OXIDATION IN TRADITIONAL MEDITERRANEAN MEAT PRODUCTS

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ABSTRACT

Lipid oxidation in dry-fermented sausages and dry-salted-hams, representative items of traditional Mediterranean pork products, is responsible for the production of compounds which can affect their organoleptic qualities and wholesomeness. Lipid-derived compounds make up an important share of the volatiles extracted from matured products, once the contribution of spices is removed, and contribute significantly to the flavour of old style products. The few reports available on oxysterols depict a total cholesterol oxidation rate of about 0.1%, a threshold level for toxic effects to occur in vitro but about 100 times lower of the in vivo toxicity dose. The value could perhaps be reduced with the use of antioxidants. Phospholipids are the main class of fats interested by lipolysis and unsaturated fatty acids are those most interested by oxidation. On that basis, the case of special feeding regimes, such as that of Iberian pigs, and the possible relevance of muscle fibre type on flavour development are discussed.

KEY WORDS: oxidation, cholesterol oxides, quality, flavour, wholesomeness, fermented sausages, dry hams.

RUNNING TITLE: Oxidation in meat products.

INTRODUCTION

The interest of researchers and ordinary people for oxidative phenomena has become a major issue in latest years. The link between oxidation and health is now a topic of research and a number of metabolic disorders has been enrolled among the group of diseases directly or indirectly related with oxidation.

As a matter of fact, food scientists have been dealing with oxidation of lipids for a long time. Autooxidation of fats, known by the layman as rancidity, has been a problem ever since human beings began to preserve foods. Rancidity was seen only as a quality problem which could seriously impair foods desirability, although the perception of rancidity was probably different from ours. Rancidity, at least in its more patent form, is not any more on the agenda of food scientists but its modern version, warmed over flavour (WOF), is still a problem for some types of foods.

Traditional meat products cover a wide class of food items. The general idea of traditional meat product bring us to those products which were developed over the centuries to preserve meat from the cold to the warm season and which could be carried along in travels. Pork products, such as dry-fermented sausages and dry-salted hams, are the most representatives among traditional meat products for their eating quality, the link with local economies and the typical features of their technology.

Dry-fermented sausages and dry-salted hams, therefore, will be dealt with in the present review as paradigmatic of traditional pork products and of their processing technology.

OXIDATION AND EATING QUALITY

Dry-fermented sausages

The knowledge of the fermentation process has considerably advanced in recent years. Considerable efforts have been primarily directed at clarifying how much of what characterises and distinguishes the final product is due to the action of fermentative bacteria, how much comes from the type of minced meat and fat and how much the two factors are interdependent.

The results which have been obtained by various research groups in recent times have helped to understand the process of fermentation and maturing (Berdagué et al., 1992; Berdagué et al., 1993b; Demeyer et al., 1974; Demeyer et al., 1986; Domínguez Fernández and Zumalacárregui Rodríguez, 1991; Fernández et al., 1991; Hierro et al., 1997; Johansson et al., 1994; Johansson et al., 1996; Meynier et al., 1998; Molly et al., 1996; Montel et al., 1993; Samelis et al., 1993; Stahnke and Zeuthen, 1992; Stahnke, 1994; Stahnke, 1995; Talon et al., 1996; Verplaetse, 1994).

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The relative importance of lipid oxidation can be appreciated if spices or smoke are omitted or not counted upon. In that case molecules originating from lipid oxidation make up about half or more of the compounds identified (Berdagué et al., 1993b; Meynier et al., 1998, Stahnke, 1995).

Lipid oxidation accounts for the production of non-branched aliphatic compounds such as alkanes (from pentane to decane), alkenes, methyl ketones (from propanone to 2-octanone), aldehydes (from pentanal to nonanal), some alcohols and some furanic molecules (Berdagué et al., 1993b; Meynier et al., 1998). The polar fraction of aldehydes and ketones, with a clear dry-sausage smell, will have the greatest impact on flavour due to their low flavour threshold compared with hydrocarbons, alcohols and furans. Berger et al. (1990), however, were of the opinion that lipid oxidation and lipolysis could not be the only pathway for ketone and aldehyde formation because the typical autooxidation intermediates, the seven-to-ten carbon alkenals and alkadienals, were not detected. Molly et al. (1996), in fact, presented evidence that bacteria played a role in the formation of aldehydes originating from the carbohydrate fraction but not from the lipid fraction.

The importance, and the limits, of lipid autooxidation products has been confirmed by Stahnke (1995) for "old fashioned sausage" (fermented at low temperature, only added nitrate) compared with "modern sausage" (fermented at high temperature, added glucose, P. pentosaceum and nitrite). The former appear to contain lower levels of volatile acids and higher amounts of ethyl esters, short chain aldehydes and lipid autooxidation products. Some of such components may impart negative notes to the aroma if present in large amounts, e.g. hexanal, while other components are likely to have positive influences. The presence of ethyl esters appears to be linked with the activity of microorganisms over long maturing times (Edwards et al., 1998).

The results obtained with the sniffing analysis carried out on the effluent obtained from gas chromatographic separation of salame Milano volatiles (Meynier et al., 1998) have confirmed the importance of spices and lipid oxidation compounds. Odours which could be traced back to spices were about one third of total, the remaining part being made up by some aldehydes, two esters, one alcohol and the 2,6-dimethylpirazine. One important outcome of the sniffing test has been that the importance of volatiles for flavour could be linked more with their perception threshold and their chemical nature than with their concentration. Indeed, some odours were identified by panel members but had no counterparts at the chemical analysis. The main conclusion, in agreement with chemical data and literature reports, was that variations in flavour among different brands and products of various quality levels could be ascribed primarily to variations in the formulation of ingredients, spices in the first place.

Dry-salted hams

Processing of dry-salted hams does not require mincing and mixing meat with various additives but it is based on the slow diffusion of salt from the uncovered muscular surfaces of intact anatomical pieces. Bacterial fermentation is not generally considered to be a determinant factor in maturing, although there are indications that micro-organism could be involved in the production of some volatile compounds (Hinrichsen and Pedersen, 1995). Dry hams, therefore, can be considered to provide suitable conditions for the understanding of the endogenous contribution of muscle and fat to flavour development. A great deal of research has been carried out in recent years on the most representatives dry-salted hams from France, Italy and Spain (Antequera, 1990; Córdoba, 1990; Berdagué et al., 1991; Barbieri et al., 1992; López et al., 1992; Ventanas et al., 1992; Berdagué et al., 1993a; Buscailhon et al., 1993; Careri et al., 1993; Buscailhon et al., 1994a; Buscailhon et al., 1994b; Buscailhon et al., 1995; Hinrichsen and Pedersen, 1995; Hansen-Møller et al., 1997; López et al., 1992; Virgili et al., 1997)

The volatiles extracted from dry-salted hams are very similar to those of dry-fermented sausages, with the exception of terpenes if pepper is not spread over muscular surfaces. The same chemical families have been observed: aliphatic and aromatic hydrocarbons, aldehydes, ketones, alcohols, esters, carboxylic acids and sulphur compounds (Antequera, 1990; Berdagué et al., 1991; Barbieri et al., 1992; López et al., 1992; Buscailhon et al., 1993; Hinrichsen and Pedersen, 1995). Most volatile molecules identified in dry-salted hams are lipid related. Lipolysis and lipid oxidation have, therefore, been considered to be key processes.

It has been shown that, during curing of hams, lipases stay active for several months and the activity of lysosomal acid lipase, in particular, stays high enough to produce considerable amounts of free fatty acids (Motilva et al., 1992; Verplaetse A., 1994). Significant increases of the free fatty acids have been observed in all types of dry-salted hams studied, but they do not appear to be related with sensory properties (Buscailhon et al., 1995). Volatiles which could come from the oxidation of free fatty acids include n-alkanes, most of aldehydes, ketones and alcohols, and altogether make up half or more of the molecules identified (Antequera, 1990; Berdagué et al., 1991; Barbieri et al., 1992; López et al., 1992).

Proteolysis in dry-salted hams, mainly due to cathepsin B and L, is rather intense resulting in the production of small peptides and free amino acids (Rico et al., 1991), the latter in particular being precursors of some volatile compounds. Some branched-chain aldehydes could derive from the oxidative deamination-decarboxylation of amino acids (Strecker degradation), but also ketones, alcohols, alkanes and sulfur compounds have been linked with aminoacid catabolism (Barbieri et al., 1992; Ventanas et al., 1992; Buscailhon et al., 1993). The hypothesis that methyl-branched aldehydes might be produced via the Strecker degradation pathway has not been shared by Hinrichsen and Pedersen (1995).

Investigations on the production of volatiles during the various phases of dry-salted ham processing have shown that autooxidation products (aldehydes in particular) reach a maximum at mid ripening and decrease afterwards, whereas in the second half of ripening methyl-branched oxy- compounds (mainly 3- and 2-methylbutanal) increase significantly (Antequera, 1990; Ventanas et al., 1992; Buscailhon et al., 1993; Hinrichsen and Pedersen, 1995). The production of methyl-branched aldehydes has been attributed to the activity of micro-organisms on substrates such as L-leucine, L-isoleucine and L-valine. The same microbial origin has been proposed for the formation of ethyl esters, from ethanol and carboxylic acids, and for dimethyl trisulfide from peptides or amino acids (Hinrichsen and Pedersen, 1995).

To complete the picture, it has been observed that short-chain volatile compounds with a lateral methyl group, together with lysine, tyrosine and aspartic acid as free amino acids, were the most related to aged flavour of representative Parma hams (Careri et al., 1993). Similarly, methyl-branched aldehydes, methyl ketones, secondary alcohols, ethyl esters and dimethyl trisulfide were the volatiles that correlated most with the sensory attributes of matured Italian-type dry-cured hams. Volatiles coming from autooxidation reactions, instead, did not correlate with flavour development (Hinrichsen and Pedersen, 1995).

The same did not apply, apparently, to French dry-cured hams as Buscailhon et al. (1994a) came to the conclusion that lipolysis and lipid oxidation play a significant role in determining dry-cured ham aroma. According to the same researchers, most identified volatile compounds related to sensory characteristics were products of lipid oxidation, particularly ketones and 1-butanol. Previously, López et al. (1992) linked the typical flavour of Iberian hams with the combined effect of volatile molecules, especially fat oxidation products, such as straight-chain alcohols, carbonyls and lactones.

LIPID OXIDATION AND HUMAN HEALTH

Food lipids oxidation is considered to be a risk factor for human health. Some lipid oxidation products, and a few cholesterol oxides (COPs) in particular, are considered atherogenic agents and appear to have mutagenic, carcinogenic and cytotoxic properties. Furthermore, COPs appear to be able to replace cholesterol molecules in membranes, perturbing permeability, stability and other membrane properties (Sevanian and Peterson, 1986; Kubow, 1990, Guardiola et al., 1996).

Cholesterol oxidation products most frequently observed in foods are the 7-derivatives (7-ketocholesterol, 7α-hydroxycholesterol, 7β-hydroxycholesterol), the 5,6-epoxides (5,6α-epoxycholesterol, 5,6β-epoxycholesterol), one triol (3β,5α,6β-trihydroxycholesterol or cholestanetriol) and two molecules deriving from side chain oxidation (25-hydroxycholesterol and 20α-hydroxycholesterol). The most cytotoxic COPs are thought to be cholestanetriol and 25-hydroxycholesterol (Addis, 1986; Kumar and Singhal, 1991; Kubow, 1990), two molecules, and the latter one in particular, which inhibit the activity of 3-hydroxy-3-methylglutaryl-coenzyme-A-reductase (HMG-CoA reductase) leading to reduced endogenous cholesterol synthesis (Guardiola et al., 1996).

It has been shown that human subjects can absorb oxysterols from food sources. Once in circulation, COPs reside briefly within chylomicrons and are rapidly transferred to other plasma components (presumably other lipoprotein fractions) (Emanuel et al., 1991).

Oxidation of lipid moieties in meat products is affected by various factors, the main ones being length and type of storage, processing procedures (heating, mincing, mixing) and additives used. Cholesterol oxidation is faster in foods produced with a drying process and/or stored for some time, such as dried egg yolk powder, milk powder products and freeze-dried pork (Gallina Toschi et al., 1994; Paniangvait et al., 1995)

Processing procedures could affect lipid oxidation in various ways. Heat treatment has negative effects on cellular structure, inactivates enzymes (including those with reducing activity) and releases oxygen from oxymyoglobin, creating in this way the conditions for hydrogen peroxide production. Cooking, especially at low temperatures for long times, has also the effect of releasing iron ions from heme groups. Shredding, mincing and mixing disrupt muscle structure and, in this way, increase the surface exposed to oxygen and other oxidation catalysts. Sodium chloride has prooxidant effects (Kanner, 1994) with still unclear mechanisms. Sodium chloride might strengthens the effect of iron ions by moving them from prosthetic groups so that they are available for oxidative catalysis. It has been shown (Lee et al., 1997) that increasing concentrations of NaCl in ground meat induce a progressive decrease of the activity of muscle antioxydant enzymes, such as catalase, glutathione peroxidase and superoxide dismutase.

Traditional meat products, such as dry-fermented sausages and dry-salted hams, are interesting models for investigations on such themes as they represent two opposite types of technology. The first ones are minced, mixed with salt, additives and spices, stuffed, fermented for fairly long times and, therefore, appear to be significantly exposed to prooxidant conditions. Dry-salted hams are whole muscle products, processed in their full integrity, with rind, subcutaneous fat and bones in place, without exposing the flesh to the air until consumption and should, therefore, be less exposed to oxidative phenomena.

Conventional indexes of lipid oxidation, i.e. peroxides and TBARS (Thiobarbituric Reactive Substances) values, are within acceptable levels (i.e. around 2-4 mequivO_2/kg fat and 0.1-0.3 mgMDA/kg tissue, respectively) in good quality dry-fermented sausages and dry-salted hams, and no objectionable odours or tastes (e.g., rancid) have been reported (Dominguez Fernández and Zumalacárregui Rodríguez, 1991; Johansson et al., 1994; Ghiretti et al., 1997; Chizzolini, 1998; Novelli et al., 1998; Zanardi et al., 1998). Only in Iberian ham high peroxide values (>20) have been reported during and at the end of maturing in *Semimembranosus,* a superficial muscle. Peroxides, though, were much lower (<10) in *Biceps femoris,* an internal muscle protected from contact with the atmosphere (Antequera, 1990). A consumer test has associated the tastes of rancid, oily and butter-like with Corsican hams and, to a lower extent, with Iberian and Serrano hams, but no data on peroxide or TBARS values were reported (Virgili et al., 1997).

Cholesterol oxidation in salame Milano and Parma ham was found to be limited both as type of oxysterols encountered and as total levels of oxidation. The oxysterols constantly identified were 7β-hydroxycholesterol, 5,6α-epoxycholesterol and 7-ketocholesterol. Occasionally, that is in three samples of salame bought from commercial premises, the 25-hydroxycholesterol has been observed at low concentrations. Cholesterol oxidation was found to be around 0.1% of total cholesterol content with values varying from 0.03% to 0.12% in salame Milano and from 0.04% to 0.13% in Parma ham.

The oxidation levels observed in salame Milano and Parma ham are similar to those measured in mortadella, in frozen stored pork (shoulder, belly) and in cooked pork chops (Novelli et al., 1998; Zanardi et al., 1998). Higher oxysterols concentrations (0.3-0.8%) were reported by Pie et al. (1991) in beef, veal and pork, fresh, 3 months frozen and cooked. Higher values were, also, measured in cooked ground pork stored under refrigeration (Monahan et al., 1992).

A correct appreciation of the impact on human health of the observed cholesterol oxidation rate can be estimated from the results reported by Bösinger et al. (1993). The values observed in salame Milano and Parma ham would correspond to the minimum level considered to be able to induce toxic effects in *in vitro* trials with cultured cells but they would be about 100 times lower than the toxic level for *in vivo* experiments. On the one hand, therefore, serious dangers for human health do not appear to exist but, on the other, it could be worthwhile to verify if oxidation of cholesterol could be reduced through the enhancement of the antioxidant status of meat. Indeed, such a possibility has been envisaged with the use of lipid soluble antioxidants such as sesamol, mixed with the ingredients of salame Milano (Ghiretti et al., 1997), and vitamin E supplementation of pig feeds (Chizzolini, 1998).

Studies on the relationship between lipid oxidation and human health in traditional pork products from other countries, and on the effects o endogenous or exogenous antioxidants, are very few and would be very welcome.

RAW MATERIAL AND QUALITY OF TRADITIONAL PRODUCTS

The effect of raw material on the quality of traditional pork products can be exemplified by the case of Iberian hams (Antequera, 1990; Córdoba, 1990; López et al., 1992; Cava et al., 1997). Iberian pigs can be fed only on acorns and grass pasture *(montanera),* on acorns up to the last two months of life when they are put on a commercial diet composed of cereals *(recebo)* and only on a commercial diet based on cereals *(pienso)* (López et al., 1992). The different diets can have marked effects on the fatty acid composition of deposited fats since feeding with grass and acorns leads to high monounsaturated (basically oleic acid, 50-60%) and low saturated and polyunsaturated fatty acids contents (8-10% linoleic acid) (Antequera, 1990). Subcutaneous fat is soft to the point that it melts to a considerable extent during maturing. The acid composition of deposited fat has clear effects on lipid degradation products. Aldehydes, and hexanal in particular, were found to be the most abundant compounds among headspace extracted volatiles of Iberian hams (López et al., 1992; Antequera, 1990). Changes in feeding regimes, such as those occurring between *montanera, recebo* and *pienso,* have resulted in significant differences in the amount, although not in the type, of volatiles extracted from matured hams. The differences were more marked between *montanera* and *pienso* and were mainly due to aldehydes and alcohols, the molecules, that is, which derive from the breakdown of hydroperoxides produced by oxidation of unsaturated fatty acids (López et al., 1992).

What has just been reported is important since it underlines a fundamental aspect of the lipid-based flavour volatiles in meat products, i.e. that their origin is primarily from unsaturated fatty acids, but is also important because the differences observed between products are only quantitative, non qualitative.

Muscular unsaturated fatty acids, especially the polyunsaturated ones, are mainly confined to phospholipids, the structural components of membranes. The entire problem of lipid oxidation in traditional meat products, therefore, might acquire a new perspective if analysed in the light of phospholipid content and composition of the muscles used.

The crucial point is that phospolipid content and composition are related to muscle metabolic type. The oxidative muscles contain more phospholipids than the glycolytic ones and phospholipids of the former exhibit a higher proportion of cardiolipin and phosphatidyl ethanolamine (PE) and a lower proportion of phosphatidyl inositol (PI) and phosphatidylcholin (PC) than those of the latter (Leseigneur-Meynier and Gandemer, 1991; Alasnier et al., 1996). The phospholipids of oxidative muscles contain more long-chain polyunsaturated fatty acids than those of glycolytic ones because their phosphatidyl ethanolamine has a high proportion of these fatty acids (Alasnier and Gandemer, 1998). Phospholipases are active in muscles, more in oxidative fibres than in glycolytic ones, and most free fatty acids produced during lipolysis in raw meat, dry sausage or dry hams come from phospholipids. (Gandemer and Meynier, 1995). The high proportion of long-chain polyunsaturated fatty acids in PE and the high amount of PE in oxidative muscles, therefore, could be one of the reason for the high propensity of these muscles to oxidise (Alasnier and Gandemer, 1998). Indeed, the phospholipid fraction extracted from chicken meat was found to be responsible for about 90% of the malonaldehyde measured in total fat (Pikul et al., 1984). Earlier on, Wilson et al. (1976), working on warmed-over-flavour (WOF), reported that red muscles were more susceptible to oxidation than white ones and suggested that phospholipids played a major role in the development of WOF in cooked meats. Gandemer (1990), also, observed that phospholipids were very susceptible to oxidation with cooking and were the main compounds involved in lipid oxidation of mechanically deboned poultry meat. Finally, Hernández et al. (1998), besides confirming the higher phospholipid content of oxidative muscles, have demonstrated that lipases are also related with muscle metabolic type, being more active in the oxidative ones.

The results obtained by Buscailhon et al. (1994b), on the changes occurring to intramuscular lipids during dry-cured ham maturing, strongly support the importance of phospholipids. The above mentioned authors observed that the composition of the free fatty acids produced was close to that of phospholipids throughout the process. Moreover, there was a close relationship between the decrease in phospholipid content and the increase in free fatty acids during processing. It was evaluated that lipolysis affected around 8% of the muscle lipids and concerned chiefly the phospholipids, of which two thirds were degraded.

The possible importance of muscle fibre type, and, therefore, of the breed, on flavour characteristics of traditional pork products is open for investigation. Buscailhon et al. (1995), though, failed to observe significant relationships between histological and sensory characteristics measured in matured hams. Berdagué et al. (1993a) extracted the volatile compounds from hams produced from pigs of different breeds (Landrace X Large-White, Duroc X Gascon-Meishan, Piétrain X Gascon-Meishan and Large-White X Gascon Meishan). The effect of the breed on volatiles and flavour was limited to 7 out of 42 volatiles, the most significant being some odorous compounds such as 1-octen-3-ol, 2,3-butanedione and acetoin. The authors observed that the amount of 1-octen-3-ol, an oxidation product of unsaturated fatty acids, was lower in the fattest hams in which the unsaturation of lipids was lower due to the lower ratio between phospholipids and glycerides. No measurements, though, were reported on fibre type distribution among the breeds. A relationship between the number of Type IIb fibres and colour of green and matured hams was observed by Bellatti et al. (1996) who also reported a link between pale soft fresh muscles and more dehydrated and salted matured hams.

No other data appear to be available on the subject, and the paucity of those mentioned does not allow any clear conclusion, but deeper investigations might be useful in the light of the changes which have taken place in pig breeds since the 1950s. Selection for faster growth and muscular development has produced animals with hypertrophic muscles, especially those of the hind limb and the loin, which are rich in white fibres (Monin and Ouali, 1991; Sainz and Cubbage, 1997). Moreover, anabolic drugs, repartitioning agents and similar substances stimulate growth rate, increase protein deposition and lower fat content. Animals treated with some of such substances, e.g. β-agonists, have shown changes in muscle fibres distribution, namely a conversion of the smaller FTa (fast twitch A) to the larger FTb (fast twitch B) fibres, an hyperthrophy of the FTb fibres and, to a minor extent, a ST (slow twitch) to FT (fast twitch) fibre conversion (Oksbjerg et al., 1990, 1994).

It might well be that significant differences in fibre types do not exist any more in pig breeds actually used. Selection and breeding practices seem to have standardised to a great extent European breeds. A research carried out a few years ago in Italy on six pure breeds (Large-White, Italian Landrace, Belgian Landrace, Piétrain, Duroc and Cinta Senese) has shown that red fibres were about 1/3-1/4 higher in Cinta Senese, an old local breed recalling in some way the Iberian pigs, compared with the other breeds. Differences among the other five breeds were limited and more pronounced in fibre diameters (e.g. higher in Piétrain) than in fibre type distribution (Cantoni, personal communication). Previously, Rahelic and Puac (1981) observed, in *L. dorsi,* that the percentage of red fibres decreased and mean fibre diameter increased from "wild" and "primitive" to "highly selected" breeds. It cannot be excluded, therefore, that significant differences existed in muscle fibre composition of old local breeds and that such differences were important for the development of traditional products and for lipid oxidative patterns linked with processing.

CONCLUSIONS

Lipid degradation, mainly through oxidation of free unsaturated fatty acids, is an important part of traditional pork products maturation. The incidence of oxidation products on flavour development appears to be different in dry-fermented sausages and dry-salted hams, probably as a consequence of microbial activity. The effect of raw materials on variations in flavour characteristics and compounds, among products from different production areas or technologies, might be masked by the use of spices and/or smoke. Some differences have been observed in dry-salted hams of different geographical origin but the role played by the type of meat used has not been clarified. Investigations on lipid oxidation in relation with muscle metabolic type might be useful to understand the pathways of volatile molecules formation in pork products, especially in dray-salted hams. The results could be used to control and optimise processing procedures.

Further research would be needed on possible harmful molecules produced from the oxidation of some lipid compounds. The effect of natural antioxidants, present in the muscles from the diet or added during manufacturing where possible, has not been thoroughly studied, yet. The interaction between organoleptic features, toxic compounds, lipid oxidative and antioxidative pathways in meat remains an interesting field of study.

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