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Analysis of volatile compounds from Iberian hams: a review

By **M. Narváez-Rivas, E. Gallardo** and **M. León-Camacho***

Food Characterization and Quality Department. Instituto de la Grasa (C.S.I.C.).
Avda. Padre García Tejero, 4. 41012 Seville, Spain.
*Corresponding author: mleon@cica.es

RESUMEN

Análisis de los compuestos volátiles del jamón ibérico: revisión

En este artículo se proporciona información sobre el estudio de los compuestos volátiles del jamón ibérico tanto fresco como curado. Se presentan los diferentes compuestos volátiles identificados por distintos autores. Además, se evalúan los métodos analíticos que han sido utilizados para determinar dichos compuestos volátiles en este tipo de muestras. Todos los compuestos identificados y descritos en esta revisión (un total de 411 compuestos volátiles) han sido agrupados en diversas tablas de acuerdo a las diferentes familias a que pertenecen: hidrocarburos, aldehídos, cetonas, alcoholes, ésteres y éteres, lactonas, terpenos, compuestos halogenados, compuestos nitrogenados, compuestos de azufre y ácidos carboxílicos. Debido a la complejidad de este estudio, la presente revisión puede ser muy útil en investigaciones posteriores.

PALABRAS-CLAVE: Cerdo ibérico – Compuestos volatiles – Cromatografía gaseosa – Jamón – Proceso de curado.

SUMMARY

Analysis of volatile compounds from Iberian hams: a review

This article provides information on the study of the volatile compounds in raw and dry-cured Iberian hams. Different volatile compounds are identified and studies carried out by different authors are presented. This article reviews the analytical methods that have been used to determine the different volatiles of these samples. Furthermore, all volatile compounds identified (a total of 411 volatiles) have been collected in several tables according to different series of compounds: hydrocarbons, aldehydes, ketones, alcohols, esters and ethers, lactones, terpenes and chloride compounds, nitrogenous compounds, sulfur compounds and carboxylic acids. This review can be useful in subsequent research due to the complexity of the study.

KEY-WORDS: Dry-cured Process – Gas Chromatography – Hams – Iberian Pigs – Review – Volatile compounds

1. INTRODUCTION

Dry-cured Iberian ham is an expensive meat product with an extraordinary consumer acceptance in Spain and around the world. Consumer preference highly depends on the sensory quality of slices, which is mainly determined by aroma, taste and texture. The main factors that impact the characteristic intense flavor of this product are the meat quality as well as the conditions of the ripening process. The factors that affect the raw meat characteristics are the rearing system, mainly during the final fattening period, the age of the animals and pig genotype (Dirinck *et al*., 1997; Sabio *et al*., 1998; Jurado *et al*., 2007; Ramírez and Cava, 2007). However, the fattening diet of animals is the factor that determines the ham prices on the market. According to the feed type, there are three different types of dry-cured Iberian ham: "Montanera" (fed only on acorns and pasture), "Recebo" (fed on acorns, pasture and concentrated feed) and "Cebo" (fed on concentrated feed), the first being the most expensive. The production of Iberian pig is deeply bounded to the Mediterranean ecosystem. The outdoor rearing system has a positive image for consumers since it is associated with an increase in animal welfare, reduced environmental impact and protection for a traditional production system (Rey *et al*., 2006).

Traditional dry-curing of this kind of hams is a long process, over 24-36 months, in which humidity and temperature are controlled (Flores and Toldrá, 1993). During this period, raw hams undergo four stages: salting with dry salt, washing, post-salting for salt equalization and ripening-drying (in a cellar) (Flores and Toldrá, 1993). In the salting and post-salting stages, the hams are kept at low temperatures to reduce the risk of bacterial spoilage. However, in the ripening-drying stage, they are left to mature under environmental conditions (temperatures range from 20 to 35 °C).

It has been postulated that chemical or enzymatic reactions such as lipolysis, chemical or enzymatic oxidation, proteolysis, Strecker degradation and Maillard reactions are present in the dry-curing process of Iberian hams (Narváez-Rivas *et al*., 2007), and that these chemical processes are the origin of volatile compounds (Toldrá, 1998; Toldrá *et al*., 2009) which are especially generated in the latest stages (Flores, 1997).

A large number of volatile compounds have been reported in dry-cured Iberian hams by several authors. Among these compounds, there are hydrocarbons,

aldehydes, ketones, alcohols, acids, esters, terpenes, sulphur compounds, nitrogenous compounds and others. However, only a limited number of volatile compounds actually contribute to the overall ham aroma, such as aldehydes and ketones (Carrapiso *et al*., 2002). A detailed study of the volatile compounds will be carried out in this review.

All the information possible concerning volatile compounds of raw and dry-cured ham is necessary in order to monitor the quality of the flavor and to provide quality control for these processed products.

Several techniques have been used to isolate the volatile compounds from Iberian hams which will be explained in this review, along with the procedures employed for their separation, identification and quantification.

2. ANALYSIS OF VOLATILE COMPOUNDS

The determination of volatile compounds is complex due to different factors, such as the high number of compounds, differences in volatility and the great amount of functional groups. The different techniques that exist lead to the collections of volatile profiles, which may differ for the same product, depending on the extractive power and selectivity of the technique with respect to one type of compound or another. Furthermore, food aroma research is difficult due to the ability of volatile compounds to bind to the solid matrix of food and to their degree of ease in releasing from it. This aspect is particularly important in Iberian ham, since the ham does not lose practically any of its original structure during the dry-curing process due to the presence of salt; therefore this is a very complex matrix with a wide range of components that interact with each other or with the volatile compounds and prevent a full extraction process.

The profile of volatile compounds from Iberian hams has been used to differentiate different types of pig feedings (Narváez-Rivas *et al*., 2010b; Timón *et al*., 2002; Narváez-Rivas *et al*., 2011), genotypes (Iberian x Duroc) (Ramírez and Cava, 2007) and breed types (French, Iberian and White) (Sánchez-Peña *et al*., 2005), to study the effect of salt content and processing conditions (Andrés *et al*., 2007), and to study the length of the process (Dumont and Ada, 1972).

2.1. Sampling

The analysis of volatile compounds in dry-cured Iberian hams has been carried out using samples taken from different anatomical locations. Several authors (Sabio *et al*., 1998; Ramírez and Cava,

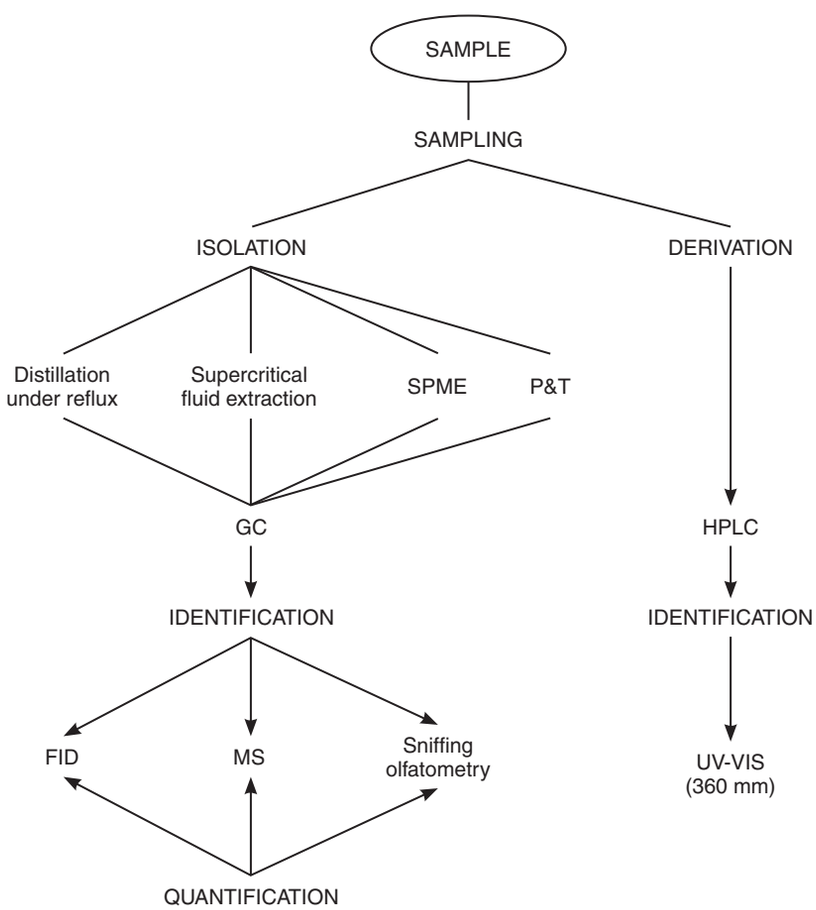

Figure 1
Summarized scheme of different steps and techniques used in the analysis of volatile compounds.

2007; Carrapiso *et al*., 2002; López, *et al*., 1992; Timón *et al*., 1998) have used bicep femoris muscle for this analysis. Others (García *et al.*, 1991; Jurado *et al*., 2009) used semi-membranosous and bicep femoris muscles. García-González *et al*. (2008) and Sánchez-Peña *et al*. (2005) analyzed the part located along and behind the femur, composed essentially of subcutaneous fat and bicep femoris, semi-membranosous and semitendinosous muscles. In other studies, the muscles selected were only semi-membranosous and semi-tendinosous (Narváez-Rivas *et al*., 2010a, 2010b), which were minced before analysis. In addition, the volatile profile of subcutaneous (Timón *et al*., 2002; Narváez-Rivas *et al*., 2010a; Timón *et al*., 2001) and intermuscular fat (Timón *et al*., 2001) from dry-cured Iberian ham has been the object of study (Narváez-Rivas *et al*., 2011).

Samples from ham have been taken using different procedures. In some cases, a cylindrical stainless steel tool was used to extract a sample along the thickness and this was then cut into small slices (Sánchez-Peña *et al*., 2005) or ground (Jurado *et al*., 2009). Several authors have carried out the analysis by cutting a portion of ham (muscle, fat or muscle and fat), which was blended and minced (Sabio *et al*., 1998; Ramírez and Cava, 2007; Carrapiso *et al*., 2002; Narváez-Rivas *et al*., 2011; López *et al*., 1992; Timón *et al*., 1998; García *et al.,* 1991; García-González *et al*., 2008). Instead of cutting a portion of ham, slices have been taken, minced and mixed (Narváez-Rivas *et al*., 2010b; Narváez-Rivas *et al*., 2010a; Ruiz *et al*., 1999) or directly analyzed (Ruiz *et al*., 1998). On the other hand, a sample of fat has been taken and directly analyzed, without subsequent treatment (Timón *et al*., 2002; Timón *et al.,* 2001). There are techniques that avoid preparation of the sample and allow a direct extraction of volatiles from hams (Andrés *et al*., 2007; Ruiz *et al*., 2001; Andrés *et al*., 2002), as we will see later.

Ham is a solid and heterogeneous material, so the volatile compounds found can be different depending on the part of the ham sampled and how the sampling is carried out. If sampling is carried out not only in different parts of the ham but also with different procedures (cut in slices, minced, etc.), the results may vary.

2.2. Isolation

Certainly, the key the complexity of the analysis of volatile compounds is in their isolation and preconcentration prior to the gas-chromatographic analysis. The low level of concentration of these compounds, the wide distribution of vapor pressures and the large difference in structures and functional groups have motivated the development of the different techniques of isolation and preconcentration of these compounds, which has been directed towards making the procedure of analysis as accurate, reproducible and repetitive as possible.

Several methods have been developed for volatile compound extraction and much of them have been used to study the Iberian ham. These techniques are the aim of this section.

2.2.1. Distillation under high vacuum

The first methods used for the recovery of volatile compounds consisted of the use of distillation followed by extraction with organic solvents (dichloromethane, carbon disulphide).

In 1991, García *et al.* (1991) used the method of Dumont and Ada (1972), in which the sample was transferred to a flask that was connected to an ice-trap cooled with liquid nitrogen and maintained at low pressure 5 hours. After distillation, the trap was carefully washed using distillate water. Then, the eluted fraction was extracted with dichloromethane and the resulting extract was concentrated with a column. The principal problem of this technique arises from the interference that exists between the solvent front and the compounds that elute with it, since the solvent means more than 99% of the sample, in spite of its low response in flame ionization detection system (saturation of column stationary phase). This method is lengthy and involves a great deal of sample handling, and for these reasons, other methods that are not so long and tedious have been more widely used to study volatiles from Iberian hams. Furthermore, in addition to odorant compounds, the utilization of organic solvent in the extraction can carry other food components, particularly lipids, which may make subsequent operations difficult. On the other hand, these solvents promote a selective extraction of volatiles depending on the polarity of the solvent and volatiles.

2.2.2. Supercritical fluid extraction

Timón *et al*. (1998) obtained aroma extracts from Iberian ham using a supercritical fluid (carbon dioxide) as the extraction technique for volatiles. They used a Hewlett-Packard 7680A supercritical fluid extractor. The extraction was carried out for 15 min. Different temperatures (40-60 °C) and pressures (77-218 atm) were tested, and finally, it was concluded that larger numbers and higher concentrations of volatile compounds were achieved at 40 °C and at 91 atm. It has been reported that flavor compounds obtained by this method showed a great similarity to the original source (Merkle and Larick, 1994). This helps to reduce or eliminate the use of halogenated solvents and to extract samples more quickly and efficiently than the distillation under reflux method. Besides, this technique allows for the analysis of thermally unstable samples.

2.2.3. Solid-phase microextraction

The static headspace solid-phase microextraction (SPME) technique is used in the analysis of volatile

compounds when the number of compounds is not too large and they are at a considerable concentration. However, the employment of SPME improves the chromatographic analysis, since by using a fiber of absorbent material, a sample pre-concentration takes place. The compounds present in the headspace are absorbed by this fiber and the volatile compounds released from the bounded phase to reach equilibrium with the vapor phase. Strictly speaking, the technique in question cannot be considered as a static headspace. Nevertheless, SPME can be classified in this group of techniques since there is no steam distillation and it is carried out in a closed system.

The adsorption SPME technique, developed by Arthur et al. (1990, 1992), is one of the most commonly used techniques to isolate volatiles from Iberian hams (Ramírez and Cava, 2007; Toldrá, 1998; Sánchez-Peña *et al*., 2005; Andrés *et al.,* 2007; Jurado *et al*., 2009; García-González *et al.,* 2008; Ruiz *et al.,* 2001; Andrés *et al.,* 2002; Andrade *et al*., 2009; Zhang and Pawliszyn, 1993), since it is solvent free, inexpensive, easy to use and relatively fast (Andrade *et al.,* 2009). SPME involves absorbing the analyte from the sample onto a modified solid support (fiber). Samples are placed into glass vials tightly capped with a septum, in which the SPME fiber, previously preconditioned at a high temperature, is inserted and then exposed to the headspace. During this process, two equilibria should be reached by the analytes: between the matrix and the headspace and between the headspace and the coating of the fiber (Ruiz *et al*., 1999). To reduce the equilibration time, agitation and heating have been proposed (Ruiz *et al*., 1999). Therefore, the extraction is carried out in an oven to ensure a homogeneous temperature for sample and headspace. When the process is completed, the fiber is inserted into the injector port of the gas chromatograph and the analytes are then desorbed by thermal means. The fibers chosen for the analysis of volatiles from Iberian hams are coated with divinylbenzene-carboxen-poly(dimethylsiloxane) (DVB/CAR/PDMS) (Ramírez and Cava, 2007; Sánchez-Peña *et al*., 2005; García-González *et al*., 2008) or carboxen-poly(dimethylsiloxane) (CAR/PDMS) (Andrés *et al*., 2007; Jurado *et al*., 2009; Ruiz *et al.,* 2001; Andrés *et al*., 2002; Andrade *et al*., 2009), because of their high sensitivity and varying thicknesses of the fiber used, which have been measured at 50/30 (Ramírez and Cava, 2007; Sánchez-Peña *et al*., 2005), 75 (Andrés *et al*., 2007; Jurado *et al*., 2009; Ruiz *et al*., 2001) and 100 µm (Andrade *et al*., 2009). A higher number of volatile compounds was found using CAR/PDMS as fiber (between 61 and 107 volatiles), but there is no relation between the thickness of the fiber and the number of volatiles and the highest number of volatiles (107 compounds) was found when using a thickness of 75 µm (Andrés *et al*., 2002) and the lowest (30 compounds) was found with a thickness of 50/30 µm (Sánchez-Peña *et al*., 2005). This is one of the techniques that require less sample handling and thus less interference in the collection of volatile compounds.

SPME has been coupled to a direct extraction device (DED) (Andrés *et al*., 2007; Ruiz *et al*., 2001; Andrés *et al*., 2002), avoiding preparation of the sample. The operating mode involves placing the needle of the SPME holder into the DED, and thereafter this is introduced into the core of ham the without damaging the fiber and avoiding physical sampling of the hams (Ruiz *et al*., 2001).

One of the advantages of static headspace sampling is the ability to analyze a sample for low molecular weight volatiles without the presence of a solvent peak. Besides, this technique can be easily automated which provides increased repeatability over manual approaches. Other additional advantages of the static headspace technique are relatively low cost per analysis, simple sample preparation, and the elimination of reagents (Wampler, 2002).

The main limitation of SPME is the relatively small amount of sorbent material available on the fiber. Another disadvantage related to this technique is that, for very low levels of analyte concentration in the original sample material, it may have a lack of sensitivity required for the determination, since the concentration in the headspace is in equilibrium with the sample matrix and only a portion of the headspace is withdrawn and transferred. This can be improved by elevating the temperature of the sample to increase the volatility of the analytes. Nevertheless, most static headspace instruments have the capability of heating samples to only about 150 °C, which limits the detection of analytes with higher boiling points. Finally, reproducibility depends on analyzing a sample after it has reached equilibrium, and the time required to achieve this point may, especially for less volatile compounds, be a drawback for some analyses (Wampler, 2002).

2.2.4. Dynamic headspace (Purge and trap)

In dynamic headspace (DHS), the sample is purged (swept) with an inert gas, such as nitrogen or helium, which strips aroma constituents from the sample. The volatiles in the purge gas must then be trapped from the gas stream.

When an inert carrier gas is bubbled through the sample, forcing the release of the volatiles from the matrix, the technique is also referred to as "purge and trap". This technique has certainly been the most commonly used in the analysis of volatile compounds by various authors, although many authors think that volatiles obtained by DHS better represent the real volatile fraction that reaches the human receptors when a sample is smelt.

The volatile compounds from Iberian ham have also been isolated by the purge and trap technique and adsorbed in a capillary trap (Sabio *et al*., 1998; Carrapiso *et al*., 2002; Narváez-Rivas *et al*., 2010b; Timón *et al*., 2002; Narváez-Rivas *et al*., 2011; Dumont and Ada, 1972; López *et al*., 1992; Narváez-Rivas *et al*., 2010a; Timón *et al*., 2001). In this method, the sample is introduced into a dynamic headspace vial which is thermostated for a time to increase the fugacity of volatile compounds, and subsequently, for a few

minutes the volatile substances are purged with purified helium and adsorbed into a capillary Tenax trap held at a low temperature with liquid nitrogen. After adsorption onto a sorbent, the trapped compounds are desorbed by heating and then cryofocused at the head of the gas chromatograph-column (Pillonel *et al*., 2002). The analytes can also be eluted with a solvent (Burger and Munro, 1987; Olafsdottir *et al*., 1985) but recovery is not always satisfactory (Boren *et al*., 1985) and is difficult to automate. However, thermal desorption shows the following advantages: analysis of 100% of the trap content, no solvent peak, no waste and no contamination from the solvent (Pillonel *et al*., 2002).

One of the main problems of dynamic headspace is the adsorption of water in the trap, which can damage the MS-detector and induce a modification of the spectrum, rendering identification difficult. So, it is necessary to use one or a combination of the following solutions: dry purge, condensation of water in a cold water trap (condenser), hygroscopic trap and drying of the sample, and permeation (Nafion membrane) (Pillonel *et al*., 2002).

All authors that have used this technique to isolate the volatiles from Iberian hams have used an automatic Purge and Trap concentrator, in which a thermal desorption mode is used.

The use of different temperatures and times in each step has shown differences among the studies. For example, using the same kind of sample (bicep femoris muscle), Sabio *et al*. (1998) and López *et al*. (1992) extracted a different number of volatile compounds (88 and 64 respectively), which can be due to the use of different temperatures and times in the purge step (35 °C for 1 h and 29 °C for 45 min, respectively).

Dynamic headspace techniques offer many of the same advantages of static headspace, including elimination of the solvent peak, analysis of just the volatiles, automation, and easy sample preparation. In addition, the trapping stage of the analysis offers increased sensitivity, permitting the analysis of volatiles at parts per billion (ppb) levels routinely. Furthermore, sorbents offer some selectivity within the range of volatiles collected, so it may be possible to select a combination of sorbent and temperature which permits the collection and concentration of specific analytes while venting others, thus simplifying the analysis (Wampler, 2002).

On the other hand, purge-and-trap instrumentation is more complex since it requires the monitoring of several steps, and may be more expensive than others (Wampler, 2002). The sources of error in purge and trap are purge time, trap drying, trap transfer, trap temperature, capping material and sample storage (Washall and Wampler, 1990).

2.3. Gas chromatography

Once the volatile compounds have been isolated their matrix, their analysis is carried out by gas chromatography (GC) using a fused silica capillary column. Different columns (low and high polarity) have been used in this analysis, and their properties can be seen in Table 1. The stationary phase of the low polar

Table 1
Different columns used in the analysis of volatile compounds of dry-cured Iberian hams

Column	Stationary phase	Polarity	Length (m)	Internal diameter (mm)	Film thickness (µm)	References
HP-5 (Hewlett-Packard)	(5%-Phenyl)-methylpolysiloxane	Low polar	50	0.32	1.05	3,8,12,16,18,19,20,21,22
HP-5 (Hewlett-Packard)	(5%-Phenyl)-methylpolysiloxane	Low polar	50	0.32	0.52	10
HP-FFAP (Hewlett-Packard)	Nitroterephthalic acid modified polyethylene glycol	High polarity	30	0.32	0.25	3, 21, 22
HP-FFAP (Hewlett-Packard)	Nitroterephthalic acid modified polyethylene glycol	High polarity	50	0.25	0.25	9
DB-5 (Agilent J&W)	(5%-Phenyl)-methylpolysiloxane	Low polar	50	0.32	1.05	1, 5, 15
DB-WAX (J&W Scientific)	Polyethylene glycol	High polarity	60	0.25	0.25	7, 13
SE54 (J&W)	(5%Phenyl)(1%Vinyl)-methylpolysiloxane	Low polar	60	0.32	1	11
Rxi®-5ms (Restek)	(5%-Phenyl)-methylpolysiloxane	Low polar	30	0.25	1.00	2, 17
Supelcowax^{m}-10 (Supelco)	CARBOWAX® 20M poly(ethylene glycol)	High polarity	60	0.25	0.25	4, 6, 14

In references: 1: Sabio *et al.,* 1998; 2: Ramírez and Cava, 2007; 3: Carrapiso *et al.,* 2002; 4: Narváez-Rivas *et al.,* 2010; 5: Timón *et al.,* 2002; 6: Narváez-Rivas *et al.,* 2011; 7: Sánchez-Peña *et al.,* 2005; 8: Andrés *et al.,* 2007; 9: López *et al.,* 1992; 10 = Timón *et al.,* 1998; 11: García *et al.,* 1991; 12: Jurado *et al.,* 2009; 13: García-González *et al.,* 2008; 14: Narváez-Rivas *et al.,* 2010; 15: Timón *et al.,* 2001; 16: Ruiz *et al.,* 1999; 17: Ruiz *et al.,* 1998a; 18: Ruiz *et al.,* 2001; 19: Andrés *et al.,* 2002; 20: Andrade *et al.,* 2009; 21: Aparicio-Ruiz and Morales, 1998; 22: García-González *et al.,* 2006.

columns was 5%-Phenyl-methylpolysiloxane, except in SE54 (J&W), in which it was (5%Phenyl, 1%Vinyl-methylpolysiloxane. On the other hand, the stationary phases used in high polar columns were polyethylene glycol and nitroterephthalic acid modified polyethylene glycol. As shown in this table, the most commonly used column has been the HP-5 (50 m × 0.32 mm, 1.05 µm), although Carrapiso et al. (2002) made a comparison between this low polar column and a high polar column (HP-FFAP, 30 m × 0.32 mm, 0.25 µm), finding that coelutions of some compounds exist using this first one and concluding that the use of the second column is advisable to avoid wrong assignments of odor descriptions to abundant compounds with clear mass spectra that may co-elute with others. This coelution also existed in other columns of low polarity auch as the Rxi®-5ms (Restek) (Ruiz *et al*., 1998). However, there are different studies on the same type of sample (subcutaneous fat) carried out by several authors (Timón *et al*., 2002; Narváez-Rivas *et al*., 2010a) using two columns (high and low polarity, respectively) and the amount of volatile compound identified was totally different (105 and 52 compounds, respectively).This can be due to the temperature used in the isolation (45 and 40 °C, respectively) rather than the use of different columns. Therefore, the use of columns with different polarity and dimensions can have an influence on the resolution of some peaks but not in the number of them, which is influenced by the different techniques of isolation used previously and the conditions employed.

Nitrogen (Timón *et al*., 2002; Narváez-Rivas *et al*., 2010a), hydrogen (Narváez-Rivas *et al*., 2010b; Sánchez-Peña *et al*., 2005; García-González *et al*., 2008, Narváez-Rivas *et al*., 2010a) or helium (Sabio *et al.,* 1998; Ramírez and Cava, 2007; López *et al*., 1992; Timón *et al*., 1998; Andrade *et al.,* 2009) have been used as carrier gas. As can be observed, helium is the most commonly used carrier gas, but according to the van Deemter equation, hydrogen is better since the chromatographic column has better efficiency when the molecular weight of the carrier gas is lower (van Deemter *et al*., 1956). Several oven temperature programs have been employed, starting at 30 °C (López *et al*., 1992), 35 °C (Sabio *et al*., 1998; Carrapiso *et al*., 2002; Timón *et al*., 2002; Timón *et al*., 1998; Timón *et al*., 2001) or 40 °C (Ramírez and Cava, 2007; Narváez-Rivas *et al*., 2010b; Sánchez-Peña *et al*., 2005; Andrés *et al*., 2007; García *et al.,* 1991; Jurado *et al*., 2009; García-González *et al*., 2008, Narváez-Rivas *et al*., 2010a; Ruiz *et al*., 2001; Andrés *et al*., 2002; Andrade *et al*., 2009) and increasing up to 175 °C (Sabio *et al*., 1998), 180 °C (López *et al.,* 1992), 200 °C (Sánchez-Peña *et al*., 2005; Andrés *et al*., 2007; García-González *et al*., 2008; 28), 220 °C (Narváez-Rivas *et al*., 2010a, 2010b), 230 °C (Timón *et al*., 1998), 240 °C (García *et al*., 1991) or 250 °C (Ramírez and Cava, 2007; Carrapiso *et al*., 2002; Timón *et al*., 2002; Jurado *et al*., 2009; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrade *et al*., 2009). Splitless mode injection is the most widely used by authors who study the volatile compounds of Iberian ham, but the split injection mode has also been used although only by Narváez-Rivas *et al*. (2010a, 2010b). In accordance with a study made by Schomburg *et al*. (1983), high precision and accuracy of relative and absolute peak areas can be achieved with both the cold splitless and the cold on-column modes, and with the cold split mode technique the performance of quantitative analyses is also improved but a certain discrimination by volatility and a slightly increased standard deviation for the peak area data still cannot be avoided. However, split injection is required when a cold trap is not used between the desorption system and chromatographic column (Narváez-Rivas *et al*., 2010a, 2010b).

2.4. High-performance liquid chromatography (HPLC)

The volatile aldehydes from hams were studied during the ripening process by Antequera *et al*. (1992) using HPLC according to the method of Reindl and Stan (1982). These aldehydes produced during processing were converted into 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives prior to mixing the meat (5-10 g) with cold ethanol. After centrifugation under refrigeration (0 °C), the supernatant was distilled under vacuum (2.5-4 kPa) and this distillate was filled with a 2,4-DNP solution and mixed with n-hexane; the solvent was then removed using a rotary evaporator. The dry 2,4-DNP derivatives were dissolved in methanol and separated using reversed-phase HPLC (Supelcosil LC 18 column, 4.6 mm × 250 mm, 5 µm) with an isocratic elution of 1 ml/min. The eluent was acetonitrile:water:tetrahydrofuran (75:24:1) and the temperature in the column was 40 °C. A UV-Vis detector was used and the detection took place at 360 nm. The aldehydes identified during the maturation of Iberian hams were hexanal, heptanal, octanal, nonanal, 2-nonenal, 2,4-nonadienal and 2,4-decadienal, with the most abundant being hexanal and nonanal.

The use of this technique is not the most adequate since GC with any sample preparation technique is an easier method of analysis for these analytes. Thus, all of the cited aldehydes can be analyzed in an easy and rapid way by GC.

2.5. Identification and quantification

The compounds can be identified (i) by comparison with commercial reference compounds (Narváez-Rivas *et al*., 2010b; Sánchez-Peña *et al*., 2005; López *et al*., 1992; Narváez-Rivas *et al*., 2010a), (ii) by comparison of Kovats indices (Sabio *et al*., 1998; Ramírez and Cava, 2007; Carrapiso *et al*., 2002; Timón *et al*., 2002; Andrés *et al*., 2007; García *et al*., 1991; Jurado *et al*., 2009; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrés *et al*., 2002; Merkle and Larick, 1994; Andrade *et al*., 2009) with those described by other authors (Kondjoyan and Berdagué, 1996; Kerscher and Grosch, 1997; Rychlik *et al*., 1998; Reiners and Grosch, 1998; Kovats, 1965; Berdagué *et al*., 1991; Berdagué *et al*., 1993; Buscailhon *et al*.,

1993; Hinrichsen and Pedersen, 1995; Acree and Arn, 1997) and on the web at http://webbook.nist.gov/ (Ramírez and Cava, 2007), and (iii) by comparison of their mass spectra with those contained in libraries, such as NBS (National Bureau of Standards) (López *et al*., 1992), Wiley (Ramírez and Cava, 2007; Carrapiso *et al*., 2002; Narváez-Rivas *et al*., 2010b; Andrés *et al*., 2007; Timón *et al*., 1998; Jurado *et al*., 2009; Narváez-Rivas *et al*., 2010a; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrés *et al*., 2002), NIST/EPA/NIH (Carrapiso et al., 2002; Narváez-Rivas et al., 2010b; Timón *et al*., 2002; Andrés *et al*., 2007; Timón *et al*., 1998; Jurado *et al*., 2009; Narváez-Rivas *et al*., 2010a; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrés et al., 2002; Andrade *et al*., 2009) and MassLab v.1.3. (Sánchez-Peña *et al*., 2005).

The mass spectra have been obtained by electronic impact at 70 eV, with a multiplier voltage of 1756 V (Timón *et al*., 2002; Andrés *et al*., 2007; Timón *et al*., 1998; Timón *et al*., 2001; Ruiz *et al.,* 2001; Andrés *et al*., 2002), 1675 V (Carrapiso *et al*., 2002) or 1650 V (Ramírez and Cava, 2007; Andrade *et al.,* 2009) and a collected data rate of 1 scan s-1 over the m/z range of 30 to 500. The transfer line to the MS is held at high temperatures at 150 °C (Narváez-Rivas et al., 2010a, 2010b), 200 °C (Timón *et al*., 2001), 210 °C (Carrapiso *et al*., 2002) or 280 °C (Timón *et al*., 2002).

The quantification of volatiles can be done with a mass selective detector (MS) or a flame ionization detector (FID) (Sánchez-Peña *et al*., 2005), using an internal or external (Sánchez-Peña *et al*., 2005) standard and calculating the different response factors for each compound with respect to the standard. The peak area of the analyte is used as an analytical signal. In addition, the quantification of individual volatile compounds has been carried out by evaluating the corresponding relative percentages according to the area normalization method (Narváez-Rivas *et al*., 2010a, 2010b; García *et al*., 1991; Ruiz *et al*., 2001).

GC-sniffing/olfactometry has been employed to determine the odor and the sensory characterization of volatile compounds. In table 2, the sensory attributes

Table 2
Odor-active volatile compounds of dry-cured Iberian hams and their sensory attributes

Volatile compound	Sensory atribute	Reference
Hexane	Spicy	3
	Alkane	2
Heptane	Alkane	3, 2
	Sweet	3
Octane	Alkane	2, 3
	Sweet	3
Methyl benzene	Strong	2, 3
	Plastic, glue	3
Ethyl benzene	–	2
	Dry, glue, unpleasant	3
2-Propanone	–	2
	Fruity, apple, pear	3
2-Butanone	Ethereal	2, 3
2,3-Butanodione	Buttery	2, 3, 4
	Vanilla/caramel-like	1, 3
	Sweet	1, 4
2-Pentanone+ 3-pentanone	Sweet	3
	Fruity, green	1, 3, 4
	Tropical fruit	1, 4
1-Penten-3-one	Rotten, sewer-like, fruity	1
3-Mercapto-2-pentanone	Cured ham, toasted	1
	Fruity, sewage-like, fatty	1, 4
2-Heptanone	Spicy, blue cheese	2, 3
	Acorn	3
	Nutty, dry-cured ham-like, toasted	4
2-Octanone	Fruity, green, floral, fresh	3
Octen-2-one	Green herbaceous	1
Octen-3-one	Spicy,	3
	Mushroom, dirty	1, 3, 4, 5
	Rust-like	4
	Dust	1

Volatile compound	Sensory atribute	Reference
2-Nonanone	Floral, fruity	3
	Blue cheese	2, 3
Propanal	Almond-like, green	4
2-Methyl propanal	Toasted	1, 4, 5
	Fruity	1
	Pungent	1, 4
	Alcoholic	5
	Nutty	4
2-Methylbutanal	Rancid, almond-like, toasted	1, 5
	Fruity	5
3-Methylbutanal	Acorn	3
	Nutty	2, 5
	Almond, toasted	1
	Cheesy, salty	2, 3
	Fruity	1, 3
	Pungent	5
	Malty	4
Pentanal	Nutty, toasted	1, 2, 4
	Fruity	1, 2
Hexanal	Rancid	2
	Fatty	3
	Fruity	1, 5
	Acorn	1, 4
	Green	1, 2, 3, 4
	Grassy	2, 3, 5
Heptanal	Oily	2, 3
	Toasted	1, 2
	Fruity	1, 2, 4
	Sewage	1, 4
	Cured ham-like	1, 2, 3
	Fatty	1, 2, 3, 4
2-hexenal	Fruity, strawberry	1, 4
	Olive oil-like	4
	Apple-like	1
3-hexenal	Green, acorn-like	1, 4
	Fruity	1
2-Heptenal	Green, fatty,	3
	Fried food-like	1
	Fruity, almond	1, 3
Octanal	Green, fresh	2, 3
	Meat	3
	Stew-like, boiled meat-like, rancid	1
	Grass, fruity	5
	Rancid, sewage, roasted	4
2-octenal	Leaves, pungent, fatty	3
	Rancid	1
	Tropical fruit-like	1, 4
	Fruity	1, 3, 4
Nonanal	Rancid, fatty	2, 3
2-Nonenal	Fatty, waxy	3
Decanal	Penetrating, Sweet, floral	2
	Citrus, waxy	2, 3
2,4-Decadienal	Fatty, rancid	3
Benzaldehído	Almond	2
	Bitter almond, penetrating	3

Volatile compound	Sensory atribute	Reference
Phenylacetaldehyde	Flower, solvent-like, fruity	5
Etanol	Alcohol	3
	Sweet	2, 3
2-Propanol	Buttery taste	2, 3
	Alcohol, dry	3
2-Methyl propanol	Wine, penetrating	3
Butanol	Medicinal	2, 3
	Fruity	3
2-Butanol	Wine	3
3-Methyl butanol	Green	2
	Wood, acorn, pleasant green	3
2-Methyl-3-buten-2-ol	Earthy	3
Pentanol	Pungent	3
	Strong, balsamic	2, 3
	Somewhat sweet	2
Hexanol	Fruity, green	2, 3
2-Heptanol	Oily, sweet	3
1-Octen-3-ol	Mushroom	2, 3, 4
	Earthy	1
	Dust	1, 3
	Rust-like	4
Octanol	Fatty	2
	Strong	3
	Acid	3, 2
Nonanol	Fatty, green	3
Limonene	Lemon, wood	2
	Citric, fresh	3
α-Pinene	Sharp, pine	3
2-Ethyl furane	Sweet	3
2-Penthyl furane	Green fruity	3
Butyl acetate	Fruit	3
Acetic acid	Sweat, acid	5
Propanoic acid	Sweat, acid, foot-like	5
Butanoic acid	Fatty	2
	Rancid	3
	Cheesy	3, 2
2-Methyl propanoic acid	Iron, fishy	3
3-Methyl butanoic acid	Foot-like, acid, spoiled ham	5
Pentanoic acid	Meaty, roasted, spoiled ham	5
Hexanoic acid	Fatty, cheesy, sweat	2
2-Methyl-3-furanothiol	Cured ham, toasted, nutty	1, 4
Methanethiol	Rotten eggs, meat or fish, cheesy	1, 5
2-Furfurylthiol	Rotten eggs, meat or fish, cheesy	1
Methional	Boiled meat, cured ham,	1
	Potato-like	1, 5
	Stew-like	5
Hydrogen sulfide	Boiled or rotten eggs, sewage	1
Dimethyl disulfide	Cauliflowers, vegetables	3
	Rotten, spoiled ham, burnt	5

Volatile compound	Sensory atribute	Reference
Dimethyl trisulfide	Rotten egg	1, 5
	Burnt	1
	Sewage-like	5
2-Acetyl-1-pyrroline	Overheated meat-like, cured ham	1
	Roasted	1, 4
	Nutty, popcorn	5
	Toasted	4, 5
2-Propionyl-1-pyrroline	Stew-like, boiled meat	1
	Rancid	1, 4
	Sewage, roasted	4
Ethyl butanoate	Fruity	5
Ethyl 2-methylpropanoate	Fruity	1, 4, 5
	Toasted	1, 4
	Pungent	1
	Strawberry-like	5
Ethyl 2-methylbutirate	Fruity	1, 5, 4
	Apple-like	1
	Strawberry-like	1, 5
	Olive oil-like	4

In references: 1: Carrapiso et al., 2002; 2: Sánchez-Peña et al., 2005; 3: García-González et al., 2008; 4: Carrapiso and García, 2004; 5: Carrapiso et al., 2010.

of volatiles from dry-cured Iberian ham are shown, including aldehydes, ketones and alcohols as the most abundant odor-active volatile compounds in this kind of product.

The method employed for the assignment of the odor potencies of the volatile compounds is as follow: during GC-olfatometry, assessors (experienced in sensory analysis and trained in GC-olfatometry) are asked to give a description of each perceived odor, its length and intensity, to aid in odorant identification (Carrapiso *et al*., 2002; García-González *et al*., 2008, Carrapiso and García, 2004; Carrapiso *et al.,* 2010).

According to Aparicio-Ruiz and Morales (1998), only a small percentage of volatiles are odor-active and their sensory characteristics can change with their concentration and possible synergy with other compounds from the matrix. The chemical knowledge of these attributes may help to establish the basis for a harmonized procedure of a sensory assessment of dry-cured hams (García-González *et al*., 2006).

Carrapiso *et al*. (2002) found that 28 volatiles are the most odor-active compounds in Iberian ham, including 11 aldehydes, 7 sulfur-containing compounds, 5 ketones, 2 nitrogen-containing compounds, 2 esters and an alcohol (see Table 2). Among them, the highest odor potencies were found for 2-methyl-3-furanthiol, 2-heptanone, 3-methylbutanal, methanethiol, hexanal, hydrogen sulfide, 1-penten-3-one, 2-methylpropanal, ethyl 2-methylbutyrate, and (E)-2-hexenal. Furthermore, they found that none of the numerous or abundant hydrocarbons (neither aliphatic nor aromatic hydrocarbons) reported in previous studies performed on dry-cured hams were potent odorants. It would be stood out that the presence of 2-propionyl-1-pyrroline in foodstuffs as an odorant seems to be infrequent, but this could due to its co-elution with octanal.

García-González *et al*. (2008) studied the relationship between 45 volatile compounds and 17 sensory attributes of dry-cured Iberian hams (see table 2). They determined the odor thresholds of the volatile compounds and their sensory characterization by dilution analysis. Six sensory attributes (acorn odor and flavor, rancid odor, rancid taste, fat rancid and fat pungent flavors) were explained by regression equations (adjusted $-R^2 \geqslant 0.70$) based on ten compounds: benzaldehyde, 2-heptanone, hexanal, hexanol, limonene, 3-methylbutanal, 3-methylbutanol, 2-nonanone, octanol, pentanol. Moreover, they found that the most noteworthy volatile compounds, in terms of basic contribution to the ham flavor matrix, are the following: Hexanal, 3-methylbutanal, limonene, hexanol, octanol and E-2-nonenal. The first two are in agreement with authors mentioned above (Carrapiso *et al*., 2002).

In the study carried out by Sánchez-Peña *et al*. (2005), the hams produced in Spain and France could be distinguished by 4 odor-active volatile compounds from semitendinosus muscle (2-butanone and 2-octanone) and the subcutaneous fat (methyl benzene and octanol). On the other hand, the volatile composition was influenced by the breed type (Iberian and White). Iberian hams were clearly characterized by the information from two volatile compounds: Octanol (from subcutaneous fat) and 3-methyl-1-butanol (from bicep femoris).

In 2004, the odorants from the inter-muscular fat of Iberian ham were characterized and compared with those of lean meat samples (Carrapiso and García, 2004). Sulfur-containing compounds (specifically hydrogen sulphide, methanethiol and 2-methyl-3-furanthiol) were clearly involved in the typical odor of lean meat samples but not in the inter-muscular

fat odor, and were probably the main compounds responsible for odor differences. However, certain aldehydes (propanal, 2-hexenal, 2-octenal), ketones (1-octen-3-one, 2-pentanone, 2,3-butanedione, 2-heptanone) and esters (ethyl 2-methylpropanoate, ethyl 2-methylbutanoate), as well as some unknown compounds, contributed to the overall observed differences. Propanal and 2,3-butanedione were found as odorants of inter-muscular fat but not of lean meat samples.

Carrapiso *et al*. (2010). made a study in which they characterized the most odor-active compounds of markedly bone tainted Iberian hams and compared them with those of unspoiled hams, finding that those with a putrid, strawberry-like odor or a putrid, yeast-like odor were compounds usually found in the unspoiled product and in other dry-cured hams, most being odorants of Iberian ham. Ethyl-2-methyl propanoate, phenylacetaldehyde and acetic, butanoic, 3-methylbutanoic and pentanoic acids were only found in the spoiled samples. In addition, they found several new odor-active compounds in Iberian ham, such as ethyl butanoate, phenylacetaldehyde and acetic, propanoic, 3-methyl-butanoic and pentanoic acids, all of which appeared only in the spoiled samples, with the exception of the first one.

As well as the factor related to the initial characteristics of the raw material, from an analytical point of view, the differences in composition of volatile compounds could be probably due to the isolation and enrichment method and of course to the sampling because it is important to note that ham is a solid, heterogeneous material and in this case, the differences in sampling contribute largely to the final results.

Other techniques that would be adequate in this kind of sample, such as two-dimensional GC, have not been employed in any case to a better purification and separation of volatile compounds.

3. VOLATILE COMPOUNDS

In Iberian dry-cured hams, a total of 411 volatile compounds have been identified using the different techniques explained above. These compounds were grouped into aldehydes, alcohols, ketones, esters and ethers, nitrogenous compounds, n-alkanes, aromatic and cyclic hydrocarbons, sulphur compounds, terpenes, lactones, carboxylic acids, chloride compounds and amides. They have been listed in several Tables (1.4-1.8) for better comprehension. Differences in results of the different authors are related to the various extraction techniques applied, and to other factors related to raw material (such as different feedings, anatomical locations, pig genotypes) or ripening conditions.

There are some studies which conclude that the amount of volatile compounds is higher in hams from pigs fed on "Montanera" than in hams from pigs fed on concentrate feeds ("Cebo") (Timón *et al*., 2002; López *et al*., 1992). The particular fatty acid composition of subcutaneous fat of "Montanera" hams causes these differences, since lipid oxidation gives rise to volatile compounds (García *et al*., 1991). However, despite the fact that the fatty acid profiles of hams from pigs fed on concentrate feeds and those from pigs fed on concentrate feeds but with α-tocopherol supplementation, the volatile content of the second group is situated between "Montanera" and "Cebo" hams (Timón *et al*., 2002). Therefore, these differences would be caused by α-tocopherol supplementation and antioxidant presence ("Montanera" and α-tocopherol supplementation) and could contribute to a high intensity and quality of aroma of hams (Timón *et al*., 2002; Cava *et al*., 1999). No significant differences have been found due to the sex of the animal (Ramírez and Cava, 2007).

Some authors have demonstrated that there are important differences among different types of dry-cured hams depending on the type of raw material and the technology used and that hams with longer processing times are richer in volatile compounds (Iberian and Corsican) (Sabio *et al*., 1998).

3.1. Hydrocarbons

This group is numerous, a total of 62 n-alkanes have been detected (Table 3). However, only 18 of them have been identified by several authors (Sabio *et al*., 1998;

Table 3
Volatile hydrocarbons previously reported in dry-cured Iberian ham

Aliphatic hydrocarbons	Nonadecane[10]
2-Methyl-2-butene[3,13]	Heneicosane[10]
Pentane[10,17,18]	Docosane[10]
2-Methylpentane[2,4,14,19]	Myrcene[8]
3-Methylpentane[2,19]	***Aromatic and cyclic hydrocarbons***
3-Ethylpentane[19]	Methyl cyclopentane[1,15,16,18]
4,4-Dimethyl-2-pentene[19]	Butyl cyclopentane[3,13]
1,3-Pentadiene[17]	Ethyl cyclopentane[15]
Hexane[1,4 ,6,9,12,14,17-19]	1,2,3,4-Tetramethyl-cyclopentane[3,13]
3-Methylhexane[3,13,15,19]	1,2-Diethyl-cyclobutane[3,13]

2,2,5-Trimethyl-hexane[3,13]	Benzene[15]
2,2,5,5-Tetramethyl-hexane[3,13]	Cycloalkene[16]
Heptane[1,2,4,6,9,11,12,15,17-19]	Methylbenzene (toluene) [1,3,4,5,6,9,12-18]
Methylene heptane[4]	1-Methylethylbenzene[17]
3-Methylheptane[14,15]	Ethyl benzene[1,6,8,12,14,18]
2,4-Dimethyl-heptane[3,5,13]	Ethenylbenzene[4,15]
2,4,6-Trimethyl-heptane[3,13]	Propylbenzene[3,9,13,15,17]
2,2,4,6,6-Pentamethyl-heptane[5]	Pentylbenzene[18]
Octane[1, 4,6,9,11,12,15,16]	2,4-Diphenyl-4-methyl-2(Z)pentene[16]
2,2,4,4-Tetramethyl-octane[5]	1,2-Dimethylbenzene (o-xylene)[1,3,5,8,13,15]
1-Octene[17,18]	1,3-Dimethylbenzene(m-xylene)[1-5,13,14-16,18]
4-Octene[15]	1,4-Dimethylbenzene(*p*-xylene) [3-5,8,13-16,18]
2-Octene[3,4,13-15,17]	Diethyl benzene[1]
1,3-Octadiene[15]	Ethyl toluene[1]
1,3,6-Octatriene[16]	Trimethyl benzene[1]
Nonane[3,4,9,8,13-15,18]	1,2,2-Trimethyl benzene[1]
2,6-Dimethyl-nonane[2]	1,2,3-Trimethyl benzene[3,8,13]
2,2,3-Trimethyl-nonane[3,13]	1,2,4-Trimethyl benzene[3,13,15]
5-(1-Methyl-propyl)-nonane[3,13]	1,3,5-Trimethyl benzene[3,5,13,15]
Decane[2,4,9,10,14-16,18]	1-Ethyl-2-methylbenzene[15]
2-Methyldecane[9]	1-Ethyl-4-methylbenzene[3,4,13-15]
5-Methyldecane[9]	5-Methyldodecane[9]
2,6,7-Trimethyl-decane[5]	2-Ethyl-1-dodecene[9]
2,3,5,8-Tetramethyl-decane[3,13]	1-Methyl-3-(1-methyl-ethyl)-benzene[3,13]
4-Methyl-1-decene[3,13]	1,3-Dimethyl-3ethyl-benzene[8]
Undecane[1,9,10,18]	3-Ethyl-1,2-dimethylbenzene[8]
3-Methyl-5-undecene[3,13]	4-Ethyl-1,2-dimethylbenzene[3,9,13]
4-Methyl-1-undecene[3,13]	3-Ethylfurane[12]
Methylundecane[10]	2-Butylfurane[13]
2,6-Dimethylundecane[2,3,5,13]	1,3,4,5-Tetramethylbenzene[9]
Dodecane[1,3,9,10,13,14,18]	1-Ethyl-1-methyl-cyclohexane[3,13]
1-Dodecene[9]	1-1'-Biphenyl[19]
2-Dodecene[9]	1,4-bis(1,1-dimethylethyl)benzene[19]
3-Dodecene[9]	Methylcyclohexane[19]
Methyldodecane[10]	2-Ethenylcyclohexane[3,4,13,14]
4-Methyldodecane[2]	Propylcyclohexane[15]
Cyclododecane[9]	Octyl-cyclohexane[3,13]
Tridecane[10,17,18]	Tetramethyl benzene[3,13]
6-Methyl-tridecane[5]	Heptylbenzene[3,13,17]
1-Ethyl-3,5-dimethylbenzene[9]	Nonylbenzene[17,18]
2-Ethyl-1,3-dimethyl-benzene[3,13]	2-Ethylfurane[13,15]
Tetradecane[9,10,14,17,18]	2-Pentylfurane[7,11-13,16-18]
1-Tetradecene[9]	2,3-Dihydrofurane[13]
2-Tetradecene[9]	4-Propyl-2-methylfurane[15]

3-Tetradecene[9]	2-Methyl-4,5-dihydrofurane[8]
Pentadecane[9,10,17,18]	2,2,4-Trimethyl-2,5-dihydrofurane[8]
5-Methyl-pentadecane[3,13]	2,5-Dimethyltetrahydrofurane[8]
Hexadecane[9,10,18]	Naphthalene[9,3]
1-Hexadecene[9]	Decahydro-naphthalene[3,13]
3-Hexadecene[9]	2-Methyl-decahydronaphthalene[3,13]
Heptadecane[9,10,18]	Germacrane B[3,13]
Octadecane[9,10]	Styrene[8,17-19]
1-Octadecene[9]	

In references: 1: Sabio *et al.,* 1998; 2: Ramírez and Cava, 2007; 3: Narváez-Rivas *et al.,* 2010b; 4: Timón *et al.,* 2002; 5: Narváez-Rivas *et al.,* 2011; 6: Sánchez-Peña *et al.,* 2005; 7: Andrés *et al.,* 2007; 8: López *et al.,* 1992; 9: Timón *et al.,* 1998; 10: García *et al.,* 1991; 11: Jurado *et al.,* 2009; 12: García-González *et al.,* 2008; 13: Narváez-Rivas *et al.,* 2010a; 14: Timón *et al.,* 2001; 15: Ruiz *et al.,* 1999; 16: Ruiz *et al.,* 1998a; 17: Ruiz *et al.,* 2001; 18: Andrés *et al.,* 2002; 19: Andrade *et al.,* 2009.

Ramírez and Cava, 2007; Narváez-Rivas *et al*., 2010a, 2010b; Timón *et al*., 2002; Sánchez-Peña *et al*., 2005; López *et al*., 1992; Timón et al., 1998; García *et al*., 1991; Jurado *et al*., 2009; García-González *et al*., 2008; Timón *et al*., 2001; Ruiz *et al*., 1999; Ruiz *et al*., 2001; Andrés *et al*., 2002; Andrade *et al*., 2009). They are pentane, 3-methyl pentane, 2-methyl pentane, hexane, 3-methyl hexane, octane, 2-octene, nonane, decane, undecene, 2,6-dimethylundecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane. In spite of being a large group, they are not potent odorants. (Carrapiso *et al*., 2002).

58 aromatic and cyclic hydrocarbons have been detected (Table 3). Seventeen of them: methyl cyclopentane, methyl benzene, ethyl benzene, propyl benzene, 1,2-dimethtylbenzene, 1,3-dimethylbenzene, p-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1-ethyl-4methylbenzene, 4-ethyl-1,2-dimethylbenzene, 2-ethenylcyclohexane, tetramethylbenzene, heptylbenzene, 2-pentylfurane and styrene have been detected by more than 3 authors [Sabio *et al*., 1998; Ramírez and Cava, 2007; Narváez-Rivas *et al*., 2010a, 2010b; Timón *et al*., 2002; Sánchez-Peña *et al*., 2005; Andrés *et al*., 2007; López *et al*., 1992; Timón *et al*., 1998; Jurado *et al*., 2009; García-González *et al*., 2008; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrés *et al*., 2002; Andrade *et al*., 2009).

Several authors (Ramírez and Cava, 2007; Toldrá, 1998; López *et al*., 1992; García *et al*., 1991; González and Ockerman, 2000; Martín *et al*., 2006) have reported that hydrocarbons are probably products derived from the oxidative decomposition of lipids, which may be catalyzed by hemocompounds such as hemoglobin and myoglobin.

The 2-pentylfurane content was studied by Andres et al. (2007) in hams processed according to a modified system, and significant differences were observed. This compound was highly concentrated in hams processed with a modified system (with lower temperatures at the drying stage). The salt level also affected the content of 2-pentylfurane at day 177, those hams with a higher salt content and lower content of this compound (Andrés *et al*., 2007).

The large quantities of branched alkanes found in the aged hams could potentially be interesting because very few branched hydrocarbons have been reported in studies of other cured meat volatiles (Berdagué *et al*., 1991; Gray and Pearson, 1984). As these molecules are also found in fresh meats (Shahidi *et al*., 1986), one possible source of them might be the unsaponifiable fraction from the feed of Iberian pigs (acorn and other vegetable products). These compounds have been used to discriminate hams according to the fattening system and five compounds (2,4-dimethyl-heptane, 2-octene, 2,2,5,5-tetramethyl-hexane, dodecane, 2,4,6-trimethyl-heptane and germacrane B) which show significant differences between hams from "Montanera" and "Cebo" (Narváez-Rivas *et al*., 2010b). On the other hand, the contents in 2,2,4,6,6-pentamethyl-heptane, m-xylene, 2,4-dimethyl-heptane, 6-methyl-tridecane, o-xylene and 2,6-dimethyl-undecane allow the differentiation of three fattening diets (Montanera, extensive cebo and intensive cebo), together with 1-metoxy-2-propanol, isopropyl alcohol, 3-ethyl-2,2-dimathyl-oxirane, 3-methyl-3-pentanol and limonene (Narváez-Rivas *et al*., 2011). At any rate, it is believed that saturated and unsaturated hydrocarbons do not play a significant role in the flavor of meat (Min *et al*., 1979).

Martín *et al*. (2006) suggested that methyl hydrocarbons could be synthesized by molds as a product of secondary degradation of triglycerides.

3.2. Aldehydes

A total of 41 aldehydes have been identified in the Iberian ham volatile compounds (see Table 4). These carbonyl compounds play an important role in the aroma of the dry-cured ham because they have a low perception threshold.

The important linear aldehydes which have been detected in several studies are: butanal, pentanal, hexanal, heptanal, 2-heptenal, 2,4-nonadienal, octanal, 2-octenal, nonanal, 2-nonenal, decanal, 2-decanal, 2,4-decadienal, 2-undecenal and dodecenal (Sabio *et al*., 1998; Ramírez and Cava, 2007; Carrapiso *et al*., 2002; Timón *et al*., 2002; Sánchez-Peña *et al*., 2005;

Table 4
Volatile aldehydes, ketones and alcohols previously reported in dry-cured Iberian ham

Aldehydes	3-Decen-2-one[9]
Acetaldehyde[1,11]	2-Decanone[14,18]
2-Methyl propanal[1,2,3,11, 16-18 ,19]	Dihydro-2(3H)-furanone[2,11,17]
Butanal[5,9,10, 14,18,16,19]	5-Ethyldihydro-2(3H)-furanone[2,11,13,16]
3-Methyl butanal[1,2,3,5,7,8,9-16,18, 19]	5-Butyldihydro-2(3H)-furanone[11,16]
2-Methyl butanal[1,2,3,5, 8,9-11,13-16,18, 19]	Dihydro-5-pentyl-2(3H)-furanone[16]
3-Methyl-2-butenal[4,5,14,17]	6,10-Dimethyl-(E)5,9-undecadien-2-one[16]
2-Methylbutenal[15,17]	2,6-bis(1,1-dimethyl)-2,5-cyclohexadiene-1,4-dione[16]
4-Methyl-2-pentenal[4]	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione[19]
2-Methyl-2-pentenal[4]	5-Methyl-2-(1-methyl-ethyl)-cyclopentanone[13]
Pentanal[1,2,3-5,7,9,10,11,13,14, 16,17,18]	Alcohols
Hexanal[1,2,3-8,9-18]	Ethanol[1,2,4,7,12,14,17,18,19]
2-Hexenal[3,4,13]	2-Etoxy-etanol[13]
3-Hexenal[3]	Propanol[17,18]
Heptanal[1,2,3-8,9-18]	2-Propanol[2,4-7,12-14,16]
2-Meptenal[2,3,5,12-15,17,18]	1,2-propanediol[17]
2,4-Heptadienal[13]	2-Methyl propanol[1,12,15,18,19]
1-Ethyl-2-methyl cyclopentane[1]	2-Methyl-2-propanol[19]
1-Ethyl-3-methyl cyclopentane[6]	2-Aminopropanol[17]
Methional[3,16]	1-Methoxy-2-propanol[6]
Benzaldehyde[1,4,7,9-12,15,16,18,19]	3-Ethoxy-1-propanol[17]
Ethylbenzaldehyde[19]	Butanol[7,12,13,17]
2,4-Nonadienal[1,5,14]	2-Butanol[12]
Octanal[1,2,3-8,9,11-18]	2-Methyl-3-buten-2-ol[1]
2-Octenal[1,3,5,12-14,18]	1-Penten-3-ol[1,2,13-15,17,18]
2,4-Octadienal[5,14]	1-Pentanol[1,2,4-7,10-14,16-18,20]
Phenylacetaldehyde[1,2,4,5,9,11,14,16,18,19]	2-Pentanol[1,13]
Nonanal[1,2,4-8,9,10-14,16,17,18]	1,3-Butanediol[9]
2-Nonenal[1,5,10,12-14,16- 18]	2,3-Butanediol[9,11]
6-Nonenal[13]	1,4-Butanediol[20]
Decanal[1,2,4,7,9,10,12,14,16-18]	Tetradecan-1-ol[10,16]
2-Furaldehyde[4]	Hexadecanol[16]
2-Decenal[4,5,13,14,16-18]	3-Methyl butanol[1,2,4,7,9-12,14,18,19,20]
2,4-Nonadienal[9,18]	2-Methyl butanol[1,4,10,11,14,15,18-20]
2,4-Decadienal[9,10,12,13,16-18]	2-Methyl-2-butanol[19]
Undecanal[16]	2,3-Dimethyl-2-butanol[6]
2-Undecenal[5,14,16-18]	2-Methyl-3-buten-2-ol[12]
Dodecanal[4,9,14,16]	3-Methyl-3-buten-2-ol[14,15]
2-Dodecenal[4]	2-Methyl-1-pentanol[19]
Tetradecanal[18]	2-Methyl-2-pentanol[6,19]
Pentadecanal[16]	3-Methyl-3-pentanol[6]
Hexadecanal[10]	4-Methyl-2-pentanol[9]
Octadecenal[16,18]	1-Hexanol[1,2,4,7,9-15,18,20]
5-Ethylcyclopent-1-enecarboxaldehyde[13]	2-Hexen-1-ol[13]
Ketones	Ciclohexanol[18,19]
Propanone[1,2,5,7,11,12,14,17,18,19]	*cis*-3-hexen-1-ol[20]
2,3-Butanedione[1,3,7,10,12,18]	2-Methyl-3-hexanol[17]

Butanone[1,2,7,10,12,13,17,18,19]	3-Methyl-3-hexanol[19]
2-Pentanone[1,2,3-5,11-15,17,18,19]	2-Ethyl-1-hexanol[9,13]
3-Pentanone[12]	2-Butoxiethanol[10]
1-Hydroxy-2-propanone[9]	Heptan-1-ol[4,10,14,18]
3-Methylbutan-2-one[10]	2-Heptanol[1,2,12]
3-Hydroxy-2-butanone[2,9,10,17,18,19]	3-Methyl-4-heptanol[9]
3,3-Dimethyl-2-butanone[19]	4-Methyl-2-heptanol[19]
1-Penten-3-one[3,13]	5-Methylheptan-2-ol[20]
3-Penten-2-one[1,9]	Ethyl phenol[1]
Pentan-2,3-dione[5,10,14]	1-Heptenol[1]
4-Methyl-3-penten-2-one[9,19]	1-Octanol[4,7,11,12,14,16-18,20]
3-Methyl-2-pentanone[3,15,18,19]	2-Butyl-1-octanol[13]
3-Ethyl-cyclopentanone[13]	3,5-Octadien-2-ol[13]
Cyclopentanone[13]	1-Octen-3-ol[1,2,3,4,7,10-14,16-18,20]
3-Hexanone[1,9]	Nonanol[12]
2-Hexanone[1,2,5,14,15,17,18,19]	8-Methyl-1,8-nonanediol[19]
4-Hydroxy-4-methyl-2-pentanone[9]	4-Methyl-5-decanol[13]
Cyclohexanone[1,9,18,19]	1-Decanol[20]
4-Heptanone[1,9,17,18]	2-Decen-1-ol[13]
2-Heptanone[1,2,3,5,7,8,9-18]	1-Undecanol[14]
4-Methyl-2-heptanone[9,19]	Dodecanol[1,9,16,17,20]
3,5-Heptanedione[5,14]	4-Methylphenol[17]
5-Hydroxy-3-methyl-3-hexanone[9]	3-Methylphenol[15]
1-Octen-3-one[3]	2-Ethylphenol[13]
3-Octen-2-one[4,5,14]	3-Ethylphenol[15]
4-Octen-3-one[1,13]	Benzyl alcohol[16]
6-Octen-2-one[13]	Benzenemethanol[9,11,18]
6-Methyl-5-hepten-2-one[1,13,16]	4-Ethyl-1,3-benzenediol[19]
3-Methyloctan-3-one[10]	Phenylethanol[9-11,16,18,19]
2-Octanone[1,2,5,7,8,12-15,17,18]	BHT[10,16]
3-Octanone[5,12,15]	2,4-bis(1,1-dimethylethyl)phenol[19]
2,3-Octanedieone[2,5,14-17]	3-Ethyl-2,2-dimethyl-oxirane[6]
3,5-Octadien-2-one[5,13,14]	2-Hydroxymethyl-2,3,3,-trimethyl-oxirane[13]
8-Nonen-2-one[1,2]	Furfurylalcohol[20]
3-Nonen-2-one[9]	Diethylenglycol[18]
2-Nonanone[1,2,7,12-14,16-18]	

In references: 1: Sabio *et al.,* 1998; 2: Ramírez and Cava, 2007; 3: Carrapiso *et al.,* 2002; 4: Narváez-Rivas *et al.,* 2010b; 5: Timón *et al.,* 2002; 6: Narváez-Rivas *et al.,* 2011; 7: Sánchez-Peña *et al.,* 2005; 8: Andrés *et al.,* 2007; 9: Timón *et al.,* 1998; 10: García *et al.,* 1991; 11: Jurado *et al.,* 2009; 12: García-González *et al.,* 2008; 13: Narváez-Rivas *et al.,* 2010a; 14: Timón *et al.,* 2001; 15: Ruiz *et al.,* 1999; 16: Ruiz *et al.,* 1998a; 17: Ruiz *et al.,* 2001; 18:Andrés *et al.,* 2002; 19: Andrade *et al.,* 2009, 20: López *et al.,* 1992.

Andrés *et al*., 2007; López *et al*., 1992; Timón *et al*., 1998; García *et al*., 1991; Jurado *et al*., 2009; García-González *et al*., 2008; Narváez-Rivas *et al*., 2010a; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrés *et al*., 2002; Andrade *et al*., 2009). These types of aldehydes come mainly from an oxidative degradation of the unsaturated fatty acids: oleic, linoleic, linolenic and arachidonic (Sabio *et al*., 1998; Frankel *et al*., 1981; Chan and Coxon, 1987).

On the other hand, the major formation pathway of the branched chain aldehydes seems to be the oxidative deamination-decarboxylation, probably via Strecker-degradation. The branched chain aldehydes detected in Iberian ham by numerous authors were: 2-methyl propanal, 3-methyl butanal, 3-methyl-2-butenal, benzaldehyde and phenylacetaldehide (Sabio *et al*., 1998; Ramírez and Cava, 2007; Carrapiso *et al*., 2002; Timón *et al*., 2002; Sánchez-Peña *et al*., 2005; Andrés *et al*., 2007; López *et al*., 1992; Timón *et al*., 1998; García *et al*., 1991; Jurado *et al*., 2009; García-González *et al*., 2008; Timón *et al*., 2001; Andrés *et al*., 2002; Andrade *et al*., 2009).

Hams from pigs fed on concentrate feeds with α-tocopherol supplementation present the lowest concentrations of aldehydes, since the most abundant aldehydes (hexanal and pentanal) are found in low quantities in these hams (Timón *et al*., 2002). These low concentrations could be due to the delayed formation of these aldehydes during maturation owing to the α-tocopherol action that would affect polyunsaturated fatty acids (PUFAs) (Timón *et al*., 2002; Mitsumoto *et al*., 1993). The antioxidant effect would be reduced by the largest percentages of PUFAs in the subcutaneous fat of "Montanera" hams, since these fatty acids are the most susceptible to oxidation (Wang *et al*,, 1996).

Hexanal, heptanal, octanal, nonanal, 3-methylbutanal, and 2-methylbutanal have been used to study the effect of salt content and processing condition during the ripening of Iberian ham (Andrés *et al*., 2007). Salt level did not significantly affect hexanal content at any of the samplings days. The type of processing significantly affected octanal and nonanal contents at day 163 (drying stage), and heptanal, octanal and nonanal contents at days 219 and 252 of processing. The type of processing has a significant effect in 2-methylbutanal content, those hams elaborated with lower temperatures at the drying stage showed lower levels on days 163 and 177 and higher levels on day 308. However, the 3-methylbutanal did not change with the type of processing. Moreover, the effect of salt level on the amount of these two aldehydes was also studied but no significant differences were found.

The pig genotype affects (E)-hepten-2-al and octanal (which adds pleasant notes to the aroma of dry-cured products), showing the highest contents in hams from ♂Iberian x ♀Duroc (this last genotype corresponding to pigs selected for the production of dry-cured meat products, with a high level of fattening) (Ramírez and Cava, 2007).

Ripening time had a marked effect on 2-methylpropanal and 2-methylbutanal, whose abundances increased throughout processing (Jurado *et al*., 2009), and a positive and significant correlation between 2-methylbutanal and cured flavor was found (Dumont and Ada, 1972). In the finished product, 3-methylbutanal was found to be the most abundant volatile compound (Jurado *et al*., 2009).

No significant effect of the feeding system on lipid oxidation aldehydes (such as hexanal, heptanal, octanal and nonanal) was found (Jurado *et al*., 2009). However, acetaldehyde, which has been identified as an odorant of Iberian ham, was affected by the feeding system, being more abundant in Cebo hams than in Montanera (Jurado *et al*., 2009).

Nonanal is the most important aldehyde derived from oleic acid (Grosch, 1987) and it is in higher concentrations in "montanera" hams than in "cebo" hams. Moreover, other alehydes like 2- and 3-methylbutanal, related to the aged flavor of hams (Chan and Coxon, 1987), present the highest contents in the "montanera" hams (Ruiz *et al.,* 2001). Although some authors have suggested a microbial origin for 3- and 2-methylbutanal, the Strecker degradation of leucine and isoleucine respectively appears to be the more probable source for these compounds in dry-cured ham (Andrés *et al*., 2007).

Perhaps these are the compounds that have a higher number of possible ways of formation. Linear chain aldehydes could be formed by the breakdown of hydroperoxydes derived from unsaturated fatty acids (Sabio *et al*., 1998; Sánchez-Peña *et al*., 2005; García *et al*., 1991; González and Ockerman, 2000). Other aldehydes found in ham probably have different origins, such as the products of lipid degradation (Ramírez and Cava, 2007; Toldrá, 1998; Sánchez-Peña *et al*., 2005; García *et al*., 1991; Timón *et al*., 2001; González and Ockerman, 2000), proteins and carbohydrates (López *et al*., 1992; García *et al*., 1991; González and Ockerman, 2000). According to several authors (Sabio *et al*., 1998; Ramírez and Cava, 2007; Sánchez-Peña *et al*., 2005; Andrés *et al*., 2007; López *et al*., 1992; García *et al*., 1991; Zhang and Pawliszyn, 1993; González and Ockerman, 2000; Martín *et al*., 2006; Grosch, 1987; Ventanas *et al*., 2007), the main route of formation for branched chain aldehydes, such as 2-methyl-butanal, 3-methyl-butanal and phenyl acetaldehyde, seems to be the oxidative deamination-decarboxylation of amino acids via Strecker degradation, suggesting that the Maillard reaction could be the principal vector by which these compounds are generated. In addition, some studies (Dumont and Ada, 1972; Martín *et al*., 2006) propose that microorganisms play an important role in the formation of these branched aldehydes, with microbial activity being other possible origin.

3.3. Ketones

Forty-eight ketones have been identified (see Table 4). But only 20 of them have been detected by the majority of authors (Sabio *et al*., 1998; Ramírez and Cava, 2007; Carrapiso *et al*., 2002; Timón *et al*., 2002; Sánchez-Peña *et al*., 2005; López *et al*., 1992; Timón *et al*., 1998; García *et al*., 1991; Jurado *et al*., 2009; García-González *et al*., 2008; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrés *et al.,* 2002; Andrade *et al*., 2009): propanone, 2,3-butanodione, butanone, 2-pentanone, 3-hidroxy-2-butanone, pentan 2,3-dione, 3-methyl-2-pentanone, 2-hexanone, cyclohexanone, 4-heptanone, 2-heptanone, 2-octanone, 3-octanone, 2,3-octanedione, 3,5-octadien-2-one, 2- nonanone, dihydro-2(3H)-furanone, 5-ethyldihydro-2(3H)-furanone.

The contents of 2-heptanone and 2-octanone were used to study the effect of processing type at different stages of ripening from dry-cured Iberian ham and it was observed that the processing system significantly affected the content of 2-heptanone and 2-octanone at day 219. Hams elaborated using a modified process (with lower temperatures at the drying stage) showed higher contents of these compounds than those processed under a traditional system. The origin of 2-heptanone and 2-octanone is the oxidation and decarboxilation of lipids (Berdagué *et al*., 1991).

1-Etoxy-heptan-2-one was affected by the genotype of animals, showing the highest contents hams from ♂Iberian x ♀Duroc, this last genotype corresponding to pigs selected for the production of dry-cured meat products, with a high level of fattening (Ramírez and Cava, 2007).

Ketones are basically present as methyl-ketones, which are products either of β-keto acid decarboxylation (Toldrá, 1998; Andrés *et al*., 2007; González and Ockerman, 2000) or of saturated fatty acid β-oxidation (Ramírez and Cava, 2007; Toldrá, 1998; Andrés *et al*., 2007; Timón *et al*., 2001; González and Ockerman, 2000). These compounds may also result from free fatty acid chemical oxidation (auto-oxidation) (Ramírez and Cava, 2007). In accordance with Sabio *et al*. (1998) and Sánchez-Peña *et al.* (2005), this last case occurs when the microbial population is small.

3.4. Alcohols

As can be observed, the major group was the alcohols from a quantitative point of view. A total of 66 different alcohols have been detected. Most of them have been previously detected by only 1 or 2 authors (Table 4). There are various alcohols: ethanol, 2-propenol, 1-penten-3-ol, 1-pentanol, 3-methyl-butanol, 1-hexanol, 1-heptanol, 2-heptanol, 1-octen-3-ol, dodecanol, phenylethanol and benzemethanol that have been identified in most of the articles (Ramírez and Cava, 2007; Timón *et al*., 2002; Sánchez-Peña *et al*., 2005; López *et al*., 1992; García *et al*., 1991; Jurado *et al*., 2009; García-González *et al*., 2008; Narváez-Rivas *et al*., 2010a; Timón *et al*., 2001; Ruiz *et al*., 2001; Andrés *et al*., 2002).

Usually, the aroma of these compounds is very pleasant, with fruity and floral notes. Their odor threshold value is usually higher than, for example, aldehydes so their influence in the aroma must be lower. However, unsaturated alcohols, such as 1-penten-3-ol and 1-octen-3-ol, each had a lower threshold value; they may play an important role in odor (Sabio *et al*., 1998). In particular, 2-propanol, the most abundant alcohol obtained, has been related to longer-ripened hams (Timón *et al*., 2001).

Pig genotype affects the content of hexan-1-ol, with hams from ♂Iberian x ♀Duroc showing the highest content (this last genotype corresponding to the pigs selected for the production of dry-cured meat products, with a high level of fattening) (Ramírez and Cava, 2007). 2-Methyl-1-butanol and benzene methanol were significantly affected by ripening time, being more abundant at the end of the process (Jurado *et al*., 2009). On the other hand, 1-octen-3-ol (which is an odor-active compound, was affected by the feeding system, being more abundant in "Montanera" hams (Jurado *et al*., 2009). As mentioned above, others alcohols (such as 1-methoxy-2-propanol, isopropyl alcohol and 3-methyl-3-pentanol) together with other compounds allow for the differentiation between Montanera, extensive cebo and intensive cebo feeding (Narváez-Rivas *et al*., 2011).

Linear alcohols are products of the oxidative decomposition of lipids, according to several authors (Ramírez and Cava, 2007; Toldrá, 1998; Sánchez-Peña *et al*., 2005; López *et al*., 1992; García *et al*., 1991). The branched alcohols may come from either a reduction in branched aldehydes (Martín *et al*., 2006) or a catabolism of amino acids (Dumont and Ada, 1972), such as phenylalanine, by means of Strecker degradation reactions (Ramírez and Cava, 2007; García *et al*., 1991; Timón *et al*., 2001). In accordance with Sánchez-Peña *et al*. (2005), microorganisms can act on 3-methyl butanal formed by the Strecker degradation of amino acids during proteolysis to give rise to 3-methyl-1-butanol. In addition, Sabio *et al*. (1998) told that a microbial activity could be involved.

3.5. Esters and ethers

While 51 ether and esters have been identified, only two esters have been detected by 3 authors at least, they are: ethyl-2-methyl butanoate, and ethyl-hexanoate (Sabio *et al*., 1998; López *et al*., 1992; Timón *et al*., 1998; García *et al*., 1991). The rest of the esters and ethers have been identified by only 1 or 2 authors (see Table 5).

Hexanoic acid-1-methylethyl ester and butanoic acid-1-methylethyl ester were affected by genotype, hams from ♂Iberian x ♀Duroc showing the highest contents (this last genotype corresponding to pigs selected for the production of dry-cured meat products, with a high level of fattening) (Ramírez and Cava, 2007). Hams from the genotype ♀Iberian x ♂Duroc showed the significantly highest content of butanoic acid-1-methylethyl ester (Ramírez and Cava, 2007). Moreover, 3-ethyl-2,2-dimethyl-oxirane together with other volatiles can differentiate between different fattening diets (Montanera, extensive cebo and intensive cebo) (Narváez-Rivas *et al*., 2011).

Probably, esters arise from the esterification of several alcohols and carboxylic acids (Sabio *et al*., 1998; Ramírez and Cava, 2007; Toldrá, 1998; López *et al*., 1992; García *et al*., 1991; Martín *et al*., 2006). There are authors (Ramírez and Cava, 2007) who do not rule out that the action of microorganisms is involved in the formation of esters. They have fruity notes, mainly those formed from short-chain acids. Esters with long-chain acids have a slight fatty odor.

3.6. Lactones

Although 8 lactones have been identified (see Table 5), only three of them have been detected by more than one author. These lactones are: γ-butyrolactone, γ-octalactone, γ-nonalactone and were observed by Andrés *et al*. (2007), López *et al*. (1992), Timón *et al*. (1998), García *et al*. (1991) and Andrés *et al*. (2002).

The influence of the processing system on the content of γ-octalactone was significant on days 163, 191(drying stage), 219 and 308 (cellar stage) (Andrés *et al*., 2007). The trends were similar to those of 2-pentylfuran: Higher amounts of γ-octalactone during the drying phase and initial days of the cellar stage

Table 5
Volatile esthers, ethers, lactones, terpenes, carboxylic acids and chloride, nitrogenous and sulphur compounds previously reported in dry-cured Iberian ham

Esthers and ethers	***Chloride compounds***
Ethyl acetate[1,19]	Dichloromethane[18,19]
Methyl carbamate[9]	Trichloromethane[11,19]
Linalyl acetate[9]	Trichloroethane[16]
Butyl acetate[13,16]	Tetrachloroethane[16]
Ethyl propanate[1]	2,2-Dichloroethanol[17]
2-Ethyl-hexyl-2-propenoate[5,14]	2-Chloronaphthalene[11]
2-Methyl propanoate[10]	Chloroform[10,17,18,20]
Ethyl 2-methyl propanoate[1,3]	***Nitrogenous compounds***
Ethyl 2-methyl butanoate[1,11,16]	*N*-Methylene ethenamine[1,16]
Methyl butanoate[16]	2-Nitrobutane[17]
Acetic acid ethyl ester[18]	2-Propionyl-1-pyrroline[3]
Acetic acid butyl ester[18]	2-Acetyl-1-pyrroline[3]
Butanoic acid methyl ester[18]	Pyrrol[1,14]
Butanoic acid 1-methylethyl ester[2]	Pyridine[2,19]
Hexanoic acid methyl ester[18]	Piperidine[14]
Ethyl 3-methyl butanoate[1,16]	Methane-1,1-(bis)-methylthio[16,18]
3-Methylbutyl acetate[16,19]	2-Ethenyl-pyridine[14]
1-Penten-3-ol acetate[1]	Dibutylamine[19]
2-Methylpropyl acetate[16]	3-Methylbutamine[10]
Methyl hexanoate[1,16]	Cyclobutylamine[6]
Ethyl hexanoate[1,9,11,14,16]	Phenylethylamine[9,19]
Ethyl-2-metylbutyrate[3]	4-Methylpentanenitrile[17]
Hexyl butyrate[9]	Hexanenitrile[1,14,16]
Propanoic acid, 2-methyl-1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester[20]	2,6-Dimethyl pyrazine[2,12,17,19]
Hexanoic acid 1-methylethyl ester[2]	3-Ethyl-2,6-dimethyl pyrazine[17]
1,2-Benzenedicarboxylic acid, dibutyl ester[20]	Trimethylpyrazine[2]
1,2-Benzenedicarboxylic acid, butyl 2-methylpropyl ester[20]	3,5-Dimethylisoxazole[16]
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester[20]	N,N-Dimethyl-2-buthoxi-Isopropylamine[14]
1,2-Benzenedicarboxylic acid, bis(2-methoxyethyl) ester[20]	Hexadecanonitrile[17]
1,4-Benzenedicarboxylic acid, dimethyl ester[20]	Acetamide[17]
1-Methoxy-pentane[14]	Propanodiamide[9]
Ethyl heptanoate[1]	Isovaleramide[9]
Ethyl octanoate[1,11]	***Sulphur compounds***
Propyloctanoate[17]	Dimethylsulphide[19]
Methyl decanoate[17]	Diphenylsulphide[19]
Ethyl decanoate[11,17]	Hidrogen sulphide[3]
Propyl decanoate[17]	Carbon disulphide[1,6,14,17,20]
Butyl decanoate[17]	Dimethyl disulphide[1,12-14,16-19,20]
Ethyl tetradecanoate[17]	Dimethyl trisulphide[1,3,16,17,20]
Pyrrol[1,14]	Dimethyl tetrasulphide[17]
Pyridine[2,19]	Diprophenyldisulphide[2,5]
Piperidine[14]	Methyl *n*-pentyl disulphide[1]

Ethyl hexadecanoate[11]	Methyl *n*-hexane disulphide[1]
Dimethyl phthalate[17]	3-Methylthio propanol[11,20]
Diethyl phthalate[17]	3-Methylthio propanal[2,5,12,20]
2-Ethoxyethoxy ethanol[11]	Methane-1,1-(bis)-methylthio[16,18]
Phthalic acid alkyl ester[11]	Benzothiazole[19]
Phthalic acid alkyl ester[11]	Ethanethioc acid, methyl ester[5]
Hexyl octyl ether[14]	2-Methyl-3-furanthiol[3]
Diethyl ether[19]	2-Furfurylthiol[3]
Eucalyptol[14]	Methanethiol[3,12,18,20]
Di-(3-methyl-buthyl)ether[14]	***Carboxylic acids***
2-D-2-pentadecyl-1,3-dioxolane[14]	Acetic acid[2,9,10,12,17-19]
Lactones	Propanoic acid[10]
γ-Butyrolactone[9,10,11,19]	2-Methylpropanoic acid[2,13,19]
γ-Valerolactone[11]	Butanoic acid[2,7,9,10,12-14,18,19]
γ-Hexalactone[11]	2-Methylbutanoic acid[2,10,17-19,20]
δ-Hexalactone[19]	3-Methylbutanoic acid[2,10,12,17-19]
β-Octalactone[18]	Pentanoic acid[9,10]
γ-Octalactone[8,11,19]	Hexanoic acid[2,7,9,10,18,19]
γ-Nonalactone[11,19]	2-Methylhexanoic acid[19,20]
γ-Lactone[17]	Isohexanoic acid[9]
Terpenes	Heptanoic acid[10,18,19]
Canphene[1]	Octanoic acid[2,9,10,18,19]
β-Phelandrene[1]	Isooctanoic acid[9]
3-Carene[1,17,19]	Benzoic acid[10]
4-Carene[4,14]	Nonanoic acid[10,18,19]
Limonene[1,2,4-7,10,13-17,19]	Decanoic acid[10,18,19]
Cineol[1]	Dodecanoic acid[10,18,19]
β-pinene[5,15,16]	Tetradecanoic acid[10]
α-pinene[13,5,16,17,19]	Pentadecanoic acid[11]
	4-Hydroxybenzenesulfonic acid[17]
	Benzenedicarboxylic acid[10]

In references: 1: Sabio *et al.,* 1998; 2: Ramírez and Cava, 2007; 3: Carrapiso *et al.,* 2002; 4: Narváez-Rivas *et al.,* 2010b; 5: Timón *et al.,* 2002; 6: Narváez-Rivas *et al.,* 2011; 7: Sánchez-Peña *et al.,* 2005; 8: Andrés *et al.,* 2007; 9: López *et al.,* 1992; 10: Timón *et al.,* 1998; 11: García *et al.,* 1991; 12: Jurado *et al.,* 2009; 13: García-González *et al.,* 2008; 14: Narváez-Rivas *et al.,* 2010a; 15: Timón *et al.,* 2001; 16: Ruiz *et al.,* 1999; 17: Ruiz *et al.,* 1998a; 18: Ruiz *et al.,* 2001; 19: Andrés *et al.,* 2002; 20: Andrade *et al.,* 2009.

and lower amounts in the final days of cellar. In modified and traditional systems, the effect of salt did not influence the content in γ-octalactone throughout the processing. Therefore, the type of processing did not affect the content of this compound (Andrés *et al*., 2007). γ-Octalactone may have different origins. The main origin of lactones is lipid oxidation (Slaughter, 1999), but Maillard reactions have also been proposed as a possible origin. Although their contribution to the aroma of these products has not yet been well established, in other products they show a great importance due to their aromatic notes described as fruity and very sweet, and their low olfaction threshold (Andrés *et al*., 2007; Duffose *et al*., 1994). According to Baines and Mlotkiewicz (1984), they would be related to buttery, oily, fatty, fruity and coconut-like flavors.

Lactones can be formed by lactonization (dehydration and cyclation) of hydroxyacids from fat, and also by oxidation of fatty acids and unsaturated aldehydes (García *et al*., 1991). Andrés *et al*. (2007) pointed out that the main origin of lactones is lipid oxidation, but the Maillard reaction is also proposed as a possible origin.

3.7. Terpenes

Eight terpenes have been found in Iberian ham (Table 5). 3-Carene, limonene, β-pinene, α-pinene are the compounds detected by several authors

(Sabio *et al*., 1998; Ramírez and Cava, 2007; Timón *et al.,* 1998; García-González *et al*., 2008; Timón *et al*., 2001; Andrés *et al*., 2002; Andrade *et al*., 2009).

The presence of limonene and other terpenes is usually described in hams because these compounds are normal constituents of the unsaponifiable fraction of vegetable fat. Thus, they come from the feed and they are accumulated in the animal's body (Sabio *et al*., 1998; Ramírez and Cava, 2007; Timón *et al*., 2002; Sánchez-Peña *et al*., 2005). In fact, limonene, together with others volatile compounds, allows for the differentiation between the three types of fattening diets (Montanera, extensive cebo and intensive cebo) (Narváez-Rivas *et al*., 2011).

Although it is generally accepted that hydrocarbons do not contribute significantly to flavor, some terpenes (xylene, pinene and limonene) present very particular aromas such as sweet, woody or lemony (Timón *et al*., 2002).

3.8. Nitrogenous compounds

Twenty-three nitrogenous compounds have been detected as volatile compounds in Iberian ham (see Table 5). n-Methylene ethenamine, pyrrol, pyridine, phenylethylamine, hexenenitrile, 2,6-dimethyl pyrazine, trimethylpirazine were detected by two author at least (Sabio *et al*., 1998; Ramírez and Cava, 2007; López *et al*., 1992; Andrés *et al.,* 2002; Andrade *et al*., 2009). The rest of nitrogenous compounds were detected by only one author.

2-Methylpyrazine has been affected by both ripening time and feeding system, so it could be used as indicator of both factors (Jurado *et al*., 2009).

Nitrile compounds have been detected in sausages (Stanhke, 1995) and nitrite-cured cooked pork (Mottram *et al*., 1984). The latter proposed their formation at the expense of the corresponding aldehydes during lipid oxidation involving nitrite. With respect to the volatile amines found, they are frequently cited as being of microbial origin in meat sausages (Dainty and Blom, 1995). However, amines can also originate from the decarboxylation of amino acids at a low pH, as occurs in cheese (Belitz and Grosch, 1986). They can also be formed during the pyrolysis of amino acids (MacLeod and Seyyedain-Ardebii, 1981), but the temperatures reached during processing are not high enough to allow for such reactions. An increase in volatile basic nitrogen during the ripening of Iberian hams has been described previously (Ventanas *et al*., 1992), and López *et al*. (1992) have detected an amine in Iberian ham volatiles.

These compounds, such as pyrazines, are compounds found in many meats and meat products prepared by cooking at high temperatures (Mussinan and Walradt, 1974). The high temperature promotes a reaction between diketo compounds and amino compounds, leading to pyrazine formation (Shibamoto and Bernhard, 1976). However, during dry-cured ham processing low temperatures are used, so it is likely that the formation of these compounds is favored by the dehydration process (Sabio *et al*., 1998). Martín et al. (2006) suggest that pyrazines are generated by the microbial population.

These compounds come from the breakdown of proteins, free amino acids and nucleic acids (Sabio *et al*., 1998; Ramírez and Cava, 2007; Dumont and Ada, 1972). The presence of an oxazole in ham is surprising, considering that they normally are found only in heated meat (Chan and Coxon, 1987), several oxazoles have been described as nutty, sweet, green, woody, musty and vegetable-like (Mottram *et al*., 1984).

Three amides have been identified: Acetamide (Andrade *et al*., 2009), propanediamide and isovaleramide (López *et al*., 1992).

3.9. Sulphur compounds

A total of 18 sulphur compounds were detected (Table 5), but only 5 of them are commonly find in Iberian ham. They are: carbon disulphide, dimethyl disulphide, dimethyl trisulphide, 3-methylthio propanal, methanethiol.

Dimethyl disulphide was affected by ripening time and was not detected until day 230 of the process (Jurado *et al*., 2009).

These compounds may be derived from the catabolism of amino acids that contain sulfur (Sabio *et al*., 1998; Ramírez and Cava, 2007), ribonucleotides (Dumont and Ada, 1972) or generated by the microbial population (Martín *et al*., 2006).

1,1 (Bis)methylthiomethane has been found in canned beef, and is associated with other carbonyl and sulfur compounds, with the off-flavor of this heated product (Person and Von Sydow, 1973). Its origin might involve reactions between hydrogen sulfide and such compounds as ribonucleotides, but these types of reactions have only been described in heated model systems (Stanhke, 1995).

3.10. Carboxylic acids

This group is formed by 21 different compounds (see Table 5). Nevertheless, 11 carboxylic acids have been identified in more than one work. They are: acetic acid, 2-methylpropanoic acid, butanoic acid, 2-methylbutanoic acid, 3-methylbutanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, dodecanoic acid b (Ramírez and Cava, 2007; Sánchez-Peña *et al*., 2005; López *et al*., 1992; Timón *et al*., 1998; Jurado *et al*., 2009; García-González *et al*., 2008; Narváez-Rivas *et al.,* 2010a; Ruiz *et al*., 2001; Andrés *et al*., 2002; Andrade *et al*., 2009).

3-Methyl-butanoic acid showed differences among batches, with the ♀Iberian x ♂Duroc (corresponding to animals selected for meat production) genotype showing the significantly highest content of this compound (Ramírez and Cava, 2007).

Ramírez and Cava (Ramírez and Cava, 2007) show that, generally, these compounds are generated by reactions of lipid oxidation. The origin of acetic acid in ham is not clear. According to some authors, this is originated from carbohydrate fermentation by

microorganisms (Kandler, 1983) and according to others from the Maillard reaction (Martín *et al*., 2006). Some branched acids have been identified in ham as a product of the microbial metabolism of amino acids (Ventanas *et al*., 2007). Other authors have attributed the origin of these compounds to the action of molds, like in the case of fermented meat products (Bruna *et al*., 2001). However, they could be also originated from the oxidation of their respective Strecker aldehydes, for example, 2-methyl butanal would come from the degradation of isoleucine amino acid and 2-methyl butanoic acid would be formed from oxidation (Ramírez and Cava, 2007).

3.11. Chloride compounds

Seven chloride compounds have been identified in Iberian ham (Table 5). Most of them have been detected by only one research group. Dichloromethane was detected by Ruiz *et al*. (2001) and Andrés *et al*. (2002). Chloroform is the compound of this group that has been identified in several articles (Timón *et al*., 1998; Ruiz *et al*., 2001; Andrade *et al*., 2009). The chloride compounds found have been related to pesticide residues in the feed (Flores *et al*., 1997), except Berdagué *et al*. (1991) who attributed them to laboratory contamination.

4. CONCLUSIONS

In summary, the volatile compounds from Iberian hams are affected by the following factors: rearing system, age of animal, genotype of pig and the conditions of the ripening process (salt content, length of process, processing conditions).

In this type of hams, the SPME and purge and trap techniques have been the most used to concentrate and isolate the volatiles. Then, these volatiles are analyzed by GC and detected by using a MS-detector, sniffing/olfactometry technique or a FID. Due to the different technique of isolation used, the volatile profile can change. In fact, the quantity of these compounds is very variable depending on the temperatures and times used in each phase of the isolation process. It would be very interesting to carry out new researches to establish the optimum parameters to obtain the best results for this kind of samples. Every aroma isolation task should be approached as a unique analysis.

It can be concluded that the origin of some compounds could come from lipolysis, chemical or enzymatic reactions, proteolysis, Strecker degradation and Maillard reaction. However, the origin of others is unknown. Thus, in order to know the processes by which the volatile compounds of dry-cured Iberian ham are generated, more research needs to be done using the same pieces during the dry-curing process.

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