INFLUENCE OF FREEZING ON TYROSINE PRECIPITATE IN SPANISH RAW CURED HAM

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INTRODUCTION

In Spanish raw cured hams, tyrosine precipitates can be found in two different forms: as crystals in the flesh and white film in cut surface (Silla et al., 1985, Arnau, et al., 1986).

Several theories have been elaborated in order to explain the origin of free tyrosine in the muscle:

Artioli (1952) found some correlation between blastomicetic flora and free tyrosine in the muscle. Comi et al., (1981, 1982, 1983) in Parma hams isolate yeast species of Debaryomyces, Torulopsis and Trichosporon that could synthesize tyrosine.

However proteolytic activity of cathepsins is the more feasible theory because the microbial counts in the muscle are too small to justify the proteolysis. Melo et al., (1974) observed a decrease in catheptic activity after an aging period of six months, and holding hams in frozen storage at -29ºC for long periods were not detrimental to specific enzyme activity. Sárraga et al., (1988) found an increase of calpain activity that reaches its maximum two months after the beginning and remains constant until the end. Cathepsin L shows a constant activity during all the process and cathepsine D decreased progressively since the fourth month.

The main component of white film was tyrosine (Butz et al., 1974) and the relative proportion of phenylalanine is also increased (Arnau et al., 1987). Storage of ham slices at -18ºC inhibites white film, but it appears when ham is thawed. White film decreases as the thickness of vacuum packaged ham slices diminishes, and does not appear when cut surface is treated with high adherence products such as plastic solutions and gelatine (Arnau, et al., 1988), white film is chiefly found in muscles with the smaller percentage of salt in the beginning of the process that have the higher percentage of salt in the ham at the end of the process.

In Spain an important percentage of raw cured hams are manufactured from previously freezed hams. Thus the objective of these study was to analyze the influence of freezing on tyrosine precipitation.

MATERIAL AND METHODS

23 animals were sampled. In group I right leg hams (n=23) were frozen at -18ºC for 48 hours and thawed at 4ºC. In Group II left leg hams (n=23) were refrigerated.

Both groups were cured separately with a mixture of salt (40 g/Kg of green ham) and nitrate in a ratio of 100:1. Fifteen days later the hams were washed and hung at 3-5ºC for 30 days, and then the temperature increases 1,5ºC weekly until the six month. A twelve cm ham slice from the middle of each ham was taken in order to evaluate white film.

100 g of ham from the medium part of Biceps femoris muscle was used for chemical analysis.

23 hams were sliced, three slices per ham has been stored at three different temperatures 3-4ºC, 12-14ºC, 22-24ºC. White film has been evaluated after 15 days. Kramer test was used in order to compare the difference between tratements.

Sodium chloride was analyzed after the method of Charpentier-Volhard.

Protein content was analyzed after the Kjeldhal method. Tyrosine was determined after the technique of Wood, Sigurdsson and Dyer modified by Pearson (1968).

The Wilcoxon-Mann-Whitney Rank sums

test was used in order to compare non parametric data between high pH hams and low pH hams. The parametric data were analyzed by the analysis of variance.

RESULTS AND DISCUSSION

Group I hams has had a higher salt intake ($P < 0,05$) due to an acceleration in salt penetration in freezed hams, produced by the cellular disruption carried out by ice crystals.

In Group I the number of hams with crystals of tyrosine (n=19) was significantly higher ($P < 0,01$) than in Group II (n=1), and as shown in table II viceversa occurs for white film ($P < 0,05$).

In a similar form as the crystallization phenomenon in a solution, a high number of crystals would be found in the ham if the tyrosine concentration rises over the maximum solubility and a rapid supersaturation is produced by a rapid drying process (increasing the salt content and decreasing humidity) or a decrease in temperature. Freezing could disrupt cellular membranes and facilitate tyrosine diffusion to the surface of the crystal. As supersaturation decreases the rate of crystal formation gets down. Thus in hams as iberian serrano hams with an aging period of 18 months, the rate of crystal formation will be smaller, and the recristallization during the broad period of aging will facilitate the growth of the large crystals.

Tyrosine precipitates have been found in the inner part of the bone only in group I hams.

The hams with a pH > 6,2 in the Semimembranosus and Biceps femoris showed a small number of tyrosine crystals in freezed hams, a lower white film in refrigerated hams ($P < 0,01$) and a decrease in tyrosine concentration. It could be explicated by the increase in solubility as pH moves away from the isoelectric point (pI = 5,63). (Butz et. al., 1974; Kemp et.al., 1988) found no difference in white film samples stored at different temperatures.

In our experiment significant differences ($P < 0,01$) in white film have been found between different storage temperatures. The difference was more important when film scoring was < 3. The lower the temperature the intenser the white film, owing to the decrease of the solubility of tyrosine as temperature goes down.

Table I

	Group I	SD	Group II	SD	
pHBF1	6,06	0,45	5,94	0,40	NS
pHBF2	6,43	0,21	6,30	0,23	NS
Humidity	61,19	3,23	62,20	2,65	NS
NaCl	7,21	0,97	6,30	1,12	*
Tyrosine(3)	284	113	305	106	NS
Proteine	28,15	4,17	27,00	2,57	NS
Hams with tyrosine crystals	19	-	1	-	

pHBF1 = pH in Biceps femoris in fresh ham
pHBF2 = pH in Biceps femoris at the end of the aging process

(3) : Tyrosine in mg/100 g

Table 2. Distribution of the white film scores

	film scores					
Group	0	1	2	3	4	5
Group I	0	8	9	6	0	0
Group II	0	3	7	5	5	3

Film scoring 0=none 1=very slight 2=slight 3=moderate 4=heavy 5=very heavy

REFERENCES

Arnau, J., Hugas, M., García-Regueiro, J.A. and Monfort, J.M. 1986. A study of the development of a white film on cut surfaces of Spanish cured hams. Proceedings 32nd Europ. Meet. Meat Research Workers 313.

Arnau, J., García-Regueiro, J.A., Hugas, M. y Monfort, J.M. 1988. La tirosina en el jamón curado. In: "El jamón curado : aspectos técnicos". Arnau, J., Hugas, M. and Monfort, J.M. (Ed.), 101. Institut de Recerca i Tecnologia Agroalimentàries.

Arnau, J., Hugas, M., García-Regueiro, J.A. and Monfort, J.M. 1987. Precipitado de tirosina en la superficie de corte del jamón curado. Rev. Agroquím. Tecnol. Aliment. 27 (3):398.

Artioli, D. 1952. "Blastomicosi dei prosciutti". Arch. Vet. Ital. 3:105.

Butz, R.G., Blumer, T.N., Christian, J.A. and Swaisgood, H.E. 1974. Factors responsible for white film formation on cut surfaces of dry cured hams. J. Food Sci. 39:516.

Comi, G. and Cantoni, C. Presenza di lieviti nei prosciutti crudi stagionati. 1983. Ind. Aliment. 22:102.

Comi, G., Cantoni, C., Saronni, G. and Denozza, D. 1981. Ipostesi sulla formazione di cristalli di tirosina nei prosciutti crudi da parte dei lievitti. Ind. Aliment. 20: 879.

Comi, G., Cantoni, C. and Traldi, C. 1982. Attivitá proteolítica di lieviti isolati da granuli di tirosina di prosciutti crudi stagionati. Ind. Aliment. 21:524.

Kemp, J.D., Langlois, B.E., Akers, K., Means, W.J. and Aaron, D.K. 1988. Effect of storage temperature and time on the quality of vacuum packaged dry-cured ham slices. J. Food Science 53 (2):402.

Melo, T.S., Blumer, T.N. and Swaisgood H.E. 1974. Catheptic enzyme activity in aged country-style hams as influenced by pre-curing treatment. J. Food Sci. 39:511.

Pearson, D. 1968. Application of chemical methods for the assessment of beef quality. II Methods selected to protein breakdown. J. Sci. Food Agric. 19: 366.

Sárraga, C., Gil, M., and Cussó, R. 1988. Proteinase activities in the Spanish ham during the curing process. 14th International Congress of Biochemistry. Prague Czechoslovakia.

Silla, M.H., Innerarity, A. and Flores, J. 1985. Características de jamones con cristales de tirosina. Rev. Agroquím. Tecnol. Aliment. 25(1):95.