Lipolytic and oxidative changes during the manufacture of dry-cured lacón. Effect of the time of salting

By Rubén Garrido, María Gómez, Inmaculada Franco and Javier Carballo*

Área de Tecnología de los Alimentos, Facultad de Ciencias de Ourense, Universidad de Vigo, 32004 Ourense, Spain. (*Corresponding author: carbatec@uvigo.es)

RESUMEN

Cambios lipolíticos y oxidativos durante la elaboración del lacón crudo-curado. Efecto del tiempo de salazón.

Se determinó el índice de acidez de la grasa, el índice de peróxidos y el número de TBA (ácido tiobarbitúrico) en la grasa subcutánea y en la de la porción muscular (grasa extraída de la porción muscular obtenida tras la separación de la grasa subcutánea) (o en la porción muscular completa (grasa + magro) en el caso del número de TBA) a lo largo de la maduración del lacón crudo-curado, un producto cárnico tradicional elaborado en el noroeste de España a partir de la extremidad anterior del cerdo cortada a nivel de la articulación escápulo-humeral, siguiendo una tecnología similar a la del jamón curado. Se estudió también el efecto sobre estos parámetros del tiempo de salazón (3, 4 o 5 días).

Los valores de los tres índices aumentaron de un modo significativo (p < 0,001) a lo largo de la elaboración en todas las partidas estudiadas, tanto en la grasa subcutánea como en la de la porción muscular (o en la porción muscular completa).

El aumento del tiempo de salazón, aunque no determinó un incremento estadísticamente significativo de la concentración de cloruro sódico en las piezas al final del proceso de elaboración, determinó un incremento significativo (p < 0,001) de los valores de índice de peróxidos en todos los puntos de muestreo, tanto en la grasa subcutánea como en la de la porción muscular. Al final del proceso de elaboración, los valores del número de TBA también fueron significativamente (p < 0,001) más elevados en las partidas sometidas a un salazonado más intenso. El aumento del tiempo de salazón parece, en general, inhibir los procesos lipolíticos; sin embargo, este efecto no fue patent en todos los puntos de muestreo de todas las partidas de lacón estudiadas.


SUMMARY

Lipolytic and oxidative changes during the manufacture of dry-cured lacón. Effect of the time of salting.

The acidity, peroxide and TBA values were determined, both in the subcutaneous fat and in the muscular portion fat (fat extracted from the muscular portion minced and homogenised after discarding the subcutaneous fat), or in the whole muscular portion (fat + lean tissue) in the case of the TBA values, throughout the manufacture process of dry-cured lacón, a traditional dry-salted and ripened meat product made in the north-west of Spain from the foreleg of the pig following a similar technological process to that of dry-cured ham. The effect of the time of salting (3, 4 or 5 days) on these parameters was also studied.

Throughout the manufacture, the acidity, the peroxide and the TBA values significantly (p < 0,001) increased in all the batches studied and both in the subcutaneous fat and in the muscular portion fat or muscular portion.

The increasing of the salting time, despite the fact that did not significantly increase the NaCl contents in the pieces at the end of the manufacture process, significantly (p < 0.001) increased the peroxide values throughout the manufacture process both in the subcutaneous and in the muscular portion fat. At the end of the manufacture process, the TBA values also were significantly (p < 0.001) higher in the more intensely salted batches. The increasing of the salting time seems, in general, to have a inhibitory effect on the lipolytic phenomena; however, this effect was not consistent in all the sampling times in the batches studied.


1. INTRODUCTION

Dry-cured lacón is a traditional raw-cured meat product made in the northwest of Spain, from the foreleg of the pig by similar manufacturing processes to those used in the production of dry-cured ham.

Dry-cured lacón is a product that is well appreciated in the areas where it is produced, but at present there are some problems that make difficult its diffusion to wider markets. Such problems include the heterogeneity of the product and questionable organoleptic quality of some units. These deficiencies are partly due to a lack of knowledge and control of the biochemical and microbiological phenomena that take place throughout the manufacturing process and that are responsible for the organoleptic quality of the final product.

During the manufacture of raw-cured meat products made from whole pieces, different
physicochemical and chemical changes take place, of which the lipid degradation processes are probably the most important and are those that have the greatest effects on the organoleptic characteristics of the final products.

The lipids (triacylglycerols and phospholipids) are firstly hydrolysed by tissue enzymes to form free fatty acids, which under the action of different catalytic agents (light, Fe, NaCl, high temperatures) can also undergo oxidative processes and generate hydroperoxides, which are then degraded to give rise to secondary products of oxidation (aldehydes, ketones, hydrocarbons, alcohols, lactones and esters), which also contribute to the taste and aroma of the matured products (Toldrá & Flores, 1998; Gandemer, 2002).

In the manufacture of the raw-cured lacón, traditionally, and following the guidelines of the manufacture process of the cured ham, a day of salting per kilogram of weight was applied. Nevertheless, and given the specific characteristics of the lacón piece (bigger surface per unit of weight than in the ham) this salting time could not be the most appropriate in order to obtaining a product with maximum quality.

Reports on the effects of the NaCl concentration on the activity of the lipolytic enzymes and on the oxidative processes that take place during the ripening of the cured meat products are not abundant. According to Motilva and Toldrá (1993), in general, the activity of the pork muscle and adipose subcutaneous tissue lipases and esterases decreased as the NaCl concentration increased, with the exception of the muscle acid lipase which was activated with the increasing NaCl concentrations; the increasing \( a_w \) values increased the enzymatic activities, also with exception of the muscle acid lipase. With regard to the effects on the autooxidative processes, it seems that the increase of the concentration of NaCl, as a consequence of the dehydration process during ripening, causes an increase of the oxidation of the lipids (Coutron-Gambotti et al., 1999), besides the prooxidant effect of the salt attributed to the iron ions that accompany to the salt as impurities (Pearson et al., 1977; Ladikos and Lougovois, 1990).

The aim of the present study, which forms part of a wider study on the improvement of the quality of dry-cured lacón, was to obtain information about the lipolytic and oxidative changes that occur during the manufacturing process, as well as to study the effect of the time of salting on these changes.

2. MATERIALS AND METHODS

2.1. Samples

In order to carry out this study, six batches of lacón were manufactured. Each batch consisted of nine lacón pieces that in the green stage (fresh pieces) weighed 4 kg each. Before the salting process, each piece was rubbed with a mixture composed of glucose (8 g), sodium nitrite \( (E_{250}) \) (500 mg), sodium nitrate \( (E_{251}) \) (700 mg), sodium ascorbate \( (E_{331}) \) (2000 mg), and sodium citrate \( (E_{332}) \) (400 mg). Raw pieces were salted with coarse salt, forming piles alternating between pieces and salt. Two batches were salted during 3 days (0.75 days/kg), two batches during 4 days (1 day/kg) and the remaining two during 5 days (1.25 days/kg), being the temperature of the salting room between 2 and 5 °C and the relative humidity between 80 and 90%. After the salting stage, the pieces were taken from the pile, brushed, washed, and transferred to a post-salting room where they stayed for 14 days at a 2-5 °C and around 85-90% relative humidity. After the post-salting stage, the pieces were transferred to a room at 12 °C and 74-78% relative humidity where a drying-ripening process took place for 84 days.

In each batch, samples were taken from fresh pieces, after the end of the salting stage, after 7 and 14 days of post-salting, and after 7, 14, 28, 56, and 84 days of drying-ripening. Each sample consisted of one whole lacón piece. Samples were transported to the laboratory under refrigeration conditions (below 4 °C) and analysed on arrival. Once in the laboratory, the entire pieces were skinned and the subcutaneous fat was obtained; then, the pieces were boned, and the resulting muscular portion was minced in a high-capacity mincer.

2.2. Analytical methods

Moisture and NaCl contents were determined in duplicate in each sample using the methods cited by Marra et al. (1999). The water activity \( (a_w) \) was measured using a Decagon CX-1 Water Activity System apparatus (Decagon Devices, Pullman, WA, USA).

Extraction of fat (both from the muscular portion and from the subcutaneous localization) was performed according to Folch, Lees, and Stanley (1957). The acidity and the peroxide values were determined following the Spanish Official Standards UNE 55.011 and UNE 55.023, respectively (Presidencia del Gobierno, 1977). The TBA value was measured according to the method of Tarladgis et al. (1960). All the determinations were carried out in duplicate in each sample.

2.3. Statistical analysis

In order to study for each parameter the effect of the ripening time and the effect of the time of salting and localization of the fat in the piece at each sampling time, an analysis of variance (ANOVA) was performed, with confidence intervals of 95% \( (P < 0.05) \), 99% \( (P < 0.01) \) and 99.9% \( (P < 0.001) \). Means were compared by the least squares difference (LSD) test, using the computer programme Statistica® 5.1 for Windows (Statsoft Inc, 1996, Tulsa, OK, USA).
3. RESULTS AND DISCUSSION

Figure 1 shows the evolution of the NaCl concentrations (a) and of the a_w values (b) in the interior of the pieces along the manufacture of the lacón batches with different salting times. As in the rest of the figures included in this work, times in the X-axis correspond to the batches salted during 4 days; these times are plus a day in the batches salted during 5 days, and minus a day in the batches salted during 3 days.

The NaCl values in the interior of the lacón pieces (expressed as g/100 g of Total Solids) significantly $(p < 0.001)$ increased during the salting and post-salting stages, and during the 7 first days of the drying-ripening period, reaching values that remained relatively constant until the end of the manufacture process. The final average values were 11.25, 12.22 and 12.75 g/100 g of TS in the batches salted during 3, 4 and 5 days, respectively; the differences between these final values were not significant statistically.

The a_w values significantly $(p < 0.001)$ decreased in all the batches studied, reaching final average values in the interior of the pieces of 0.90, 0.89 and 0.87, in the batches salted during 3, 4 and 5 days, respectively. The differences between the values of the batches submitted to different salting times were also not significant.

Figure 2 shows the evolution of the acidity value in the subcutaneous and in the muscular portion fat during the manufacture of the lacón batches with different salting times.

The values in the muscular portion fat dropped during the salting and post-salting stages. This effect has been previously described by other authors in dry-cured lacón (Lorenzo et al., 2008a) and in dry-cured ham (Martín Cáceres, 1997).

Figure 1. Changes in NaCl contents (a) and in the $a_w$ values (b) in the muscular portion during the manufacture of dry-cured lacón salted along different times. Plotted values are the average of two batches in each salting time.
Agents and by some other processing parameters. Results from Motilva and Toldrá (1993) show that the activity of the tissue lipases is limited by the increasing NaCl concentrations and by the low environmental temperatures. The low environmental temperatures during the lacón manufacture (never above 12 °C) and the high NaCl concentrations seem to be the responsible for the low lipolysis observed in this meat product.

Regarding the effect of the time of salting on the acidity values in the subcutaneous fat, in all the sampling times, the values were higher in the batches salted during 3 days than in the batches salted during 4 or 5 days; however, these differences were not statistically significant. In the muscular portion fat, only in the post-salting stage and after 7 days of drying-ripening the values in the batches salted during 5 days were significantly (p < 0.05) lower than in the batches salted during 3 or 4 days; no significant differences were observed between the batches salted during 3 and 4 days. From these values it can deduce a certain inhibitory effect of the NaCl over the lipolytic processes. However, this inhibitory effect is not linear with the NaCl concentration in all cases.

Figure 3 shows the evolution of the peroxide values in the subcutaneous fat and in the muscular portion fat during the manufacture of dry-cured lacón salted along different times. Plotted values are the average of two batches in each salting time.

During the drying-ripening stage, the acidity values increased significantly (p < 0.001) both in the subcutaneous and in the muscular portion fat, and reached final average values of 2.29, 2.01 and 2.07% of oleic acid in the subcutaneous fat and of 4.49, 3.86 and 3.93% of oleic acid in the muscular portion fat, in the batches salted during 3, 4 and 5 days, respectively. This significant increase may be due to the environmental conditions in this stage (12 °C and 74-78% relative humidity), which may favour a certain degree of lipolysis.

The final average values in the muscular portion fat were similar to those previously reported in dry-cured lacón (end product) by Marra et al. (1999) and by Rodríguez et al. (2001). These values, however, were generally lower than those reported in ham (Antequera et al. 1992; 1993; 1994; Astiasarán et al., 1988; Flores et al., 1985), even after a manufacture time similar to the total duration of the manufacture of the dry-cured lacón. The final average values in the subcutaneous fat were also lower than those reported in the subcutaneous fat in hams (Astiasarán et al., 1988; Balderas et al., 1993; Flores et al., 1985).

The values of the acidity allow us to conclude that dry-cured lacón undergoes during its manufacture a lower degree of lipolysis than hams. During drying and maturation, hams are probably subjected to environmental conditions that are more appropriate for the activity of the tissue lipolytic enzymes (Balderas et al., 1993), which are the main responsible for the hydrolytic processes that the fat suffers during the manufacture of the raw-cured meat products made from whole pieces. The activity of these enzymes is strongly influenced by the curing agents and by some other processing parameters. Results from Motilva and Toldrá (1993) show that the activity of the tissue lipases is limited by the increasing NaCl concentrations and by the low environmental temperatures. The low environmental temperatures during the lacón manufacture (never above 12 °C) and the high NaCl concentrations seem to be the responsible for the low lipolysis observed in this meat product.

Regarding the effect of the time of salting on the acidity values in the subcutaneous fat, in all the sampling times, the values were higher in the batches salted during 3 days than in the batches salted during 4 or 5 days; however, these differences were not statistically significant. In the muscular portion fat, only in the post-salting stage and after 7 days of drying-ripening the values in the batches salted during 5 days were significantly (p < 0.05) lower than in the batches salted during 3 or 4 days; no significant differences were observed between the batches salted during 3 and 4 days. From these values it can deduce a certain inhibitory effect of the NaCl over the lipolytic processes. However, this inhibitory effect is not linear with the NaCl concentration in all cases.
In the subcutaneous fat, the peroxide values significantly ($p < 0.05$) increased during the salting stage, remained relatively constant or even decreased during the post-salting, and then significantly ($p < 0.001$) increased during the drying-ripening period. This increase, although also significant ($p < 0.05$), was less intense in the batches salted during 3 days.

In the muscular portion fat, the peroxide values significantly increased during the salting stage ($p < 0.01$) and, in a less marked way, in the post-salting stage ($p < 0.05$). In the batches salted during 3 or 4 days, the peroxide values significantly ($p < 0.05$) decreased during the first 14 days of the drying-ripening period, and then increased ($p < 0.001$) until the end of the manufacture; the decrease during the first days of the drying-ripening stage could be due to the fact that, in that period and in these batches, the degradative processes of the peroxides are more intense than the autooxidative phenomena with which the final balance is a descent of the peroxide values. In the batches salted during 5 days, the peroxide values significantly ($p < 0.05$) increased during the first 28 days of the drying-ripening period and then remained relatively constant until the end of the manufacture process.

In practically all the sampling times, and both in the subcutaneous and in the muscular portion fat, the peroxide values were significantly ($p < 0.001$) higher in the batches salted during 5 days than in the batches salted during 4 days; and in turn the values were significantly ($p < 0.001$) higher in the batches salted during 4 days than in the batches salted during 3 days. From these data, a clear prooxidant effect of the salt is deduced. In the subcutaneous fat, possibly due to the difficulties for the diffusion of the salt to this point in the pieces, and possibly also due to the lower diffusion of the oxygen, the peroxide values were significantly lower ($p < 0.05$) than in the muscular portion fat. The final average values were $7.69$, $17.79$, and $21.72$ meq O$_2$ / kg. In the subcutaneous fat, the final average value was $10.78$, $24.96$, and $26.48$ meq O$_2$ / kg. The final peroxide values in the muscular portion fat were similar to those reported by Marra et al. (1999) and by Rodríguez et al. (2001) in dry-cured lacón at the end of the manufacture process. However, these values were in general higher than those reported in Serrano (Astiasarán et al., 1988; Flores et al., 1985) and in Iberian (Antequera et al., 1992) hams after a similar curing period; the final average values in the subcutaneous fat were also higher than those reported by Flores et al. (1985) in ham. This circumstance could be related with the lower NaCl content in the hams and with the lower size in the lacón pieces that increases the surface per unit of weight and therefore the surface of contact with the air.

Figure 4 shows the evolution of the TBA value in the subcutaneous fat and in the muscular portion fat during the manufacture of dry-cured lacón salted along different times. Plotted values are the average of two batches in each salting time.

In the muscular portion fat, the peroxide values significantly increased during the salting stage ($p < 0.001$) and, in a less marked way, in the post-salting stage ($p < 0.05$). In the batches salted during 3 days, the peroxide values significantly ($p < 0.05$) decreased during the first 14 days of the drying-ripening period, and then increased ($p < 0.001$) until the end of the manufacture process; the decrease during the first days of the drying-ripening stage could be due to the fact that, in that period and in these batches, the degradative processes of the peroxides are more intense than the autooxidative phenomena with which the final balance is a descent of the peroxide values. In the batches salted during 5 days, the peroxide values significantly ($p < 0.05$) increased during the first 28 days of the drying-ripening period and then remained relatively constant until the end of the manufacture process.

In practically all the sampling times, and both in the subcutaneous and in the muscular portion fat, the peroxide values were significantly ($p < 0.01$) higher in the batches salted during 5 days than in the batches salted during 4 days; and in turn the values were significantly ($p < 0.001$) higher in the batches salted during 4 days than in the batches salted during 3 days. From these data, a clear prooxidant effect of the salt is deduced. In the subcutaneous fat, possibly due to the difficulties for the diffusion of the salt to this point in the pieces, and possibly also due to the lower diffusion of the oxygen, the peroxide values were significantly lower ($p < 0.05$) than in the muscular portion fat. The final average values were $7.69$, $17.79$, and $21.72$ meq O$_2$ / kg. In the subcutaneous fat, the final average value was $10.78$, $24.96$, and $26.48$ meq O$_2$ / kg. The final peroxide values in the muscular portion fat were similar to those reported by Marra et al. (1999) and by Rodríguez et al. (2001) in dry-cured lacón at the end of the manufacture process. However, these values were in general higher than those reported in Serrano (Astiasarán et al., 1988; Flores et al., 1985) and in Iberian (Antequera et al., 1992) hams after a similar curing period; the final average values in the subcutaneous fat were also higher than those reported by Flores et al. (1985) in ham. This circumstance could be related with the lower NaCl content in the hams and with the lower size in the lacón pieces that increases the surface per unit of weight and therefore the surface of contact with the air.

Figure 4 shows the evolution of the TBA value in the subcutaneous fat and in the muscular portion fat during the manufacture of dry-cured lacón salted along different times. Plotted values are the average of two batches in each salting time.
The TBA values significantly ($p < 0.05$) increased during the salting stage and during the post-salting period (in this period with the exception of the batches salted during 3 days). However, the highest increase in this parameter took place during the first 28 days of the drying-ripening period ($p < 0.001$), reaching the highest values after 28 days of drying-ripening (average values of 9.80, 9.01 and 10.52 mg of malonaldehyde / kg of subcutaneous fat and of 7.15, 6.56 and 6.66 mg of malonaldehyde / kg of muscular portion, in the batches salted during 3, 4 and 5 days, respectively). From these maximum values, a significant ($p < 0.01$) drop was observed in all the batches studied, more intense in the less intensely salted batches, until reaching final average values of 2.24, 3.29 and 5.83 mg of malonaldehyde / kg of subcutaneous fat and of 1.81, 2.50 and 3.95 mg of malonaldehyde / kg of muscular portion, in the batches salted during 3, 4 and 5 days, respectively.

The increase in malonaldehyde contents during the salting and post-salting stages was also reported by Melgar et al. (1990) in hams; these authors observed at the end of the post-salting stage values (1.97 mg of malonaldehyde / kg) very close to ours. However, they did not report any noticeable increase in TBA values during the drying stage. The final drop observed in our study was also reported by Melgar et al. (1990) in the subcutaneous fat of hams. This final drop was attributed to the instability of the malonaldehyde (Melgar et al., 1990).

Our final values in the different batches and localizations in the piece are slightly lower than those reported by Rodríguez et al. (2001) and by Lorenzo et al. (2008b), and of the same order of those reported by Veiga et al. (2003) in dry-cured lacón (end product).

In general, and for each batch and sampling time, the values observed in the subcutaneous fat were significantly ($p < 0.01$) higher than those observed in the muscular portion. This finding is due possibly to the fact that the malonaldehyde, coming from the peroxide degradation, is more concentrated in the lipid fraction and, when the muscular portion was analysed, not only fat but also lean tissue was analysed. In fact, Cobos et al. (2008) observed very high TBA values in the muscular portion of the dry-cured lacón when expressed as mg of malonaldehyde / kg of fat.

With regard to the effect of the time of salting on the TBA values, in general only significant differences were observed in the two last sampling times (56 and 84 days of drying-ripening), being the TBA values significantly higher ($p < 0.001$) in the batches salted during 5 days than in the batches salted during 4 days. In the batches salted during 4 days, the TBA values in these two sampling times were also significantly higher ($p < 0.01$) than in the batches salted during 3 days.

Along the ripening process, and on average, the acid value increased by a factor of 2.6, while the peroxide value increased by a factor of 5.5 and the TBA value increased by a factor of 9.6. This indicates that the manufacture of dry-cured lacón the oxidative processes predominate over the lipolytic ones.

Judging from the differences observed and also from the statistical significance of these differences it can be deduced that the increase of the salting time seems to have a greater effect on the oxidative (that are promoted) than in the lipolytic (that are inhibited) phenomena.
4. CONCLUSIONS

Throughout the manufacture of dry-cured lacón, the acidity, the peroxide and the TBA values significantly (p < 0.001) increased in all the batches studied and both in the subcutaneous fat and in the muscular portion fat (or muscular portion). Lipolytic processes in dry-cured lacón seem to be less intense than in hams, while the autooxidative phenomena appear to have more intensity.

During the manufacture of dry-cured lacón the oxidative processes predominated over the lipolytic ones, and the increase of the salting time seems to have a greater effect on the oxidative than in the lipolytic phenomena.

The results of this work, together with those carried out on the effect of the salting time on the proteolytic phenomena during manufacture, and on the sensorial characteristics of the final product, will help to decide the most suitable time of salting for the dry-cured lacón.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial assistance of the Xunta de Galicia (The Regional Government) (Projects 3830198 and PGIDT01PXI38301PR). The authors also wish to thank Mr. Juan Vidal Lago from Industrias Cánicas Portalaconsa S.L. (Porriño, Pontevedra, Spain) for his useful collaboration during this study.

REFERENCES


Aceptado: 5/2/09

Recibido: 23/12/08

GRASAS Y ACEITES, 60 (3), SPECIAL ISSUE, 255-261, 2009, ISSN: 0017-3495, DOI: 10.3989/gya.130508