PROTEOLYTIC AND LIPOLYTIC BREAKDOWN DURING THE RIPENING OF IBERIAN HAMS.

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SUMMARY
Forty Iberian hams were processed by traditional dry-cure procedure and the degradative changes of the marbling lipids and proteins during the maturing phase studied. A large amount of proteolysis and lipolysis occurs during the drying step as revealed by the increase of non-protein nitrogen (NPN) concentration and free fatty acids (FFA) content. Next, while hams are kept in the cellar, NPN and FFA levels raise continuously, whereas an intense autooxidative activity takes place, as assessed by a significative increase of peroxide value (PV). These proteolytic and lipolytic processes lead to accumulation of free amino-acids and amines, aldheydes, alcohols, hidrocarbons, lactones, ketones and esters found in the final product, which are assumed to be highly related to their particular taste.

INTRODUCTION

The Iberian pigs is a porcine breed of great economic importance in the Southwestern area of Spain. The Ministry of Agriculture Fisheries and Food estimated that about 1 million hind legs from Iberian pigs are processed into cured hams each year (MAPA, 1984). Some Iberian hams (Montanchez, Jabugo, Guijuelo) have attained a high degree of consumer acceptance due to their charasteristic and strong flavour. For these hams, pigs were fattened in pastures with acorn (Querqus ilex and Querqus suber) as basic food until a final live weight of about 140Kg. After slaughter hams are salted and, later on, left to ripen up to 12 months at environmental conditions.

No systematic work has been carried out until now on the changes taking place during the processing of these high-quality hams. This study was undertaken with the aim to elucidate the degradative processes leading to the formation of compounds responsible for the desired flavour in Iberian hams.

MATERIAL AND METHODS

Forty thighs from iberian pigs were selected and handed to a plant to be processed in the traditional way. The lot was divided into 7 groups of hams to fill in the following sampling protocol: 1. Green state (G) n=10, 2. Salted (S) n=4, 3. Post-salting 1 (PS1) n=4, 4. Post-salting 2 (PS2) n=4, 5. Dryed (D) n=8, 6 and 7. Half-cellar (HC) n=10 and aged ham (A) n=10.

Samples of Biceps femoris (BF) muscles of each ham were taken and analysed as follow:

Water activity (Aw) was determined at 20ºC by the graphic

interpolation method using saturated salt solutions as standards (Landrock & Proctor, 1951). The pH was measured in a homogeneized slurry made of 10g of sample and 10ml of distilled water. Nitrite were analysed espectrophotometrically by using the Gries reaction (AOAC, 1984a).

Protein nitrogen (PN) was determined following AOAC, (1984b) recommended method, and the non-protein nitrogen (NPN) content was analysed following the method of Johnson (1941). Peptidic (peN) and amino-acidic nitrogen (AN) contents were determined according to Moore and Steine (1948). Basic volatile nitrogen (BVN) content was measured following the method of Pearson (1968).

Free amino-acids and amines were indentified and their content measured by HPLC following the methods of Yang and Sepulveda (1985) and Edwards et al. (1983) respectively with minor modifications.

The fat was extracted according to the method of Bligh and Dyer (1959). The subsequent determinations of free fatty acids content (FFA) and peroxide value (PV) were carried out respectively by the method described by the AOAC, (1984c & d). The carbonyl (aldehyde) compounds of the hams were made into 2,4-dinitrophenylhydrazone derivatives and separated into individual compounds with HPLC. The carbonyls were identified following the method of Reindl and Stan, (1982).

The volatile compounds from mature hams were entrained in cooled traps after distillation under high vacuum. The distillate was collected with dichlorometane and analysed by combined gas-chomatography-mass-spectrometry (GC-MS) according to Dumont and Ada (1976).

RESULTS AND DISCUSSION

The time-course evolution of limiting factors for bacterial growth, proteolytic and lipolytic activity along the processing of Iberian hams is shown in Figure 1. The low temperature and the presence of residual levels of nitrate and nitrite seem to be the main bacteriostatic factors during the salting-postsalting period. When hams are placed in the natural dryer to favour flavour development, combined effects of these inhibitory obstacles (pH=6.08; Aw=0.96; NO3=374ppm; NO2=7ppm) could be enough to ascertain the absence of microbial spoilage.

The figure 2 shows the evolution of nitrogen fractions during the elaboration process. As expected, an intense proteolytic breakdown takes place when higher temperatures (25-30ºC) are reached in the drying stage as revealed by the shift increase of NPN. Next, while hams were kept in the cave, NPN levels rose more continuously. This increase in NPN was progressive apparently due to formation of free amino-acids through the corresponding peptide intermediates. However, at the end of the maturation period, the rate of formation seems to be compensated by its

degradation to volatile derivates, as revealed by the increase of BVN. Drying and aging steps resulted in a strong increase of all the amino-acids identified, except for a number of individual amino-acids (Asp, His, and Arg), presumably due to formation of their corresponding amines.

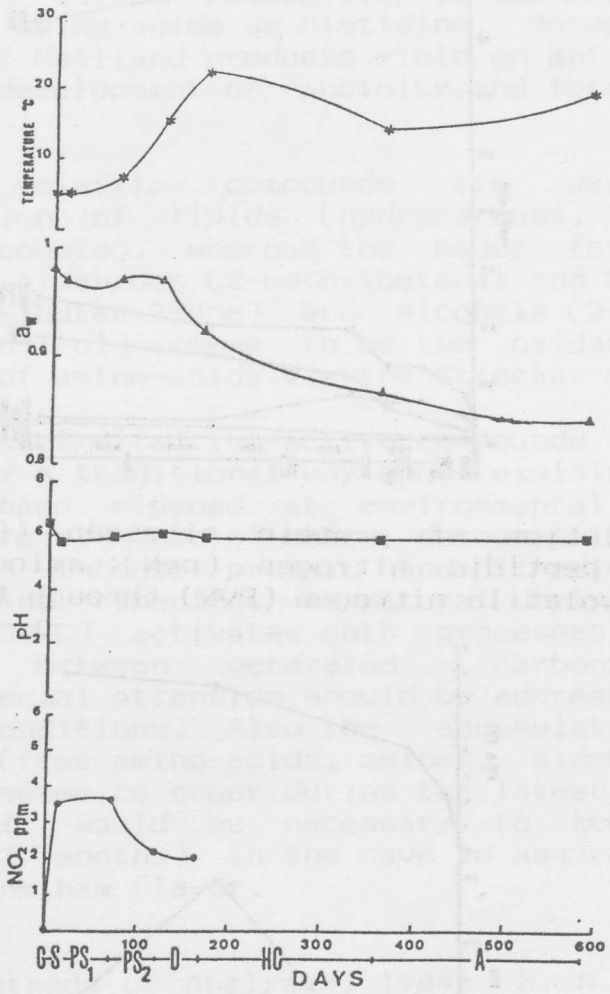

Figure 1.- Evolution of temperature; a_w; pH and nitrite along the processing of Iberian hams.

Lipidic breakdown along the processing of Iberiam hams is presented in figure 3. Lipolytic activity was stimulated in two steps of processing; first by salting and a second activation occurs by high temperatures of drying, as assesed by the increase of FFA content. Also an intense autooxidative degradation was found during salting. However, in contrast to lipid acidity (FFA), no relevant changes in the autooxidative reactions were detected during the drying period. Peroxide test (PV) values showed the highest levels at sixth month of ageing, and then decreased. Carbonyl formation through processing of Iberian hams

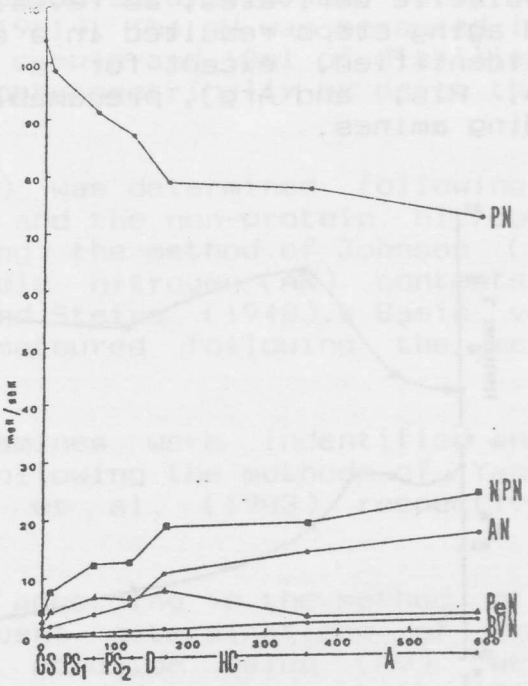

Figure 2.- Evolution of protein nitrogen (PN); non-protein nitrogen (NPN); peptidic nitrogen (peN); amino-acidic nitrogen (AN) and basic volatile nitrogen (BVN) through the maturation of Iberian hams.

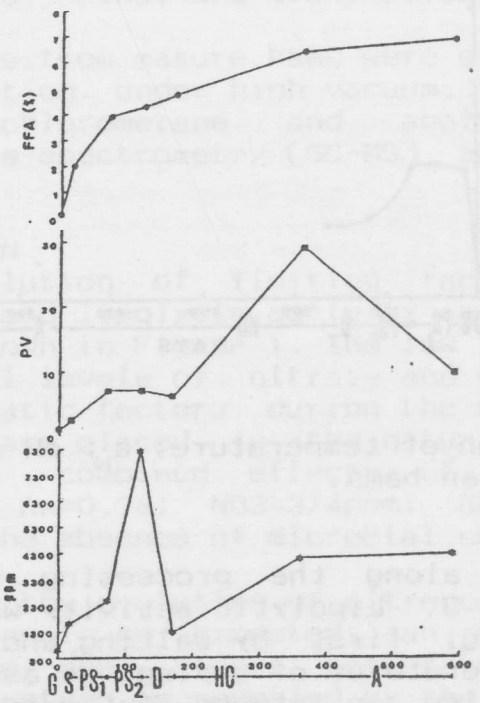

Figure 3.- Lipolytic-autooxidative decomposition during the processing of Iberian ham. FFA is expressed as a percentage of oleic acid and PV as mequiv O2/kg fat. Carbonyls represent the contents of aldehydes identified by HPLC (C6:0, C7:0, C8:0, C9:0, C9:1, C9:2 and C10:2)

also seems to be biphasic; its contents increased after salting, decreased during drying and then rose again in the latter months of ageing. The large decrease of carbonyls during the drying stage is difficult to understand. It may be due to losses through volatization that are favoured by fat melting when the hams were kept in the dryer. Other possible explanation would be a depletion of precursors or the interaction with free amino-acids. The latter possibility is supported by the small increase in some amino-acids as histidine. Moreover, it has been demonstrated that Maillard products yield an antioxidative effect and thus retard development of rancidity and formation of hexanal in foods.

Most of the volatile compounds are derived from the lipolytic-oxidation of lipids (hydrocarbons, straight chain aldehydes and alcohols), whereas the major formation route of branched chain, aldehydes (2-methylbutanal and 3-methylbutanal), Ketones (3-methylbutan-2-one) and alcohols (2-methylbutan-1-ol and 3-methylbutan-1-ol) seems to be the oxidative deamination-decarboxilation of amino-acids via the Strecker-degradation.

CONCLUSION

The large amounts of olfactive-active compounds found in Iberian hams processed by a traditional way could explain the consumer acceptance for hams ripened at environmental conditions in the processing areas. Most of these decomposition products are dependent on the intense proteic and lipydic breakdown that takes place during ripening. As natural drying (at summer temperatures 25-30ºC) activates both processes (and probably the reactions between generated carbonyls and free amino-acids) special attention should be addressed to control the stuffing conditions. Also the accumulation of several taste compounds (free amino-acids, amines, aldehydes, alcohols, lactones, etc) seems to occur during the latest steps of aging in the cellar. It would be necessary to keep the prolonged periods (up to 12 months) in the cave to assure development of desirable Iberianm ham flavor.

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