GC-MS PROFILING OF DRY-CURED HAMS FROM DIFFERENT ORIGINS

DIRINCK P., VAN OPSTAELE F., DE SMEDT A.*, VANDENDRIESSCHE F*.

Chemical and Biochemical Research Centre, Catholic Technical University St.-Lieven, Gent, Belgium. * Imperial Meat Products N.V., Belgium.

INTRODUCTION

Southern European countries (Spain, France, Italy) are the main producers of high quality hams, produced by dry-curing and long ripening and drying periods (9 months or more). These hams impart an "aged" flavour and can be differentiated from the short-ripened (3 months) brine cured products, which are the main products in northern Europe. However in some northern countries (e.g. Belgium) there is an increasing interest in using dry-curing for raw ham production.
Dry-cured ham flavour is the result of both enzymatic and nonenzymatic reactions and degradations of macromolecules (triacylglycerols, fatty acids, proteins) in the tissues of the hams during the drying and ripening periods. In addition to those pathways, secondary metabolisms of microorganisms are involved in the development of volatile aroma components (Hinrichsen and Pedersen, 1995). The volatile composition of dry-cured hams was studied in several production countries: France (Berdagué et al., 1993; Buscailhon et al., 1994), Italy (Barbieri et al., 1992; Careri et al., 1993) and Spain (Garcia-Regueiro and Diaz, 1994; Antequera et al., 1996). Dirinck et al. (1997) compared the volatile patterns of short-ripened brine-cured and long-ripened dry-cured hams using two procedures for isolation of aroma compounds: dynamic headspace isolation and simultaneous steam distillation-extraction (SDE).

OBJECTIVES

To compare the volatile composition of several Spanish, Italian and Belgian dry-cured hams using SDE-extraction, gaschromatography-mass spectrometry and multivariate statistics.

MATERIALS AND METHODS

The sampling consisted of 4 hams of each country: 3 Serrano hams (conventional Spanish technology, 9 months of ripening), one long-ripened (18-24 months) Iberico ham (produced from heavy Iberian pigs with a feeding system based on acorns and grass), 4 Italian Parma hams (12 months of ripening) and 4 Belgian dry-cured hams (DCBEL) from two different producers (9 months of ripening). Isolation and GC-MS analyses of the volatiles was performed as described before (Dirinck et al., 1997). Semi-quantitative determinations of the volatiles were obtained by relating the peak areas of the volatiles to the peak area of dodecane as internal standard and expressed as ng g^{-1} of ham. A principal component analysis was performed using Unscrambler 6.1 (Camo, Norway).

RESULTS AND DISCUSSION

The different dry-cured hams had a rather similar qualitative but a different quantitative composition. The volatile aroma compounds could be classified into several groups: saturated, unsaturated and branched aldehydes, ketones, aromatic compounds, alcohols, esters, acids, sulfur compounds and furans. Fifty-eight components were identified in the different hams and for 41 components reliable semi-quantitative data could be determined (mean of triplicate analyses). The values for mixture peaks and badly separated peaks were omitted with the exception of the mixture peak of 2-heptanone and methional, considered to be important for ham flavour.
The volatiles with the highest concentration in the extracts originated from lipid oxidation: saturated aldehydes (C_5-C_9), unsaturated aldehydes (C_5-C_{11}) and polyunsaturated aldehydes (2,4-nonadienal and the isomeric decadienals). The highest levels of saturated aldehydes were found in the Serrano hams, while the Iberico ham was characterised by high levels of unsaturated aldehydes. Because of their low volatility the contribution of the high molecular weight aldehydes (saturated $C_{14,16,18}$, unsaturated C_{18}) to the flavour should be of minor importance. Also γ-lactones, formed by dehydration and cyclisation of the γ-hydroxyacids, were related to lipid degradation. The γ-lactones are potent aroma compounds and their level was significantly higher in the Iberico ham compared to the Serrano and Parma hams. These compounds contribute to fatty, creamy and coconut-like odours.
The polyfunctional ketones (diacetyl, 3-hydroxy-2-butanone, 2,3-pentanedione) were related to the carbohydrate metabolism. Diacetyl and 3-hydroxy-2-butanone are components with a strong buttery smell.
The identified branched aldehydes (2- and 3-methylbutanal) and the aromatic phenylacetaldehyde were the result of oxidative deamination-decarboxylation of amino acids or were formed by microorganisms and could be related to proteolysis (Barbieri et al., 1992; Hinrichsen et al., 1995). Examination of the semi-quantitative data showed that proteolysis was more intense for the Serrano hams. This was especially due to the higher level of phenylacetaldehyde in this ham in comparison with the Parma hams. However, the level of the branched aldehydes was comparable for the Serrano and the Parma ham and was lower for the Iberico ham.
The group of esters (ethyl decanoate, ethyl tetradecanoate and ethyl hexadecanoate) was important for the classification of the hams. The esters were relatively more important in the Parma and the Belgian dry-cured hams. Because Likens-Nickerson extraction was used for isolation of the volatiles no low molecular weight ethyl esters were detected in this study (Dirinck et al., 1997). According to Hinrichsen et al. (1995) ethyl esters are formed enzymatically in the final stage of ripening by combining ethanol and acids. Therefore, microorganisms appear to play an important role in their formation.
In order to visualize the complex data matrix , a principal component analysis was performed on the semi-quantitative data, with the 12 hams as objects and all 40 volatile compounds as variables (figure 1). A 2-dimensional scatter plot showed clusters of the hams of different origins, explaining 58% of the total variance (PC1 44%, PC2 14%). By presenting the objects and variables in the same plane

it was possible to show which volatiles occured in a relatively greater concentration in the different types of ham. The higher amount of oxidation products observed in the Spanish hams compared to Parma hams could be attributed to the use of higher temperatures employed during ripening of Serrano hams and thus explain the higher rancidity note in the former products. Probably as a result of the feeding system a whole series of unsaturated aldehydes was dominant in the volatile pattern of the Iberico ham. As unsaturated aldehydes are known to be responsible for rancid odours, the volatile composition of the Iberico ham could explain the even higher rancidity note of the Iberico ham compared to the Spanish Serrano hams. Although ethyl esters were detected in the Iberico and in 2 Serrano hams, these compounds had the highest relative importance in the Italian Parma hams. Because of the lower amount of oxidation products in the Parma hams, esters could play a major role in the overall aroma and may be responsible for a more fruity-flowery odour character. The Belgian dry-cured products had greater similarity with the Parma hams and were more differentiated from the Spanish products. Due to lower levels of oxidation products they were situated at the left side of PC1.

CONCLUSION

As a conclusion we may state that determination of the volatile composition of hams, according to the described analysis technology, provides a better understanding of: a) the biochemical pathways influencing flavour formation in dry-cured hams; b) the volatiles responsible for the differences in flavour character of dry-cured hams from different origin and c) the influence of feeding systems and processing technology on ham flavour. These techniques could also be used for studying all kinds of parameters influencing flavour formation in hams, such as basic materials, curing technology and ripening conditions.

REFERENCES

Antequera T., Martin L., Ruiz J., Cava R., Timon L. and Ventanas J. Differentiation of Iberian hams from Iberian and Iberian x Duroc pigs by analysis of volatile aldehydes. 42th ICoMST, Meat for the consumer, L-16, 1996.

Barbieri G., Bolzoni L., Parolari G., Virgili R., Buttini R., Careri M. and Mangia A. Flavour compounds of dry-cured ham. J. Agric. Food Chem., 40 (1992) 2389-2394.

Berdagué J.L., Bonnaud N., Rousset S. and Touraille C. Influence of pig crossbreed on the composition, volatile compound content and the flavour of dry-cured ham. Meat Sci., 34 (1993) 119-129.

Buscailhon S., Berdagué J.L., Bousset J., Cornet M., Gandemer G., Touraille C. and Monin G. Relations between compositional traits and sensory qualities of French dry-cured ham. Meat Sci., 37 (1994) 229-243.

Careri M., Mangia A., Barbieri G., Bolzoni L., Virgili R. and Parolari G. Sensory property relationships to chemical data of Italian dry-cured ham. J. Food Sci., 58 (1993) 968-972G.

Dirinck P., Van Opstaele F. and Vandendriessche F. Flavor differences between northern and southern European cured hams. Food Chemistry, 59 (1997) 511-521.

Garcia-Regueiro J.A. and Diaz I. Volatile compounds in dry-cured ham produced from heavy and light Large White pigs. 40th ICoMST, The Hague, The Netherlands, S-VIA.O9, 1994.

Hinrichsen L. and Pedersen S.B. Relationship among flavour, volatile compounds, chemical changes and microflora in Italian-type dry-cured ham processing. J. Agric. Food Chem., 43 (1995) 2932-2940.

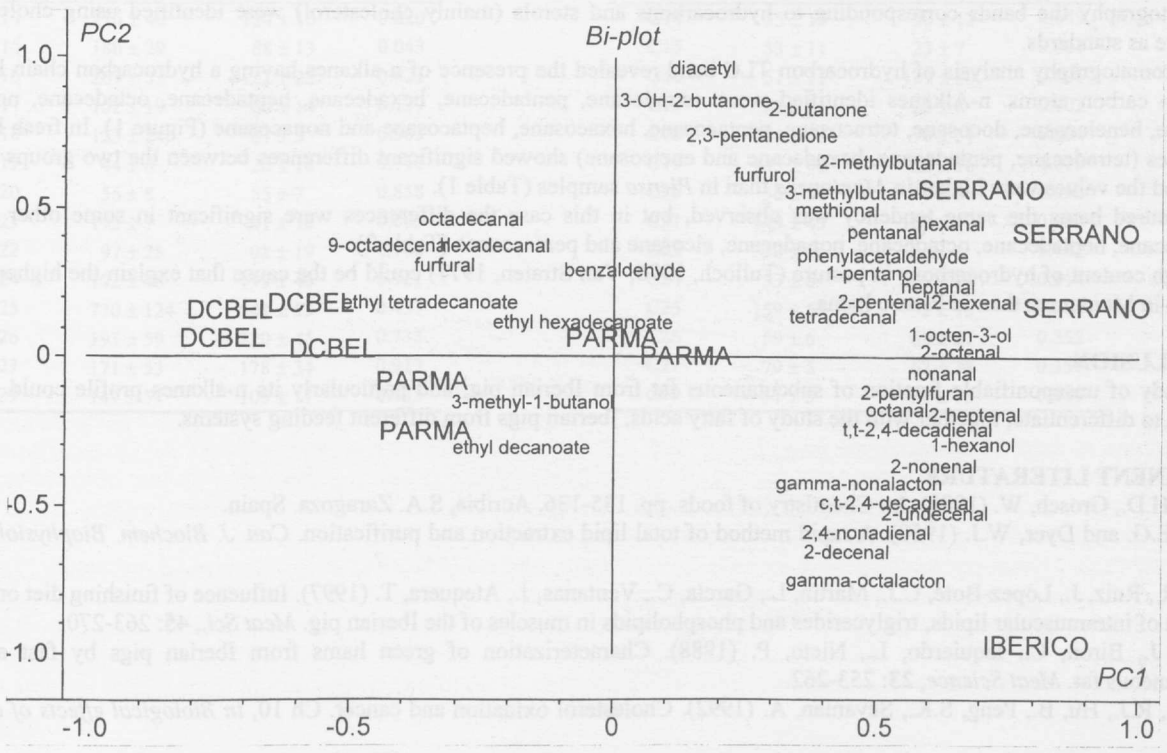

Figure 1. Principal component analysis of the volatile composition of dry-cured hams