Volatile compounds from Iberian dry-cured shoulders

Reina, R. [1], Ventanas, J.[1], García, C. [1], Silva, A.[3] and García-Casco, J.M. [2]

[1] University of Extremadura/Department of Food Technology, Cáceres, Spain
[2] AECERIBER, Zafra, Spain
[3] University of Extremadura/ Animal Production Innovation Facility, Caceres, Spain

Abstract— **Volatile compounds from three batches of dry-cured shoulders from Iberian pigs with different feeding systems: "MONTANERA" (extensive fed on acorns and pasture), "RECEBO" (extensive fed on acorns, pasture and combined whit commercial concentrate) and CAMPO (intensive fed on a commercial concentrate) were analyzed using SPME coupled to gas chromatography/mass spectrometry (GC/MS). Fourteen volatile compounds were selected for its origin formation and for its description as odorant of Iberian hams. Volatile compounds associated with lipid oxidation reactions, and even some of them as lipid oxidation markers (2,3-butanedione, pentanal, hexanal, 2-heptanone, heptanal, 2-pentylfuran, octanal, nonanal, decanal) were significant higher (*p*<0,001) in CAMPO shoulders in comparison with the other two batches, mainly for the most quantity of hexanal in this batch. Contrarily, volatile compounds derived from Strecker and Maillard reactions (3-methylbutanal, 2-methylbutanal, 5-methyldihydro-2(3H)-furanone, 5-ethyldihydro-2(3H)-furanone, 5-butyldihydro-2(3H)-furanone), were significant higher (*p*<0,001*)* in MONTANERA and RECEBO batches in comparison with PIENSO batch. These small differences were important as feeding system marks because they involve compounds that have been identified as Iberian ham odorant.**

Keywords— **Dry-cured shoulder, Volatile compounds and Flavor.**

I. INTRODUCTION

Iberian dry-cured shoulders are the great unknown of Iberian dry-cured products. As in Iberian dry-cured ham its typical flavour is an outstanding quality parameter and a major contributor to consumer acceptance [1]. Moreover, there are a lot of relevant factors that influence Iberian dry-cured products sensory characteristics, and that causes a great heterogeneity in the Iberian products quality. Most research focused on volatile compounds has been limited to the study of the most abundant compounds without elucidating their contribution to dry-cured aroma. However, it is well accepted that only a limited number of volatile compounds actually contribute to the overall food aroma [2].

It has been postulated that volatile compounds arise from different chemical and biochemical reactions [3]. A high number of compounds, comprising a great proportion of total chromatographic area, have a lipid oxidation origin. Nevertheless, compounds derived from amino acids through Strecker degradations or Maillard reactions are also very important in dry-cured products. Although is very common to link lipid oxidation compounds with off flavours, some of these volatiles show very pleasant aromatic notes and low olfaction thresholds [4]. Moreover, compounds from Strecker degradation of amino acids in dry-cured products are formed through reactions between amino acids and carbonyl compounds from lipid oxidation [5]. Therefore, those processing conditions influencing lipid oxidation and reactions between lipid oxidation compounds with amino acids will probably affect the flavour of dry-cured ham.

Amongst the factors influencing the volatiles profile in Iberian meat products, rearing system (indoors vs outdoors), feeding system (acorn and grass vs. mixed diet) and the length and conditions of the ripening process have been widely studied in dry-cured hams [6, 7]. Not studies have been carried out in dry-cured shoulders and in most cases, available information of volatiles profile could be extrapolated from dry-cured ham studies.

The objective of this study was to analyse some odour active volatiles of Iberian dry-cured shoulders affected by the feeding conditions.

II. MATERIAL AND METHODS

A. Animals

The present study was carried out with 30 pure Iberian pigs. Pigs were divided into three batches according to the type of feeding and rearing system during the finish fattening period (60 days prior to slaughter). Ten animals were reared outdoors and exclusively fed on available acorn and grass according to the traditional ‘montanera’ feeding system (IBM). Ten pigs of the second batch were reared outdoors and fed on available acorn and grass and supplemented with commercial concentrates according to the traditional ‘recebo’ feeding system (IBR). Finally, the rest of pigs were reared indoors and fed on common concentrates as a control batch according to the traditional ‘campo’ feeding system (IBC).

B. Dry-cured processing

Iberian dry-cured shoulders were placed in piles of salt at 4ºC and 80% relative humidity (RH), for 1 day/kg weight (salting) for IBC shoulders and one more day for IBR and IBM shoulders. After salting, the salt from the surface was brushed and the shoulders were processed as follows. Iberian shoulders were held at 3,5ºC and 75–80% RH for 5 days, after 3,5ºC and 78-82% HR for 60 days (post-salting step). Temperature was thereafter increased from 3,5ºC to exterior conditions at less than 1ºC per two days (it depend the time of year) during 30 days. Finally, shoulders were kept in a room under natural conditions for the rest of dry-cured process, about 10 months (drying stage).

C. Analysis of volatile compounds

Volatile compounds were extracted by a SPME (Supelco Bellefonte, PA) fibre coated with carboxen-poly(dimethylsiloxane) (85 µm thickness) coupled to a direct extraction device (DED) and subsequently analysed by GC/MS (gas chromatograph Hewlett-Packard 5890 series II coupled to a mass selective detector Hewlett-Packard HP-5791 A). Volatile extraction was carried out using 1 g of sample into a 4 ml glass vials and sealed with silicon cap. Before extraction, samples were pre-conditioned in a temperature-controlled water bath at 37ºC for 30 minutes. The stationary phase of SPME was inserted into the sample vial through the septum and then exposed to the headspace during 30 minutes. After extraction, the SPME fibre was immediately transferred to the injector of the chromatograph which was in splitless mode al 250ºC. The separation of volatiles was performed on a 5% phenyl-methyl silicone (HP-5) bonded phase fused silica capillary column (Hewlett-Packard, 50 m x 0.32 mm i.d., film thickness 1.05 µm), operating at 6,5 psi of column head pressure, resulting in a flow of 1.3 ml min^{-1} at 40ºC. Oven program was: 40ºC for 10min, 5ºC min^{-1} to 200ºC, 20ºC min^{-1} to 250ºC, and held 250ºC for 5 min. Fourteen volatile compounds were selected according to its origin formation and for its description as odorant of Iberian dry-cured hams. Volatile compounds were identified by comparing their mass spectra with those reported in the Wiley and NIST libraries and by comparing their mass spectrum and/or LRI with those reported in the literature [8], and in the NIST database [9]. Results from the volatiles analysis are given in area units (UA).

D. Statistics

Treatment of anomalous data was carried out using Grubb test, recommended by ISO rules. The statistical analysis was carried out an analysis Multivariate analysis using the statistical package SPSS software (v. 12.0)

III. RESULTS AND DISCUSSION

Among the identified compounds in three batches (n-108), fourteen volatile compounds were selected from dry-cured shoulders for its origin formation and for its description as odorant of Iberian hams (Table 1). All these volatile compounds have been previously identified in fully ripened Iberian ham [10], and previous researches on this product have investigated the effect on them of the rearing system [4, 11]. Some of these compounds contribute to the overall ham flavour as they have been reported as odorant of Iberian hams [4, 12], and also of other dry-cured hams [13, 14].

Among the 14 compounds included in Table 1, 9 of them have been associated with lipid oxidation reactions, and even some of them are lipid oxidation markers [15] and 6 compounds are generated from amino acids through Strecker and Maillard reactions

[16, 17]. he effect of the feeding system (Montanera vs Recebo vs Pienso dry-cured shoulders) on the volatile compounds was significant for most of the selected compounds. Significant effect of the feeding system on lipid oxidation was found (Figure 1). Some of them were more abundant in IBC than in the other two batches (Table 1), and they have been described as odor-active compounds of dry-cured ham [4]. These differences could be important because they involve compounds that have been identified as Iberian ham odorants, and in fact remarkable differences between the flavour characteristics of these dry-cured shoulders were found in the sensory analysis [18].

Table 1. Total selected volatile compounds (mean values ± SD).

	IBM	IBR	IBC	Origin	*p*
2,3-butanedione	1,4^{b} ± 0,5	0,7^{a} ± 0,0	2,6^{c} ± 0,8	lipid	0,000
3-methy, butanal	23,8^{b} ± 3,8	23,8^{b} ± 12,7	10,1^{a} ± 5,1	aa	0,001
2-methyl, butanal	19,8^{b} ± 8,4	13,2^{b} ± 7,4	4,5^{a} ± 2,6	aa	0,000
pentanal	13,2^{b} ± 3,7	6,3^{a} ± 1,8	13,5^{b} ± 6,7	lipid	0,002
hexanal	62,6^{ab} ± 23,3	38,6^{ab} ± 18,5	98,4^{b} ± 51,6	lipid	0,003
2-heptanone	14,2^{a} ± 4,0	13,0^{a} ± 6,2	28,7^{b} ± 14,9	lipid	0,002
heptanal	5,4^{a} ± 2,5	4,0^{a} ± 2,5	10,1^{b} ± 5,7	lipid	0,004
2(3H)-furanone, dihydro, 5-methyl	0,5 ± 0,2	0,8 ± 0,6	0,7 ± 0,4	aa	0,292
furan, 2-pentyl	1,2^{a} ± 0,3	1,5^{a} ± 0,6	2,2^{b} ± 0,4	lipid	0,000
octanal	1,6^{a} ± 0,4	2,0^{a} ± 1,1	6,2^{b} ± 3,3	lipid	0,000
2(3H)furanone, 5-ethyldihydro	1,3^{a} ± 0,6	2,0^{ab} ± 1,0	3,2^{b} ± 1,9	aa	0,012
nonanal	2,7^{a} ± 1,8	3,6^{a} ± 3,1	10,0^{b} ± 6,6	lipid	0,002
decanal	0,2^{a} ± 0,1	0,3^{ab} ± 0,2	0,6^{b} ± 0,4	lipid	0,019
2(3H)furanone, 5-butyldihydro	0,3^{a} ± 0,2	0,4^{a} ± 0,3	0,8^{b} ± 0,5	aa	0,005

[a] p: effect was considered significant at $p<0{,}05$

Five compounds coming from Strecker and Maillard reactions showed significant differences between batches. In general these compounds rose significantly with the increase of the consumption of acorn and grass during the feeding system of the animals (Figure 1). There was a marked increase from IBC to IBM in these compounds. Conversely compounds derived from lipid oxidation reactions decreased significantly when the consumption of acorn and grass were increased, especially in IBR dry-cured shoulders. A possible explanation for this would be the consumption of natural (from grass and acorns) and synthetic antioxidants (from feed) of IBR shoulders, compared with the only consumption of natural antioxidant of IBM shoulders and the synthetic of IBC shoulders.Thus, these compounds could be used as indicators of the feeding system, and with its study would be possible to estimate the Iberian dry-cured shoulder current feeding system.

Compounds derived from Strecker degradation of amino acid and Maillard reaction were higher in IBM batch. The higher proteolysis activity in the muscles of outdoor reared pigs linked to exercise [19] could explain the higher levels of volatile compounds derived from amino acid degradation in IBM dry-cured shoulders. Although in most cases differences between IBM and IBR batches were not significant.

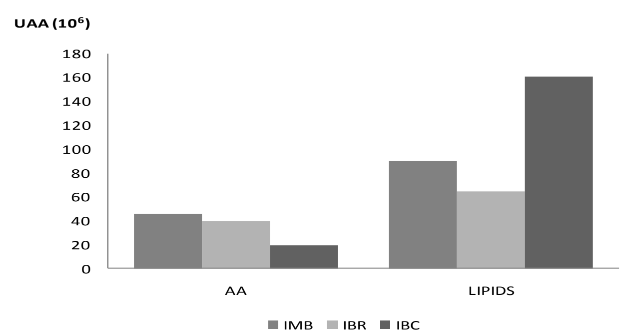

Figure 1.Total selected volatile compounds classified according to its origin formation

The present results suggest that the development of Strecker and Maillad reactions could have been more intense in IBM and IBR batches and lipid oxidation reactions in IBC batch. For this reason, these reactions are related with the higher consumer’s preferences for IBM compared to IBC dry-cured products showed in previous studies with non-trained panellist (consumers) [20], which could be partly attributed to the differences in the volatiles profiles found in the present study. Besides, the presence of α-tocopherol in acorn and grass presents in IBM and IBR dry-cured shoulders produced significant differences in the levels of some aldehydes, compounds associates with off-flavours as rancid. The protective effect of α-tocopherol against lipid oxidation, as consequence of the deposition of dietary α-tocopherol in muscle, resulted in a significant reduction in the volatile aldehyde amounts ($p<0.05$).

IV. CONCLUSSIONS

The effect of rearing system and feeding regime had a marked effect on the volatile compounds of Iberian dry-cured shoulders, especially on Strecker and Maillard volatile compounds whose abundances increased with the consumption of acorn and grass (IBM and IBR). The abundance of some of these compounds could be used as indicators of the feeding system and, therefore, as flavor development indicators.

V. ACKNOWLEDGMENT

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VI. REFERENCES

1. Ruiz J, García C, Muriel E et al. (2002). Influence of sensory characteristics on the acceptability of dry-cured ham. Meat Sci. 61:347–354.
2. Schieberle P (1995). New developments in methods for analysis of volatile flavor compounds and their precursors. Amsterdam, The Netherlands.
3. Ruiz J, Cava R, Ventanas J et al. (1998) Headspace solid phase microextraction for the analysis of volatiles in a meat product: dry-cured Iberian ham. J Agric Food Chem. 46:4688–4694.
4. Carrapiso AI, Ventanas J, Garcia C (2002) Characterization of the most odor-active compounds of Iberian ham headspace. J Agric Food Chem. 50:1996–2000
5. Ruiz J, Muriel E, Ventanas J (2002) The flavour of Iberian ham. Signpost, Trivandrum, India.
6. Ruiz J, Ventanas J, Cava R et al. (1999) Volatile compounds of dry-cured Iberian ham as affected by the length of the curing process. Meat Sci. 52:19–27
7. Jurado A, García C, Timón ML et al. (2007) Effect of ripening time and rearing system on amino acid-related flavor compounds of Iberian ham. Meat Sci 75:585–594
8. Kondjoyan N, Berdagué JL (1996). A compilation of relative retention indices for the analysis of aromatic compounds. Saint Genes de Champanelle, France.
9. NIST database at http://webbook.nist.gov/
10. García C, Berdagué JL, Antequera T et al. (1991).Volatile components of dry-cured Iberian ham. Food Chem. 41: 23-32.
11. Carrapiso AI, Jurado A, García C. (2003). Effect of Crossbreeding and Rearing System on Iberian Ham Volatile Compounds. Food Sci. Technol. Int. 9, 421-426.
12. Carrapiso AI, Garcia C. (2004). Iberian ham headspace:odorants of intermuscular fat and differences with lean. J. Sci. Food Agric 84, 2047-2051.
13. Flores M, Grimm CC, Toldrá FA et al. (1997). Correlations of sensory and volatile compounds of Spanish Serrano dry-cured ham as a function of two processing times. J. Agric. Food Chem. 45, 2178-2186.
14. Blank I, Devaud S, Fay LB et al. (2001). Odor-active compounds of dry meat: Italian-type salami and Parma ham. Washington..
15. Cava R, Ruiz J, Ventanas J, Antequera T. 1999. Effect of α-tocopheryl acetate supplementation and the extensive feeding of pigs on the volatile aldehydes during the maduration of Iberian ham. Food Sci. Technol. Int. 5, 235-241.
16. Mottram DS. (1998). Flavor formation in meat and meat products: a review. Food Chem. 62, 415-424.
17. Pripis-Nicaulau L, De Revel G, Bertrand A et al. (2000). Formation of flavor components by the reaction of amino acid and carbonyl compounds in mild conditions. J. Agric. Food Chem**, 48,** 3761-3766.
18. Jurado A, Carrapiso AI, Ventanas J et al. (2009). Changes in SPME-extracted volatile compounds from Iberian ham during ripening. Grasas y Aceites, 60:262-270.
19. Enfalt ACK, Lundstrom I, Karlsson HA, et al.(1993) Moderate indoor exercise: effect on production and carcass traits, muscle enzyme activities and meat quality in pigs. Anim Prod 57:127–135
20. Ventanas S, Ruiz J, García C et al. (2007) Preference and juiciness of Iberian dry-cured loin as affected by intramuscular fat content, crossbreeding and rearing system. Meat Sci 77:324–330.