pericarp and seed) and the effect of dehydration on this composition. Special mention is made of the nutritional aspects of the fats contained in pericarp, seed, and paprika.

EXPERIMENTAL PROCEDURES

Raw material. Ripe fruits of two varieties of pepper, *C. annuum longum* L., from eight farms were used. Four of the farms grew the variety Jaranda and the other four the variety Jariza. Two of the farms were in Valle del Alagón Spain, and the others in Valle del Tiétar, Spain. The fruits ripened at the same time, and almost all were picked during a single har-

*To whom correspondence should be addressed at Instituto de la Grasa (CSIC), Departamento de Biotecnología de Alimentos, Av. Padre García Tejero n° 4, 41012 Sevilla, Spain. E-mail: aperez@cica.es

vesting. After picking, the fruits were dried in dryers on the farm. These dryers are stone constructions of two stories, the upper separated from the lower by a wooden mezzanine allowing ventilation between them. The fruits are put into the upper part, and heat is generated in the lower by burning oak logs. The temperature reaches around 40–50°C. Dehydration of the fruits is completed in 8–10 d. The dry fruit from each dryer was milled locally, to yield eight lots of paprika, each from one farm and the corresponding dryer.

Three types of sample were collected. From fresh fruit, one sample of 2 kg was taken per farm. Seeds and stalk were removed, and the sample was sliced and homogenized; six subsamples each of 10 g were taken for the analysis of fatty acids. The total number of replicates was 24 for each variety. The dry sample was 1 kg, freed of seeds, sliced, and homogenized; three subsamples each of 2 g were used for the extraction and analysis of fatty acids. In this case, the number of replicates per variety was 12. The paprika available was 100 g from each farm, in each case, two samples of 1.5 g were analyzed, a total of eight replicates per variety.

Analysis of fatty acids. Fruit pericarp. The fatty matter was extracted using hexane as solvent. In the case of fresh and dried fruit, 10 g of sample were dehydrated using a vacuum stove and extracted for 4 h in a Sohlext apparatus. The fat content was calculated from the difference in weight of the sample before and after extraction and the amount of oil collected in the flask. In the case of paprika, the sample was 5 g, because of its higher content in fat (the result of mixing pericarp and seed), the rest of the procedure being the same.

Seed. In this case, the sample was 10 g, dehydrated in a vacuum stove. Oil extraction was as from the pericarp.

Preparation of methyl esters and chromatographic analysis. The methyl esters of the fatty acids were prepared from the oil by direct intersterification, adding 5 mL of 0.2 N MeONa solution to aliquots of oil. The sample was mixed with the reagent in a test tube, adding the appropriate amount of dissolved heptadecanoic acid as internal standard for later quantification. The reaction was carried out by heating for 15 min at 80°C in a water bath. When the reaction was finished, the tube was allowed to cool. Then, 5 mL of 15% (vol/vol) $MeOH/H_2SO_4$ was added and the mixture was heated for 15 min. The tube was allowed to cool and 1 mL of hexane was added, together with 10% (wt/vol) NaCl solution to help in the transfer of the methyl esters to the organic phase. An aliquot of this phase was placed in an Eppendorf tube for chromatographic analysis. The methyl esters were separated and quantified using a gas chromatograph (Hewlett-Packard model 5890; Las Rozas, Madrid, Spain) fitted with flame-ionization detector. The working conditions were the following: oven temperature 175°C for 20 min, with a rise of 15°/min to 240°C. The temperature was maintained for 5 min, and then returned to the initial 175°C. Both the detector and the injector were fixed at 250°C. The solution of methyl esters (1 or 2 μL) was injected on to the column (Supelcowax 10μ, 30 m; Alcobendas, Madrid, Spain), and the peak areas were measured using an integrator (Hewlett-Packard model 3396II). Quantification was performed using the area of the internal standard.

RESULTS AND DISCUSSION

Profile of fatty acids in pericarp and seed of the pepper. Table 1 shows the percentage composition of fatty acids of pepper in the different stages of preparing paprika and in the seed. As in most plants, the major fatty acids accumulated in the pepper are palmitic (16:0), oleic (18:1), linoleic (18:2), and linolenic (18:3). However, the lipid patterns are different in pericarp and seed. In the external tissue, the unsaturated acids

TABLE 1
Percentage Composition (mean ± SD) in Fatty Acids of the Pericarp and Seeds During the Processing Stages for Paprika (*Capsicum annuum* L.) Jaranda and Jariza Varieties

Fatty acid	Fresh fruit (n = 24)		Dehydrated fruit (n = 12)		Paprika (n = 8)
	Pericarp	Seed	Pericarp	Seed	
			Jaranda variety		
Lauric	2.42 ± 0.82	0.05 ± 0.03	3.22 ± 0.81	0.04 ± 0.08	0.78 ± 0.20
Myristic	7.16 ± 1.98	0.12 ± 0.02	8.66 ± 1.86	0.20 ± 0.05	1.88 ± 0.19
Palmitic	18.22 ± 0.84	11.08 ± 0.45	18.35 ± 1.49	10.76 ± 0.12	11.92 ± 0.20
Palmitoleic	0.81 ± 0.26	0.21 ± 0.03	0.85 ± 0.19	0.20 ± 0.01	0.40 ± 0.02
Stearic	4.73 ± 0.39	2.85 ± 0.08	4.18 ± 1.14	2.78 ± 0.10	2.75 ± 0.09
Oleic	8.48 ± 0.39	7.38 ± 0.29	11.28 ± 1.96	7.11 ± 0.50	8.48 ± 0.57
Linoleic	27.15 ± 2.78	77.98 ± 0.57	28.11 ± 6.99	79.45 ± 1.77	69.24 ± 1.09
Linolenic	29.93 ± 3.22	0.38 ± 0.02	23.38 ± 1.84	0.56 ± 0.09	4.12 ± 0.76
			Jariza variety		
Lauric	3.17 ± 0.95	0.03 ± 0.02	3.58 ± 0.63	0.03 ± 0.01	0.65 ± 0.11
Myristic	8.27 ± 2.64	0.14 ± 0.01	10.18 ± 2.61	0.17 ± 0.02	1.98 ± 0.17
Palmitic	18.72 ± 1.01	11.24 ± 0.46	18.98 ± 1.63	11.16 ± 0.46	12.45 ± 0.25
Palmitoleic	0.77 ± 0.08	0.21 ± 0.03	0.93 ± 0.14	0.19 ± 0.01	0.41 ± 0.05
Stearic	4.90 ± 0.66	2.71 ± 0.14	3.71 ± 0.23	2.78 ± 0.20	2.84 ± 0.06
Oleic	7.19 ± 0.98	7.32 ± 0.33	10.54 ± 2.19	7.09 ± 0.31	8.36 ± 0.45
Linoleic	25.18 ± 5.14	77.96 ± 0.67	28.77 ± 5.61	78.09 ± 0.66	68.46 ± 1.43
Linolenic	30.27 ± 4.40	0.38 ± 0.02	20.90 ± 2.65	0.49 ± 0.04	4.10 ± 0.72

18:2 and 18:3 are the major ones (in almost equal amounts), in the seed the major acid is 18:2, and 18:3 is practically absent. The biosynthetic pathways (1–4) in the two tissues lead to different fatty acid compositions. The major fatty acids in both cases are the unsaturated ones (apart from palmitic, which is the precursor of the others). As 18:2 and 18:3 fatty acids are synthesized preferentially, they probably constitute the appropriate membrane lipids in this stage of fruit ripening, particularly when the enzymes involved in the synthesis of capsanthin and capsorubin are highly linked to membranes. However, as the pigments are synthesized, they are esterified preferentially, with saturated fatty acids in the case of the red xanthophylls and unsaturated ones in the case of the yellow xanthophylls, although it is noteworthy that linolenic acid does not take part in such esterification (10). It appears that the metabolic system of the plant attempts, with this esterification, to make these pigments more accessible to the membranes by increasing their liposolubility, and to protect them from enzymatic and nonenymatic oxidative reactions (14). The nonparticipation of linolenic acid in this esterification process can be explained by the fact that the pigments esterified with linolenic acid are not as stable to oxidation. Lipoxygenases are known to selectively oxidize linolenic acid, which is followed by oxidation reactions affecting the photosynthetic pigments.

In the particular case of pepper seeds, the oil content is 18% in the varieties studied (Jaranda and Jariza). The seed is one of the most important lipid storage sites in the plant, but the presence of carotenoid pigments in the seed is minimal. Once fat accumulation has finished, the seed dehydrates and becomes ready to sustain the new plant with a source rich in energy until photosynthesis begins.

Effect of drying on the initial fatty acid composition in the fruit pericarp and seeds. The drying stage, which is the first treatment to which the fruit is subjected, does not end its metabolic life. Enzymatic processes continue for a time, depending on the moisture content of the fruit and the environmental temperature, and pigment biosynthesis and transformation are possible. In such case, cell integrity will be maintained and biosynthetic reactions can continue. During the dehydration process, there is a net increase of 19% in the total content of fatty acids in pericarp for the variety Jaranda and 30% for Jariza. In relation to individual percentages, lauric and myristic saturated fatty acids increase their relative presence in the pericarp, while palmitic remains constant; of the unsaturated acids, linoleic increases and linolenic decreases.

With regard to the fatty acid composition of the seed, there are no changes during drying (Table 1). Hence the seed milled with the pericarp to obtain paprika will have the same composition as that of the seed from fresh fruit.

Nutritional aspects. Table 2 shows different relationships between fatty acid fractions: saturated, unsaturated, sum of mono- and polyunsaturated, and total. Given the different lipid pattern of the fruit pericarp and seed, the results are discussed separately, followed by those of the prepared product, paprika.

Pericarp. The ratio of saturated/unsaturated (s/u) varies between 0.5 and 0.6. This ratio is similar to that found in the seeds of certain legumes, e.g., *Vigna sinensis* (15). Thus, two aspects must be borne in mind. The first is the higher proportion of saturated fatty acids, and the second is the high content of linolenic acid (22.14%, mean value from both varieties), with the increased risk of autoxidation of the components of the tissue in which it is found.

Seed. The small proportion of linolenic acid in the seed composition is interesting. It gives the oil both a higher resistance to rancidity caused by autoxidation and a high nutritional value. The s/u ratio in the seed is constant at around 0.16, similar to that of the oils of olive (0.17) and soybean (0.19), and better than that of palm oil (0.98).

Paprika. Paprika contains a proportion of seed ranging from 30 to 40%. Thus the fatty acid distribution in paprika is very similar to that in the seed, with a high content of linoleic (Table 1). Even so, paprika has a high nutritional value as a result of the incorporation of a large amount of linoleic, with an s/u ratio similar to that of the seed, around 0.2. The dilution effect decreases the level of linolenic acid, thus reducing the risk of autoxidation reactions, which, apart from other considerations, could affect the carotenoid fraction of the dry fruit.

Calculation of the percentage of added seed. Once the fatty acid composition of the pericarp, seed, and paprika (the product of mixing the two fruit fractions) is known, the proportion of seed to the dry fruit in the mixture can be calculated, revealing the dilution made by the manufacturer. The calculation is based on linoleic acid, the major fatty acid in

TABLE 2
Relationships (mean values) Between Different Fatty Acid Fractions of the Pepper for Paprika (Jaranda and Jariza) in the Processing Stages

Relation[a]	Jaranda variety				Jariza variety			
	Fresh fruit (n = 24)	Dehydrated fruit (n = 12)	Seed (n = 24)	Paprika (n = 8)	Fresh fruit (n = 24)	Dehydrated fruit (n = 12)	Seed (n = 24)	Paprika (n = 8)
s/u	0.49	0.54	0.16	0.21	0.55	0.60	0.16	0.22
mu/pu	0.16	0.24	0.10	0.12	0.14	0.23	0.10	0.12
s/t	0.33	0.35	0.14	0.17	0.36	0.37	0.14	0.18
mu/t	0.09	0.12	0.08	0.09	0.08	0.12	0.08	0.09
pu/t	0.58	0.53	0.78	0.74	0.56	0.51	0.78	0.73

[a]s, saturated fatty acids; u, unsaturated fatty acids; mu, monounsaturated fatty acids; pu, polyunsaturated fatty acids; t, total fatty acids.

the seed and one of the major fatty acids in the pericarp. The formula proposed is as follows:

$$C_P = x \bullet \frac{(100 - \%M)}{100} \bullet \frac{\%O}{100} C_s + (100 - x) \bullet C_{DF} \quad [1]$$

where x is the amount of seed added to 100 g of fresh fruit, $\%M$ is the percentage of moisture in the seed, $\%O$ is the percentage of oil in the seed, and C_S, C_{DF}, and C_P are the concentrations in mg/g of linoleic acid in the seed, dehydrated fruit, and paprika, respectively. Solving x, and substituting each parameter by its actual value, gives the percentage of seed added to the dry fruit.

ACKNOWLEDGMENT

The authors express their sincere gratitude to CICYT for supporting this research project, PTR95-0100.

REFERENCES

1. Murphy, D.J., Structure, Function and Biogenesis of Storage Lipid Bodies and Oleosins in Plants, *Prog. Lipid. Res. 32*:247–280 (1993).
2. James, A.T., The Biosynthesis of Long-Chain Saturated and Unsaturated Fatty Acids in Isolated Plant Leaves, *Biochim. Biophys. Acta 70*:9–19 (1963).
3. Rougham, P.G., and J.B. Ohlrogge, Evidence That Isolated Chloroplasts Contain an Integrated Lipid-Synthesizing Assembly That Channels Acetate into Long Chain Fatty Acids, *Plant Physiol. 110*:1239–1247 (1996).
4. Schmidt, H., and E. Heinz, Direct Desaturation of Intact Galactolipids by a Desaturase Solubilized from Spinach (*Spinacea oleracea*) Chloroplast Envelopes, *Biochem. J. 289*:777–782 (1993).
5. Whitaker, B.D., Growth Conditions and Ripening Influence Plastid and Microsomal Membrane Lipid Composition in Bell Pepper Fruit, *J. Amer. Soc. Hort. Sci. 116*:528–533 (1991).
6. Marion, J.E., and A.H. Dempsey, Fatty Acids of Pepper Seed Oil, *J. Am. Oil Chem. Soc. 41*:548–549 (1964).
7. Nosti Vega, M.; R. Vázquez Ladrón and R. Castro Ramos, Posibilidades de Aprovechamiento de los Subproductos de la Industria de Aderezo de Aceitunas, *Grasas Aceites 33*:135–139 (1982).
8. Camara, B., and Brangeon, J., Carotenoid Metabolism During Chloroplast to Chromoplast Transformation in *Capsicum annuum* Fruit, *Planta 151*:359–364 (1981).
9. Camara, B., and R. Monéger, Free and Esterified Carotenoids in Green and Red Fruits of *Capsicum annuum, Phytochemistry 17*:91–93 (1978).
10. Mínguez-Mosquera, M. I., and D. Hornero-Méndez, Changes in Carotenoid Esterification During the Fruit Ripening of *Capsicum annuum* cv. Bola, *J. Agric. Food Chem. 42*:640–644 (1994).
11. Biacs, P.A. H.G. Daood, A. Pavisa, and F. Hajda, Studies on the Carotenoid Pigments of Paprika (*Capsicum annuum*, L. var. Sz-20), *Ibid. 37*:350–353 (1989).
12. Mínguez-Mosquera, M.I., M. Jarén-Galán, and J. Garrido-Fernández, Effect of Processing of Paprika on the Main Carotenes and Esterified Xanthophylls Present in the Fresh Fruit, *Ibid. 41*:2120–2124 (1993).
13. Mínguez-Mosquera, M.I., M. Jarén-Galán, and J. Garrido-Fernández, Influence of the Industrial Drying Processes of Pepper Fruits (*Capsicum annuum* cv. *Bola*) for Paprika on the Carotenoid Content, *Ibid. 42*:1190–1193 (1994).
14. Daood, H.G. and P.A. Biacs, Evidence for the Presence of Lipoxygenase and Hydroperoxide-Decomposing Enzyme in Red Pepper Seeds, *Acta Aliment. 15*:307–318 (1986).
15. Mohan, V.R., and K. Janardhanan, Chemical Composition and Nutritional Evaluation of Two Little-Known Species of *Vigna, Food Chem. 48*:367–371 (1993).

[Received August 19, 1998; accepted November 23, 1998]