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Meat Science 54 (2000) 333–337

MEAT SCIENCE

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Evolution of volatile aldehydes in Iberian ham matured under different processing conditions

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Received 10 May 1999; received in revised form 14 July 1999; accepted 29 July 1999

Abstract

To evaluate the influence of the Iberian ham processing conditions in the evolution of volatile aldehydes, 35 hams were processed in two plants following different conditions of relative humidity and temperature. For this, free fatty acids, peroxide values and volatile aldehydes were quantified in the hams. The highest increases in free fatty acids were noted during the drying stage in both processing plants. The drying period also revealed the greatest increase in peroxide values, where the highest values were in those hams processed at higher temperatures. The temperature during post-salting and drying had a marked influence on the formation of volatile aldehydes, being responsible for the differences in volatile compounds of matured hams.

1. Introduction

The Iberian dry cured ham is an uncooked meat product of high sensory quality with a first rate of consumer acceptance. This seems to be related to the special characteristics of the raw material obtained from Iberian pig, fattened extensively in pastures with acorns and grass, with levels of 10–13% of intramuscular fat (Antequera, Córdoba, Ruiz, Martín, Bermúdez & Ventanas, 1993) and a high percentage of oleic acid (Cava et al., 1997; Flores, Nieto, Bermell & Alberola, 1987). In addition, the prolonged dry-cured processing of Iberian hams covering 18–24 months may also be important to the sensory characteristics of the product.

It is well known that the typical ham aroma is related to intramuscular lipid composition and to the extent of lipolysis and oxidation of lipids during processing (Berdagué, Denoyer, Le Quere & Semon, 1991; Buscailhon, Berdagué & Monin, 1993). Although oxidation of lipids during processing is usually considered to produce off-flavors and rancidity, dry-cured hams are a notable exception, because oxidation products play a definitive role in the sensory quality of the final product (García, Berdagué, Antequera, López-Bote, Córdoba & Ventanas, 1991; Flores, Grimm, Toldrá & Spanier, 1997).

Processing conditions determine the rate of lipid oxidation and the subsequent possible deteriorative effects (Ladikos & Lougovois, 1990). Carbonyl compounds are the most abundant volatiles reported at the end of processing in different types of cured hams such as country style dry-cured ham (Lillard & Ayres, 1969; Ockerman, Blumer & Craig, 1964), Parma ham (Barbieri, Bolzoni, Parolari, Virgili, Careri & Mangia, 1992), French ham (Berdagué, Bonnaud, Rousset & Touraille, 1993; Berdagué et al., 1991; Buscailhon et al., 1994) and Iberian ham (García et al.; López, de La Hoz, Cambero, Gallardo, Reglero & Ordoñez, 1992). Among the carbonyls, aldehydes have very low threshold olfactory concentrations, and therefore constitute an important group of natural flavors. Carbonyl compounds, particularly volatile aldehydes formed from oxidation or decomposition of lipids, play both positive and negative roles in lipid-rich food (Grosch, 1987). Antequera et al. (1992) studied lipid oxidation parameters during the processing of Iberian ham, but the influence of processing at different temperatures and relative humidity on the composition of volatile aldehydes has not been reported yet.

In this work, changes in the free fatty acid (FFA), peroxide value (PV) and the content of selected aldehydes were studied during two usual maturation processes of Iberian dry-cured hams.

0309-1740/00/$ - see front matter
PII: S0309-1740(99)00107-2

2. Material and methods

2.1. Selection of the hams

Thirty-five thighs were obtained from Iberian pigs that were reared extensively in pastures with acorns (*Quercus suber* and *Quercus ilex*) as their basic feed until they achieved a final weight of about 160 kg. After conventional slaughter and refrigeration for 48 h, the thighs, of homogeneous characteristics (pH and weight), were sorted out and processed for 22 months.

2.2. Processing of the hams

Hams were rubbed with salt, containing about 1% potassium nitrate and placed in piles of salt at 4°C and 80% relative humidity, for 1 day/kg weight (salting). After salting the hams were washed to remove salt from the surface and processed in two local plants under different conditions as follows.

- Batch A: For 68 days the temperature was moderately raised (1–2°C every 5 days) up to 15°C and the relative humidity was progressively lowered down to 75% to allow diffusion of the salt into the hams. The hams were then kept in a room under environmental conditions for 130 days (temperature range from 5 to 25°C and 70–50% relative humidity). Next, the hams were left to mature for 15 additional months in a cellar at temperatures ranging from 11 to 23°C and 58–80% relative humidity.
- Batch B: After washing to remove the salt from the surface, the hams were hung at low temperature (4°C) and high relative humidity (80%) for 64 days and then taken to a natural dryer at temperatures varying from 4 to 27°C and a relative humidity from 70 to 43% for 134 days. Next, the hams were left to mature for 15 months in a cellar at temperatures of 10–27°C and relative humidity of 58–80%. Changes of temperature and relative humidity during processing of the two batches are shown in Fig. 1.

2.3. Sampling procedure

The steps included in the two processes and the number of hams removed for testing at each stage (n) were as follows:

	Batch A	Batch B
Green state (G)	0 days ($n=5$)	
Post salting (PS)	80 days ($n=5$)	76 days ($n=5$)
Drying (D)	210 days ($n=6$)	210 days ($n=6$)
Matured hams (M)	665 days ($n=4$)	665 days ($n=4$)

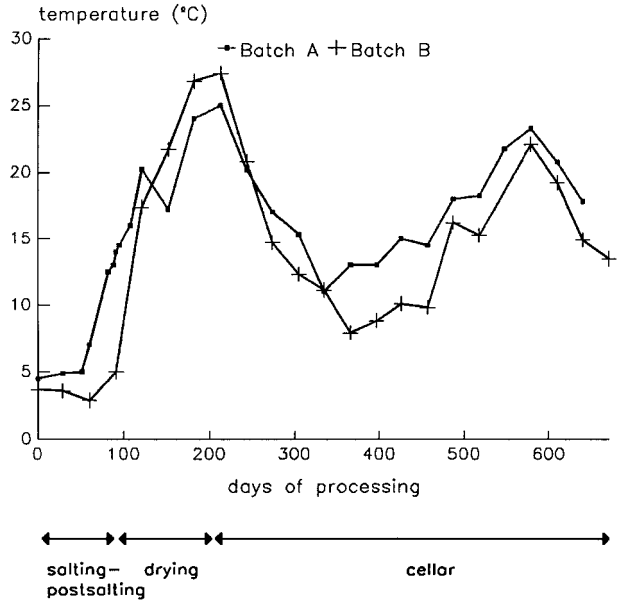

Fig. 1. Changes of environmental temperature during the processing of Iberian hams at Batch A and Batch B.

The *Biceps femoris* muscle was used for the study. It was coarsely ground and kept at −80°C until analyzed.

2.4. Analytical determination

2.4.1. Lipid extraction

Lipids were extracted from samples with a chloroform:methanol mixture (2:1) using the method of Folch, Lees and Stanley (1957).

2.4.2. Acidity (FFA). Acidity as percentage oleic acid equivalents was determined by the method 28032 recommended by AOAC (1984a).

2.4.3. Peroxide value (PV). The method 28025 recommended by AOAC (1984b) was followed for the determination of PV.

2.5. Volatile aldehydes

A Hewlett-Packard headspace automated system Mod. 1939A directly coupled to a Hewlett-Packard 5890A gas chromatograph equipped with split-splitless injector and FID detector was used to determine the volatile aldehydes. Samples (4 g) were placed into a glass vessel with 408.5 ng (0.5 μl) of 4-heptanone as internal standard. The glass vessel was hermetically closed and connected to a stream of helium at 90°C for 30 min.

The separation was performed with a Hewlett-Packard-5 capillary GC column crosslinked with 5% phenylmethyl silicone (1.05 μm, 50 m×0.32 mm). Helium carrier flow rate was 18 ml/min. The oven temperature was programmed from 35 to 200°C, at a rate of 7°C/min. The

injector temperature was 230°C and the detector temperature 240°C. The injector split ratio was 1:24. Response factors were determined for all volatile aldehydes by injecting samples containing a known amount of each aldehyde standard and 4-heptanone. The result were expressed as ng aldehyde/g of dry matter. Tentative identification was based on retention time of reference compounds (Sigma). Mass spectra were also obtained using a mass selective detector (Hewlett-Packard HP-5971 A) by electronic impact at 70 eV, a multiplier voltage of 1756 V and collecting data at a rate of 1 scan s^{-1} over the m/z range 30–300. Compounds were tentatively identified by comparing their mass spectra with those contained in the NIS/EPA/NIH and Wiley libraries.

2.6. Statistical analysis

Statistical analyses were carried out using the STATGRAPHICS 5.0 (Statistical Graphics System) statistical package run in a Hewlett-Packard PC. The comparison between means from processing A and B was made using Student t-test. Differences between stages were performed by analysis of variance using the Bonferroni test.

3. Results and discussion

Data for total free fatty acids (expressed as % oleic acid equivalents) are shown in Table 1. Although lipolysis occurred throughout the process, the highest increases were noted during the drying stage, recording a daily rise of 0.03% as oleic acid equivalents (percentage of oleic acid). There seemed to be a clear relationship between rise in temperature and increased acidity index, since in the latter months of processing, while hams were in the cellar, higher temperatures again led to increased acidity. This second rise was less intense than that of the drying stage, perhaps due to the intense autoxidation taking place at this time (Table 2). In the two processing plants A and B, the degree of acidity in the final product was about three times higher than that of the fresh meat ($p < 0.05$). While temperatures during processing were different for Batches A and B, the values recorded for this index were similar at both plants. The degree of acidity found in the final product was greater than those in previous reports for Iberian ham (Antequera et al., 1993). These differences may be due to the different processing times involved. In this sense, for "serrano" hams, Astiasarán, Beriain, Melgar, Sánchez-Monge, Villanueva and Bello (1988) reported a direct relationship between processing time and increased acidity index. Evolution of the oxidative processes during maturation is shown by peroxide value (Table 2). Generally, the PV displayed a marked rise during processing, although this evolution took place over distinct stages. The drying period revealed the greatest increase in the index, where higher values were recorded for processed hams from Batch B (Table 2). This finding may be directly related to temperature, which at this stage of the process was higher at plant B. Probably, PV values higher than those found in the final product could have been recorded if the time between successive samples had been shorter, specially in cellar stage that takes about 15 months.

In the latter months of processing the hams revealed the highest levels of FFA (Table 1). As these FFA act as an oxidation substrate, the new rise in temperature promoted the increase in PV. However, the daily increase was less intense than during the previous stage. In other studies of Iberian hams, Antequera et al. (1993) reported a similar evolution, although at the end of processing, PV values were higher in the present study. Similar values to the first peak were reported for dry-cured "serrano" ham by Flores et al. (1987), but these authors found no second increase, owing perhaps to the shorter processing times applied to this type of ham. In Iberian ham, Huertas (1990) observed maximum PV values in post-salting stage, and then a progressive decrease in the rest of the processing. This wide disparity in results for peroxide values highlights the great reactivity of these compounds, with results varying according to the moment when sampling is performed; the dynamic nature of oxidation means that as hydroperoxides are formed, they decompose giving rise to secondary products.

When studying the composition and evolution of aldehydes during the processing of Iberian hams, the following were identified: butanal, pentanal, hexanal, heptanal, octanal, 2-octenal, nonenal, 2,4-nonadienal, decanal and 2,4-decadienal. The composition and evolution of

Table 1
Means of free fatty acids (expressed as oleic acid percentage) in *Biceps femoris* muscle at Batch A and B during the ripening of Iberian hams[a]

	Stages			
Processing	Green ham	Post-salting	Drying	Maturated ham
Batch A	4.75a	3.51a	7.03b	14.55c
Batch B	4.75a,b	3.06a	7.72b	13.25c

[a] Means with different letters in the same row are significantly different ($p < 0.05$).

Table 2
Means of peroxide value (expressed as mequiv O_2 active/Kg fat) in *Biceps femoris* muscle at Batch A and B during the ripening of Iberian hams[a]

	Stages			
Processing	Green ham	Post-salting	Drying	Maturated ham
Batch A	2.91a	6.17a	28.02b	45.78c
Batch B	2.91a	6.43a	39.74b	47.70b

[a] Means with different letters in the same row are significantly different ($p < 0.05$).

aldehydes during processing of hams at plants A and B are shown in Table 3. The main precursors of these particular volatile compounds in different foods are the polyunsaturated fatty acids. The high level of marbling in fat (10–13%) in Iberian pigs (Antequera et al., 1993) and its high PUFA content in fresh Iberian pig meat (Cava et al., 1997) contribute to the presence of the above compounds. These compounds present a low olfaction threshold and are thus largely responsible for the final aroma produced in dry-cured ham. Saturated aldehydes help strengthen and intensify the aroma, while the 2-enal and 2,4-enal compounds add sweet, fruity and fatty features to the flavor and smell (Hamilton, 1989). The overall evolution of volatile headspace aldehydes showed a marked increase during maturation (Table 3). In the early stages of the process, a rise was only witnessed in the predominant aldehyde always hexanal, the remaining aldehydes roughly maintaining their original values. The gradual rise in temperature occurring during this stage did not appear to have any great influence on the formation of volatile aldehydes, but significant differences ($p < 0.05$) were found for the sum of all aldehydes between the two processing plants surveyed. The higher temperatures at which hams from Batch A were stored at the end of the post-salting stage contributed to the generation of more volatile compounds in these hams. In drying stage there was a marked increase in all the aldehydes studied. The rise in temperature occurring at this time promoted the large scale formation of volatile aldehydes, showing statistic differences respect PS stage ($p < 0.05$). In drying stage, hams of Batch B showed daily increases of volatile aldehydes (290.41 ng/g) higher than Batch A (177.34 ng/g), probably due to higher temperatures in Batch B. At the last stage of maturation there was yet another general increase in recorded volatile aldehyde levels, again coinciding with a temperature rise at the end of maturation. On comparing mean daily aldehyde increase at this stage with results from the foregoing stage it is clear that despite the time spent in cellar and the temperatures reached during this phase (close to those of the drying stage), volatile aldehyde formation was moderate. The limited oxidation produced in the last few months of maturation may be because during the latter stages of maturation there are condensation reactions between the aldehydes thus formed, in addition to reactions between aldehydes and the large quantity of free amino acids present at this stage (Córdoba, Antequera, García, Ventanas, López-Bote & Asensio, 1994), giving rise to the formation of Maillard compounds (Ventanas, Córdoba, Antequera, García, López-Bote & Asensio, 1992). The predominant aldehyde throughout the maturation process was hexanal, originating from linoleic and arachidonic acids (Tamura, Kitta & Shibamoto, 1991). The large amount of hexanal found in matured ham lends to the faintly rancid aroma so typical of high quality Iberian ham and considered a distinctive feature of these products. In addition to this rancid fragrance, hexanal has been described by some authors as the source of pleasing "grassy" or "fruity" aromas (Stahnke, 1994). Other volatile aldehydes, such as nonanal, octanal and heptanal, arise from oleic acid. These volatile aldehydes are extremely important since they add a highly pleasing sweet or fruity note to the aroma of cured ham (Specht & Baltes, 1994), and have low perception thresholds. This observation leads to the belief that their contribution to the ham's aroma is much higher than their scarce presence might indicate. Although the differences found between aldehydes in the two groups of hams were slight, certain significant differences ($p < 0.05$) were noted, more specifically for hexanal, 2-octenal, nonanal and the sum total of aldehydes; aldehyde values were

Table 3
Means of volatile aldehydes expressed as ng/g dry matter in *Biceps femoris* muscle at Batch A and B during the ripening of Iberian hams[a,b]

	Stages						
	Green ham	Post-salting		Drying		Maturated ham	
Aldehyde	Batch AB	Batch A	Batch B	Batch A	Batch B	Batch A	Batch B
C4	304ab	215a	200a	514b	422b	657b	754c
C5	1203a	1169a	955a	2505b	2161b	2612b	3180
C6	17 191a	24 071ab	18 559a	35 489b	36 239a	53 279c	89 883b
C7	1535a	1465a	1093a	3523b	3135b	2543ab	2460ab
C8	958a	1108a	697a	2558b	2397b	1494b	1800a
2-C8	781a	340b	389b	497b	426b	568a	802ab
C9	2147ab	1308a	1419a	2505bc	2831b	2041c	3050ab
2-C9	663a	887a	782	1203a	798	2091b	2115
2,4-C9	665	–	–	1069	798	933	1137
C10	927	767	745	633	650	682	764
2,4-C10	–	–	–	358a	377a	963b	1186b
Total	26 374a	31 330b	24 839a	50 854c	50 234b	67 863d	107 131c

[a] Means with different letters in the same row show significative differences ($p < 0.05$) among stages of the same processing.
[b] Underlined values in the same row show significative differences ($p < 0.05$) between curing processes in each stage.

higher in drying and cellar stage for processed hams from Batch B than those from Batch A. Cellar temperature was higher in Batch A, lending even more weight to the assumption that the influence of temperature during the final maturation stages is reduced owing to the presence of antioxidants such as some free amino acid, peptides of low molecular weight (Martín, Antequera, Ruiz, Cava, Tejeda & Córdoba, 1998) and Maillard compounds, which have been reported as possessing antioxidant effects (Chan & Decker, 1994).

Temperature during processing of Iberian ham has a marked influence on the formation of volatile aldehydes, especially during the first stages of processing (post-salting and drying). In cellar stage the formation of volatile aldehydes was lower than in the former stages probably due to the presence of antioxidant compounds. Thus, differences in temperatures in the post-salting and drying stages between processing systems lead to different amounts of volatile aldehydes, which could influence the sensory characteristics of the final products.

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