# ERIAN PIG DRY HAM VOLATILE COMPOUNDS FROM DIFFERENT HAM DEPTHS

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## MMARY

The possible role of oxigenation and fattening on the Iberian dry ham flavour development has been studied. Samples were obtained om three different depths: external (about 4 cm in depth); medium (5-8 cm in depth) and internal (depth>8 cm) layers. Over 64 mpounds were identified. Those accurately characterized were selected for comparison between layers. The selected volatiles mainly cluded aldehydes (12), alcohols (8) and short chain fatty acids (5). The external layer (the fattest and the most oxigenated) showed a gnificative ($p<0.05$) higher amount of total volatiles than those found in the other two studied layers. In general, no significative fferences ($p>0.05$) were found between volatiles from the medium an internal layers. The results suggest that the dominant volatile mpounds of Iberian pig dry hams result from the oxidation of unsaturated fatty acids, which are abundant in adipose tissue of Iberian gs.

## TRODUCTION

Iberian pigs are widely distributed in the Southwestern and part of the Western area of Spain. From them a great variety of ripened eat products (several types of dry fermented sausage, dry ham and sirloin) are produced being the dry ham the most popular and preciated by consumers. This meat product is manufactured according to basic principles (salting, surface drying and ripening). Iberian y hams have an intense and characteristic flavour which is developed after a long time of ripening (14-18 months). García et al (1991) died the volatile compounds from *biceps femoris* muscle zone (internal layer) of Iberian dry hams. These authors indicated that the rge amount and type of olfactory volatiles found in this product suggests an intense proteolytic and lipolytic breakdown during turation. The volatile compound composition of dry hams is markedly affected by the feeding the animals were fed during the fattening riod (López et al., 1992).

The ripened meat products from Iberian pigs fed on pasture and acorns (*Quercus ilex, Q. rotundifolia* and *Q. suber* ) are the most preciated by consumers reaching the highest price in the market. López et al (1992) studied the volatile compounds of Iberian dry hams om pigs fed on different diets (acorns, acorns and cereals or cereals). The results from this study suggests that the well known nsumer preference for the hams from Iberian pigs which have been fed on acorns is due to quantitative differences in the volatile mpounds rather than to qualitative ones. These variations in Iberian dry ham flavour are attributed to the different fat composition imals, since it is well known that fat is the most dependent fraction on the diet, and also to the degree of lipid breakdown during ening (Flores et al., 1988; López-Bote et al., 1990; García et al., 1991; López et al, 1992). The dominant volatile compounds found in y ham (García et al., 1991; López et al, 1992) suggest that fat oxidation phenomena play an important role in the development of erian dry ham flavour. The objetive of the present work was to investigate the olfactive-active volatile compounds of dry hams (aged 2-14 months) from different sampling depth to know the possible role of oxigenation and fattening on the flavour development.

## ATERIAL AND METHODS

### nalytical procedure

Five dry hams from Iberian pigs, which had been exclusively fed on pasture and acorns, were used. Animals were reared in the uthwestern of Spain (Fuentes de León, Badajoz) and slaughtered in a local abattoir .

Dry hams were manufactured and ripened in a local factory by the conventional technology used for these products (Carrascosa and rnejo, 1989). Samples were taken after ripening for 14 months. Given that the volatile compound analysis is a semiquantitative ethod, the conditions for volatile collection were totally standarized in order to be able to establish comparison between different mpling depth. Portions of ham were obtained from three different depths: external layer (about 4 cm in depth) composed by more than % of fat, medium layer (5-8 cm in deth) composed by around 50-60% fat and 50-40% muscle and internal layer (depth > 8 cm) mposed by around 10-20% fat and 90-80% muscle. Around 50 g of these portions were coarsely ground. The material was placed in a tical flask (500 ml) where it was allowed to equilibrate at room temperature for 30 min. The flask was then equipped with a Dreschel ttle head and a glass trap (70 mm long x 2 mm o. d. x 1.5 mm i. d.) packed with 30 mg Tenax GC 80-100 mesh attached via a screw nt on the head outlet. During collection, the system was mantained at 29°C. Volatiles were swept onto the trap using a nitrogen flow 0) ml/min) for exactly 45 min.

The sample was thermally desorbed using a Perkin-Elmer PTV (Programmed Temperature Vaporizer) by increasing ballistic (150°C/s) the injector temperature to 300°C and maintaining it there for 5 min. This temperature allowed the complete desorption of medium volatile compounds and in blank experiment only a weak background was observed (maximum temperature for Tenax 375°C). The chromatographic analysis itself was performed in a Perkin-Elmer 8320 Gas Chromatograph. Helium at 35 psig was used carrier gas. A 50 m x 0.25 mm i.d. fused silica capillary column coated with a cross-linked 0.25 μm film of FFAP was used. The col temperature was initially maintained at 30°C for 3 minutes and then programmed at 30°C/min to 180°C. Identification of peaks performed by GC-MS using a Perkin-Elmer ITD-50 Ion Trap Detector (electronic impact 70 e. v.).

Compounds were tentatively identified by computer comparison of spectra with those of the NBS (National Bureau of Standa library. Identification of some of these compounds was subsequently confirmed by matching their spectral data with those of auth reference compounds analyzed under identical conditions.

**Statistical methods**

Statistical analysis was performed using the analysis of variance and the differences between means were analyzed using the Sch F-test in a Statview SE program run in a Macintosh LC computer.

## RESULT AND DISCUSSION

A total of 64 different compounds were identified in the three layers, including the following groups: aldehydes (15), alcohols (1 short chain fatty acids (7), furan derivatives (4), lactones (1) and other miscellaneous compounds such as ketones, esters, alkan branched alkanes, alkenes, benzene derivatives, amines and amides. In some samples several of the above mentioned volatile compou were detected in trace amounts. The volatiles compounds detected in the present work were the same that those described by López e (1992). The headspace volatiles of the three layers contained essentially the same substances although there were relative differen specially between external and internal layers. The relative contribution of the major volatile compounds to the headspace of each layer shown in Table 1. The compounds selected for this table and for comparison between layers were only those accurately characterized. T selected volatiles mainly included aldehydes (12), alcohols (8), and short chain fatty acids (5).

The aldehydes were the dominant compounds in the headspace volatiles of the three layers. Most of these volatile compounds are result of oxidation, usually of C-18 polyunsaturated fatty acids such as linoleic and linolenic although the arachidonic acid may be involved (Shahidi et al , 1986). García et al (1991) have observed that hexanal was the most abundant volatile compound in dry from Iberian pigs (17% of the total). Cross and Ziegler (1965) reported that gas-chromatographic examination of the volatiles of cur and uncured ham showed that pentanal and hexanal were present in appreciable quantities in the uncured product, but they were rare detected in the volatiles of the cured meat. Hexenal can be formed by the oxidation of either esterified or free linoleic acid. Pork fat substantially high levels of linoleic acid (Flores et al., 1988; López-Bote et al., 1990; López et al, 1990). Other mechanisms can involved in the aldehydes formation such as some protein degradation products and reactions between proteins and carbohydra Branched chain and aromatic aldehydes, such as phenylacetaldehyde might be formed by oxidative deamination-decarboxylation of amin acids via Strecker degradation (Belitz and Grosch, 1987). Benzaldehyde was detected in similar concentration in the headspace volatiles the three layers. This aldehyde can be formed from the decomposition of linoleic acid (Kawada et al., 1967), although recent studie using chemically defatted meat, suggest that a nonlipid route may also be involved (Mottram and Edwards, 1983).

Pentan-1-ol, hexan-1-ol, octan-1-ol and decan-1-ol were also found in the headspace volatiles of the three layers. They may b formed by breakdown of the hydroperoxides derived from unsaturated fatty acids (Frankel, 1985).

Short-chain fatty acids released may be also considered as a marker of lipid degradation (MacLeod and Seyyedain-Ardebili, 1981).

Similar amounts of 2-methyl-4,5-dihidrofurane were found in the headspace volatile of the three layers. Furanoid compounds are n considered to contribute substantially to the basic meaty aroma (Shahidi et al., 1986). However, they contribute to the overall flavour meat products (Ho et al., 1983; Persson et al., 1973). Likewise, δ-butyrolactone was also found in similar concentration in the headspace volatile of the three layers. Lactones are known to be associated with meat aroma of all kinds. This class of compounds may be formed from the γ- or δ-hydroxy fatty acids that are known to be present in fat (Shahidi et al, 1986) and also from the oxidation of oleic acid an unsaturated aldehydes (Belitz and Grosch, 1987).

It is well know that fat may influence the meat flavour as a substrate for oxidation, with the formation of carbonyl compounds i organoleptically significant amounts. These compounds may produce desirable flavour or undesirable off-flavours, depending on their

ncentration. Because Iberian dry hams are processed for long times (14-18 months) at temperature ranges about from 15 to 30° C, it s expected that the different aldehydes, alcohols, and short-chain fatty acids found in the headspace volatiles from the three layers of erian hams suggests intense lipids breakdown during maturation.These results are in agreement with those obtained by García et al 991). These authors reported that curing of Iberian hams involves the addition of salt alone and, in some cases, low quantities of nitrate. hough nitroso compounds seem to retard the formation of several high molecular weight aldehydes, such as hexanal, the relatively high mperature together with the long ripening period of Iberian hams, contributed to lipolytic and oxidative degradation of unsaturated fatty ids.

Table 1 shows the differences for selected volatile compounds. The differences observed in all three layers were mainly due to the ncentrations of volatile compounds rather than to the types of volatile substances present. These quantitative differences are obviously ated to the intensity of the lipid degradation process, which is higher in the external layer because this layer is the fattest and the most igenated. It can explain the significative differences ($p<0.05$) observed between the volatiles collected from this layer and from the other o ones. Alcohols, short chain fatty acids (excepting hexanoic) and the aldehydes pentanal, hexanal, heptanal, phenylacetaldehyde, tanal, 2-hexenal and 2-furaldehyde were significatively more abundant in the headspace volatile of the external layer. As it can be see in able 1, no significative differences ($p> 0.05$) were found , in general, between volatiles from the medium and the internal layers.

The differences observed between the layers may be attributed to the available oxygen and to the different chemical composition xternal layer was composed around 90% of fat; medium layer by 40-50% muscle and 60-50% of fat and internal layer by 90-80% uscle and 10-20% of fat). The lipid oxidation in the medium (5-8 cm in deph) and internal layers (> 8 cm in deph) is mainly conditioned y oxygen difussion processes. However, the internal and medium layers contain a higher concentration of phospholipids and saturated fatty acids than the external layer (López et al., unpublished). Mottram et al. (1982) reported that the relation between the vels of volatiles and of adipose fat suggests that the triglycerides of the adipose tissues may not be the major source of the volatiles and at the intramuscular triglicerides and phospholipids may adquire a greater important. It can explain that the headspace volatiles of the ree layers contained essentially the same components. The fat from internal and medium layers are more prone to oxidation but this

**Table 1.- Selected compounds (Peak Height in Analoge-to-Digital Converter Counts) of Headspace Volatiles of Iberian Dry Hams from "Internal", "Medium" and "External" Layers.**

| | LAYER | | | | | |
|---|---|---|---|---|---|---|
| COMPOUND | INTERNAL | | MEDIUM | | EXTERNAL | |
| **CARBONYLS** | | | | | | |
| pentanal | 20695 ± 3644 | a | 19766 ± 3405 | a | 48365 ± 9786 | b |
| hexanal | 190605 ± 24736 | a | 264599 ± 19247 | a | 1407824 ± 202720 | b |
| heptanal | 183074 ± 22946 | a | 593714 ± 73131 | b | 1498269 ± 150514 | c |
| phenylacetaldehyde | 4602 ± 517 | a | 3816 ± 465 | a | 18514 ± 2496 | b |
| octanal | 48593 ± 6762 | a | 132880 ± 21235 | a | 367409 ± 43856 | b |
| 2-hexenal | 13583 ± 1538 | a | 23599 ± 2649 | a | 94485 ± 14516 | b |
| nonanal | 87703 ± 10128 | a | 99694 ± 11441 | a,b | 144611 ± 18791 | b |
| decanal | 30622 ± 3789 | a | 59123 ± 8949 | a,b | 74997 ± 13486 | b |
| 2-furaldehyde | 7755 ± 915 | a | 7005 ± 997 | a | 14606 ± 1884 | b |
| 2-decenal | 16570 ± 1737 | a | 15266 ± 1851 | a | 22576 ± 2754 | a |
| benzaldehyde | 18532 ± 2632 | a | 21092 ± 2583 | a | 28143 ± 3178 | a |
| dodecanal | 5185 ± 687 | a | 5150 ± 717 | a | 5813 ± 501 | a |
| **ALCOHOLS** | | | | | | |
| 2-methylbutan-1-ol and 3-methylbutan-1-ol | 14166 ± 1820 | a | 9729 ± 1079 | a | 25329 ± 2274 | b |
| pentan-1-ol | 16187 ± 2195 | a | 17134 ± 2071 | a | 47451 ± 2311 | b |
| hexan-1-ol | 100678 ± 13921 | a | 133960 ± 14766 | a | 453339 ± 45938 | b |
| cis-3-hexen-1-ol | 4766 ± 715 | a | 6313 ± 402 | a | 12600 ± 1830 | b |
| octan-1-ol | 35778 ± 4120 | a | 45501 ± 5719 | a | 175492 ± 17526 | b |
| decan-1-ol | 42459 ± 6473 | a | 52154 ± 7084 | a | 241418 ± 32179 | b |
| furfurylalcohol | 95643 ± 8967 | a | 375619 ± 39088 | b | 423033 ± 56222 | b |
| **SHORT CHAIN FATTY ACIDS** | | | | | | |
| acetic | 59124 ± 7051 | a | 145080 ± 19299 | b | 166919 ± 29464 | b |
| butanoic | 18977 ± 2667 | a | 25068 ± 2599 | a | 76289 ± 9217 | b |
| pentanoic | 20800 ± 2690 | a | 54843 ± 7382 | b | 67856 ± 11569 | b |
| hexanoic | 2060228 ± 269533 | a | 14302044 ± 5285044 | a | 11356468 ± 1376864 | a |
| octanoic | 168775 ± 18799 | a | 100175 ± 13564 | a | 627076 ± 75130 | b |
| **MISCELLANEOUS** | | | | | | |
| 2-methyl-4,5-dihidrofurane | 19989 ± 1650 | a | 17182 ± 1378 | a | 24176 ± 2524 | a |
| ∂-butyrolactone | 23767 ± 5033 | a | 42634 ± 9220 | a | 34064 ± 7311 | a |

Each value is the average (means±standard error) from five dry hams
a, b, c: Values in a row with different letter differ significantly ($p\leq 0.05$)

phenomenon is dependent of the oxygen difussed from outside. However, in the external layer is more possible the lipids degradation because this layer is the fattest and the most oxigenated.

Moreover, other factors can also affect the lipid oxidation in medium and internal layers such as nitrite difussion and some factors may show a prooxidant activity such as methemoproteins (Rhee et al., 1985; Rhee, 1989), nonheme iron (Rhee, 1989; MacDonald et al., 1980), lipid peroxidizing enzyme system (Rhee, 1989), salt concentration (Ellis et al., 1968; Rhee et al., 1983), low Aw (Jacobson et al., 1989). Dry ham manufacturing involves the addition of salt together with low quantities of nitrate (Carrascosa and Cornejo, 1989). The low quantities of nitrite formed may act as a powerful antioxidant and thus it may contribute to a partially control of the oxidative reactions during the long time of ripening. All these factors may effect to the lipid oxidation deped either promotioning or reducing the lipid oxidation during the ripening. The combination of the volatile compounds from the controled lipid oxidation, with probably others volatile compounds from different origins and with some non-volatile substances, gives rise to the typical flavour of the Iberian hams.

The results suggest that the dominant volatile compounds of Iberian pig dry hams result from the oxidation of unsaturated fatty acids which are abundant in the adipose tissue of Iberian pigs.

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