VOLATILE COMPOUNDS IDENTIFIED IN ALTERED DRY-CURED HAM

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SUMMARY

One of the most frequent alterations in dry-cured hams is putrefaction, which is characterized by off-flavour production. The volatile compounds present in altered dry-cured ham have been studied in this work. The volatiles were isolated with a dynamic head-space technique using a purge-cold trap-injection system, and then, identified by mass spectrometry coupled to gas chromatography. 36 compounds of the following families were identified: ketones (8), aldehydes (5), alcohols (4), sulphur compounds (4), aromatic hydrocarbons (4), n-alkans (3), nitrogen compounds (2), furanes (1), ethers (1), esters (2), and contaminants (2).
The volatile compounds profile of putrescent samples is very different from that found in the non-altered ones. From a quantitative point of view, the most important change is the increase on ketones, alcohols, and sulphur derived compounds, and the reduction on aldehydes. The large number of ketones and amino acid derived compounds obtained suggest that there is a high degree of lipolysis and proteolysis, probably due to the action of microorganisms.

INTRODUCTION

Although there has been an important development on the technology applied in the dry cured ham processing, there are still many alterations that produce important economical losses in Spain mainly due to the following reasons:

1.- There are many parameters to be controlled in the process.
2.- Consumers require less salted products.
3.- The scalding step introduce a risk of contamination in the processing.

The origin of ham alterations might be due to: (Bello, 1985):
1.- The use of non adequated raw meat, as well as problems on feeding, transport, and slaughtering yield to DFD, PSE or off- flavour meat.
2.- Failures in the control of some important steps in the technological process (e.g. Temperature, relative humidiuty, non-hygenic conditions, incorrect bleeding).

Undesirable characteristics such as off-flavour, decoloration, disliking appearance and short shelf-life might occur in dry-cured ham for the reasons mentioned above. Bello (1985) has described sixteen different kinds of alterations, the most common ones might be divided into three groups (Cantoni, 1987):

- inner putrescent alterations
- penetrating putrescent alterations
- appearance deffects

Inner putrescent alteration of bacteriologic or enzymatic origen are the most frequent (Simonetti et al., 1983). They are generally due to a lower salt penetration, pH>6 in raw material, an incorrect bleeding or a cold chain break. Much research has been done in order to establish the relationship between microorganisms presence and development of subsequent alteration (Cantoni et al., 1969, Marín, 1990, Hechelmann et al., 1980). In contrast, little research has been done on the study of the volatile compounds responsible for off-flavour developed in hams affected by inner putrescence phenomenon.

The purpose of this paper has been to isolate and identify the volatile compounds that occur in the head space of Iberian dry-cured ham with inner putrescence and to compare them with the volatile composition of non-putrescent dry-cured ham. Since the samples studied have been only a few, the results obtained should be only considered as a guidance to further research.

MATERIALS AND METHODS

Samples

All samples were taken from Biceps Femoris muscle of Iberian pig ham after 18 months of curing proccess, vacuum packaged and stored at -30°C until analysis.

6 g of frozen samples were minced with a home mincer for the analysis.

Isolation of volatile compounds

The isolation of volatile compounds has been carried out with a Purge and Cold Trap Injection System (PTI) of Chrompack (Badings et al., 1985). The purge conditions were:

- Sample temperature: 45°C
- Purge flow: 10 ml/min of Helium
- Purge time: 15 min

Separation and identification

GC_MS analysis of the volatile compounds were performed with a Hewlett Packard 5890 Serie II Chromatograph coupled to a Hewlett Packard 5971 mass spectrometer. Mass spectrum were acquired using a vectra Hewlet Packard 386/25 computer, which also controls the running conditions of the analysis.

Gas Chromatography was performed on a 50m x 0.32mm id fused silica column coated with a Phenyl-methyl-silicone of 1.05 μm, using Helium as the carrier gas. The column was held at 50°C while transferring the headspace components; after 5 min the oven temperature increased 5°C/min until it reached 210°C and then it was held for 1 min. The mass spectrometer was scanned from 10 m/z to 400 m/z. The ion source was maintained at 280°C and the spectra was obtained by electron impact (70ev). The spectrum was identified by comparation with a Wiley library.

RESULTS AND DISCUSSION

Table 1 shows the average of area/10^6 of the volatile compounds identified in the head space of all samples analyzed. In atltered hams 36 compounds clustered in the following chemical families were identified: sulphur compounds (4), aldehydes (5), ketones (8), alcohols (4), esters (2), n-alkanes (3), aromatics hidrocarbons (4), ethers (1), furanes (1), nitrogen compounds (2) and contaminants (2).

The main difference between spoiled and non-spoiled hams is that the amount of sulphur compounds found in the first ones is higher than that in non-spoiled ones, which indicate a larger degree of proteolysis. The most abundant compound present is metanothiol followed by 2-propanone. Metanothiol can derive from free methionine by demethylase activity of microorganisms such us *corinebacteriaceae* and can produce dimethyl disulfide, which has been detected in altered samples in considerable concentration. Moreover, the growth of microorganisms, such as *Brevibacterium linens*, also raise the amount of dimethyl trisulfide (Jollivet et al., 1992).

Another important difference between spoiled and non spoiled ham samples is the amount of ketones. It should be noted that a higher number and concentration of ketones are found in altered hams. The formation pathway of this family might be the β-oxidation of free fatty acids. Probably, microorganism enzymes are involved in this mechanism (Karahadian et al., 1985, Kranz et al., 1992).

When inner putrescence alteration takes place, there is a reduction in the number and concentration of aldehydes, and, in some cases, such as hexanal and pentanal, the aldehyde dissappear completly.

As for alcohols, there is an increment in number and concentration in altered hams. 3-methylbutan-1-ol and 2-methylbutan-1-ol increase in concentration, whereas 2 -methylpropan-1-ol, normally absent in non-altered hams, appears. These compounds might have been produced by amino acids degradation due to microorganisms activity. Probably, the aldehydes are an intermediate step in the transformation route and they are quickly reduced to the corresponding alcohols (Fernandez & Frutos, 1988). The reduction of acetaldehyde due to microorganisms activity might produce ethanol (Marshall, 1984). The pathway for the biosynthesis of 1-pentene-3-ol might involve microbiological degradation of polyunsaturated fatty acids (Karahadian et al., 1985).

Eters, furanes and nitrogen derived compounds appear in spoiled dry-cured ham, whereas terpenoids dissappear. The aromatics hidrocarbons and n-alkanes do not present a clear pattern.

Most of these changes might play an important role on off-flavour detected in the altered hams, specially those observed in ketones, sulphur , and nitrogen compounds.

The results suggest that off-flavour found in altered ham might be due to microbiological contamination, probably *enterobacteriaceae*, lactic bacteria, *micrococaceae* and *staphylococus* (Hechelmann, 1980; Sanabria et al., 1994). The contamination might be owed to failures in the technology applied.

CONCLUSIONS

The volatile compounds profile of putrescent samples is very different from that found in the normal ones. From a quantitative point of view, the most important change is the increment of ketones, alcohols, and sulphur derived compounds, and the reduction of the aldehydes. The large number of ketones and amino acid derived compounds obtained suggest that there is a high degree of lipolysis and proteolysis, probably due to the action of microorganisms.

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