Effect of meat quality on tyrosine precipitates in dry cured hams

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SUMMARY: The effect of meat quality, different breeds and comercial lines of the Pig Improvement Company on tyrosine precipitates was evaluated. Tyrosine concentration was significantly lower in DFD hams, but no difference was found between PSE and normal hams. The incidence of hams with tyrosine crystals and white film decreased as the pH increased. A higher number of tyrosine crystals were found in hams from halothane positive pigs and the conformated line. The formation of the white film and tyrosine crystals could be explained as a crystallisation process.

INTRODUCTION: Tyrosine precipitates can be found in dry cured hams in two different forms: as crystals in the flesh and white film in cut surface (Silla et al., 1985; Butz et al., 1974; Arnau et al., 1987). DFD hams show a lower tyrosine concentration, white film and tyrosine crystals (Arnau et al., 1989). Some breeds (Pietrain and Belgian Landrace) presents a high level of tyrosine precipitates (Stazione Sperimentale, 1988). Several theories have been elaborated in order to explain the origin of free tyrosine (Artioli, 1952; Comi et al. 1981, 1983, Melo et al. 1974). The objective of this study is to analyse the effect of meat quality and genetics of the ham on tyrosine precipitation. An hypothesis that would explain the formation of tyrosine crystals and white film from free tyrosine is presented.

MATERIAL AND METHODS: **Processing:** 36 fresh hams (9 PSE, 15 normal and 12 DFD), 67 freezed pure breed hams (12 Large White (LW^-), 10 Duroc (D^-), 10 Pietrain (P^+), 12 Belgian Landrace (LB^+), 11 Landrace halothane positive (LS^+) and 12 Landrace halothane negative (LS^-)) and 30 freezed hams of the commercial lines of the Pig Improvement Company (10 L15, Duroc; 10 L10, high muscular development; 10 L03, Comborough) were elaborated after traditional methods in Spain. 100 g of ham from the medium part of Biceps femoris muscle was used for chemical analysis. Sodium chloride was analyzed after the method of Charpentier-Volhard. Tyrosine was determined after the Pearson method (1968). In order to see the effect of the freezing at the end of the aging process on tyrosine precipitates, 24 hams (4 PSE, 12 Normal and 8 DFD) were salted and aged for six months. The hams were freezed for 3 days at -20 ^{0}C, then were thawed at 4 ^{0}C, deboned and vacuum packaged. After one month of storage at 4 ^{0}C the Biceps femoris muscle was analysed. White film was scored after a six point scale (0=none, 1=very slight, 2=slight, 3=moderate, 4=heavy and 5=very heavy). Data were analyzed after the General Linear Models Procedure, using the Bonferroni test (S.A.S., 1987).

RESULTS and DISCUSSION: Tyrosine concentration was significantly lower in DFD hams ($P<0,05$),

the incidence of hams with tyrosine crystals and white film decreased as the pH increased, but no difference was found between PSE and normal hams (tables 1, 2). These results agree with those found by Gil et al. (1989), finding a lower proteolytic activity in DFD hams than in normal and PSE hams. This suggest the participation of cathepsins in the proteolysis of the ham. However as the pH moves away from the isoelectric point (pI=5,63), the solubility of tyrosine increases (Butz et al., 1974), existing a lower tendency to precipitate. No tyrosine crystal has been observed in dry cured hams freezed and thawed at the end of the aging process but after one month of storage at 4 ^{0}C there were 13 hams with tyrosine crystals. Thus, the freezing at the end of the aging process favoured the formation of tyrosine crystals (table 2). This results agree with Arnau et al. (1989) that found more tyrosine crystals in hams elaborated from previously freezed hams. At the end of the process the free tyrosine concentration in the muscle is higher, thus the nucleation and growth of the crystals will be quicker. The concentration of tyrosine was higher in Pietrain hams. A higher number of tyrosine crystals and free tyrosine were found in hams from halothane positive pigs and the conformated line (L10) ($P<0,05$). The formation of the white film and tyrosine crystals could be explained as a crystallisation process. The use of previously freezed hams favours the formation of tyrosine crystals (Arnau et al. 1989), because freezing would facilitate heterogeneous nucleation (the broken membranes could act as nucleation sites) and the migration of the tyrosine, thus the growth of the crystals would be quicker. The freezing of the hams at the end of the aging process would also facilitate heterogeneous nucleation, and growth of the crystals. In nonfreezed hams the nucleation would be the critical step regulating the formation of tyrosine crystals. White film would be formed as an heterogeneous nucleation where the cut surface irregularities could act as nucleation sites, where the tyrosine would precipitate. The high adherence products such as gelatine an plastic film would eliminate the nucleation sites, thus the nucleation would not take place and white film is not formed. White film is normally not present around the tyrosine crystals, suggesting that crystal growth is controlled by diffusion and not by tyrosine integration in the crystal. If the crystal growth was controlled by integration, white film would be formed around the crystal. In order to avoid the formation of tyrosine crystals and white film there are three possibilities:

1) To control the raw material (pH and breed), process (temperature, drying rate and concentration of salt) and storage conditions (temperature and drying rate) in order to a prevent the supersaturation of tyrosine in the ham. 2) To inhibite the nucleation or the growth of the crystals (avoiding freezing). 3) To dissolve the crystal when formed. The later could not be carried out in dry cured ham. Thus the research has to be oriented towards the two first possibilities in order two control these precipitates.

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Table 1. Physicochemical parameters in dry cured ham after the meat quality.

Meat quality	pH24	pH	NaCl[x]	Tyr	White film
PSE	5,70[a] ± 0,13	6,22[a] ± 0,14	7,11 ± 1,09	280[ab] ± 24	2,7[a]
Normal	5,72[a] ± 0,21	6,17[a] ± 0,18	6,64 ± 1,01	299[b] ± 19	2,5[ab]
DFD	6,45[b] ± 0,22	6,55[b] ± 0,14	7,09 ± 1,14	230[a] ± 21	1,9[b]

a-b: Means within a column with different superscripts are significantly different (P<0,05).

Table 2. Physicochemical parameters in dry cured hams freezed at the end of the aging process.

Meat quality	n	n^w	pH	$NaCl^x$	Tyr^y	White film
PSE	4	3	$6,38^a \pm 0,07$	$5,23 \pm 0,36$	$387^a \pm 51$	$2,0^{ab}$
Normal	12	8	$6,30^a \pm 0,11$	$5,45 \pm 0,54$	$382^a \pm 34$	$2,7^a$
DFD	8	2	$6,76^b \pm 0,08$	$5,69 \pm 0,77$	$318^b \pm 27$	$0,6^b$

a-b: Means within a column with different superscripts are significantly different ($P<0,05$).
w: number of hams with tyrosine crystals.

Table 3. Results obtained from commercial lines.

Parameter	L15	L10	L03
pH	$6,03 \pm 0,13$	$6,04 \pm 0,15$	$5,92 \pm 0,09$
$NaCl^x$	$7,91^b \pm 0,36$	$7,55^b \pm 0,56$	$8,80^a \pm 0,46$
Tyr^y	$406^b \pm 101$	$545^a \pm 73$	$463^{ab} \pm 69$
Tyr crystals^z	21^b	56^a	26^b

Table 4. Physicochemical parameters in hams of different pure breeds

Parameter	LW^-	LS^-	LS^+	LB^+	D^-	P^+
$NaCl^x$	5,32	5,53	5,21	5,23	5,63	4,64
	0,56	0,64	0,49	0,59	0,48	0,82
pH	6,07	6,04	6,06	6,10	6,05	6,09
	0,07	0,05	0,10	0,09	0,03	0,12
Tyr^y	607	610	649	628	600	702
	66	64	120	85	59	118
Tyr crystals^z	37	32	52	46	29	84
White film	2,0	2,0	1,5	2,0	2,1	1,3

x: percentage in humid basis. y: mgs of tyrosine per 100 g. of ham. z: number of tyrosine crystals. a-b: Means within a file with different superscript are significantly different ($P<0,05$). The analysis were carried out at the end of the process in Biceps femoris.