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Chemical changes in volatile aldehydes and ketones from subcutaneous fat during ripening of Iberian dry-cured ham. Prediction of the curing time

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ABSTRACT

Changes in volatile aldehyde and ketone amounts from subcutaneous fat have been evaluated during the dry-curing process (987 days) of Iberian ham by purge & trap-gas chromatography–mass spectroscopy method, using the same hams for the first time. The subcutaneous adipose tissues of ten hams obtained from five Iberian pigs fed on acorns and pasture were sampled and analyzed periodically during whole processing time. Fifteen aldehydes and six ketones have been identified, all previously described except the 2,4-pentadienal that has been identified for the first time. A LDA was applied and the two discriminant functions were obtained using backward stepwise analysis retaining the variables: 4-octen-3-one, 2-methylbutanal, butanal, 2-decenal, 2-heptanone, decanal, 2,4-pentadienal, pentanal, hexanal, 2-butanone, octanal and 2-octanone. A complete separation between the three periods was obtained, indicating that the retained variables are powerful descriptors to characterize samples from these three dry-curing periods. The ratio between total aldehydes and ketones was used to predict the curing time.

1. Introduction

The Iberian dry-cured ham is an uncooked meat product with long taste and rich nutty flavor, whose production system has survived due to its highly demanded characteristics (Andersen, Oksbjerg, Young, & Therkildsen, 2005; Viera-Alcaide, Vicario, Graciani, & León-Camacho, 2007). The elaboration of this is a long process of ripening (about 2–3 years), therefore it is necessary to define analytical parameters able to attest its quality and typical traits. Its sensory quality (aroma, flavor and texture) depends on the ripening conditions (Andrés, Cava, Ventanas, Muriel, & Ruiz, 2007; Flores, Grimm, Toldrá, & Spanier, 1997; Ruiz, Ventanas, Cava, Andrés, & García, 1999) and factors that affect the raw meat characteristics, such as rearing system, mainly during the fattening period, age of animals and pig genotype (Dirinck, Van Opstaele, & Vandendriessche, 1997; Jurado, García, Timón, & Carrapiso, 2007; Narváez-Rivas, Pablos, Jurado, & León-Camacho, 2011; Narváez-Rivas, Vicario, Alcalde, & León-Camacho, 2010; Ramírez & Cava, 2007; Sabio, Vidal-Aragón, Bernalte, & Gata, 1998). During the dry-curing process, reaction of hydrolysis and oxidation take place and produce the degradation of the lipid fraction from adipose tissue (Coutron-Gambotti & Gandemer, 1999; López et al., 1992). On the one hand, hydrolysis mainly affects triacylglycerols and diacylglycerols and to a lesser extent monoacylglycerols and phospholipids (Narváez-Rivas, Vicario, Graciani Constante, & León-Camacho, 2007, 2008). On the other hand, oxidation affects the fatty acids, producing oxidized compounds that have a short life and being some volatiles responsible for the characteristic flavor of dry-cured ham (Antequera et al., 1992).

Previous works have been carried out to study the generation of volatile compounds in Iberian (Andrés, Cava, & Ruiz, 2002; Cava, Ruiz, Ventanas, & Antequera, 1999; Martín, Timón, Petrón, Ventanas, & Antequera, 2000), Serrano (Pérez-Juan, Flores, & Toldrá, 2006), Parma (Bolzoni, Barbieri, & Virgili, 1996; Hinrichsen & Andersen, 1994) and Chinese Jinhua (Huan, Zhou, Zhao, Xu, & Peng, 2005) hams, but the authors have not taken samples each month of process. In this last type of ham, the concentrations of sulphur compounds, pyrazines, aldehydes and carboxylic acids increased, while the concentrations of alcohols, ketones, alkanes, alkenes, aromatic and cyclic hydrocarbons decreased (Huan et al., 2005). In Parma ham, Bolzoni et al. (1996) examined the changes in the aromatic profile in order to identify distinctive signals for different maturing periods (6, 9, 12 months), finding that methyl esters, carbonyl compounds and alcohols were the most relevant signals and that the greatest discriminating power was ascribed to components such as 3-methylbutanal, ethyl esters and alcohols like 1-propanol, 1-butoxy-2-propanol and 2-butanol. The other study about this ham showed that flavor formation can be divided into two phases the first one (salting, drying and ripening) characterized by autoxidation and the second one (ripening and postripening)

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by secondary metabolism of microorganisms, especially aminoacid catabolism, in which methyl-branched aldehydes, secondary alcohols, methyl ketones, ethyl esters and dimethyl trisulphide were generated (Hinrichsen & Andersen, 1994). Pérez-Juan et al. (2006) studied how the generation of volatile compounds (7 and 12 months) was affected by the chemical composition of different dry-cured Serrano ham sections (shank, center, butt), and they found that the center section has the highest proportion of volatiles because of not only to the higher concentration of free amino acids but also to the oxidation of unsaturated fatty acids.

In the case of Iberian ham, the influence of processing conditions in the evolution of volatile aldehydes was study changing relative humidity and temperature (Martín et al., 2000). Temperature had a marked influence on the formation of these, especially during post-salting and drying, which could influence the sensory characteristics of the final products. In cellar stage, the formation of volatile aldehydes was lower probably due to the presence of antioxidant compounds. The effect of α-tocopheryl acetate supplementation and the extensive feeding (free-range reared on acorn and pasture) of pigs on these compounds during the maturation of Iberian ham have been also studied (Cava et al., 1999). Volatile aldehyde evolution was not affected by regime throughout ripening of hams, but both feeding regimes mentioned above significantly decreased the total and individual aldehydes at days 0, 210 and 700 in comparison with muscle samples from pigs fed on non-supplemented diet.

Several methods, such as headspace (Cava et al., 1999; Martín et al., 2000), dynamic headspace (Bolzoni et al., 1996), solid-phase microextraction (SPME) (Huan et al., 2005; Pérez-Juan et al., 2006), SPME coupled to a direct-extraction device (DED) (Andrés et al., 2002), and purge and trap techniques (Hinrichsen & Andersen, 1994), have been used to isolate the volatile compounds to study their evolution during dry-curing process. SPME-DED avoids sample handling, but the compounds cannot be quantified because the use of the internal standard method is not possible with this. Samples (between 3 and 30 g) were taken in all cases, except when SPME-DED is used, in different pieces of ham, one for each sampling. After extraction of volatile compounds, aromatic profiles were obtained by gas chromatography (GC) with flame ionization detection (FID) (Bolzoni et al., 1996; Hinrichsen & Andersen, 1994) and/or mass spectrometry (MS) (Andrés et al., 2002; Bolzoni et al., 1996; Cava et al., 1999; Hinrichsen & Andersen, 1994; Huan et al., 2005; Martín et al., 2000; Pérez-Juan et al., 2006).

In this work, changes in volatile aldehydes and ketones from subcutaneous fat were studied during the dry-curing process of Iberian ham, as first step in the investigation of aroma genesis. Understanding this could help to improve the product quality and optimize the duration of processing. Additionally, the determined volatile compounds have been used as chemical descriptors to differentiate the three dry-curing periods, which can be useful to get hams with similar quality. With this aim, several pattern recognition techniques have been applied. Principal component analysis (PCA) was applied to visualize possible data trends in the sample distribution as well as the discriminant power of the variables and linear discriminant analysis (LDA) was used to construct a suitable classification model and reduce the number of input variables. The present work is a continuation of the previous studies about the dry-curing process of Iberian ham, in which the sweaty fat and the polar and non-polar fractions of the subcutaneous fat were investigated (Narváez-Rivas, Gallardo, & León-Camacho, 2013a,b).

2. Material and methods

2.1. Chemicals and reagents

2-Butanone, butanal, 2-methylbutanal, 3-methylbutanal, pentanal, hexanal, 2-heptanone, heptanal, 2-hexenal, 2-octanone, octanal, 2-heptenal, 6-methyl-5-hepten-2-one, 2-nonanone, nonanal, 2-octenal, decanal, nonenal, 2-decenal and isoamyl butyrate were obtained from Sigma Aldrich Fluka (Steinheim, Germany). Standard solutions were prepared using fully deodorized edible oil as matrix. Concentrations were in the range 0.1–5.0 mg kg^{-1}.

2.2. Processing of hams and sampling

Ten hams (between 10.80 and 12.83 kg, mean of 11.69 kg) from the origin designation of "Los Pedroches" were obtained from five castrated Iberian pure 14-month-old pig males, fattened extensively with acorns and pastured for 90 days prior to slaughter, and were processed in an industry facility for 34 months. They are the same that those used in the previous works by Narváez-Rivas et al. (2013a,b). The stages and the number of days from the beginning of the processing were as follows: after the slaughter, hams were removed from the carcasses after 24 h refrigerated storage at 1 °C. Then they were placed in piles completely covered only with marine salt (they were not in contact with each other) at low temperature (1.0 °C) and high relative humidity (about 80%) for 12 days. After being washed to remove salt from the surface, the hams were hung at 3.0 °C and a relative humidity of 76% for 26 days, then at 4.0 °C and a relative humidity of 70% for 5 days. Next, they were kept at 6.0 °C and a relative humidity of 70% for 34 days and after this, they were kept at 7.0 °C and a relative humidity of 70% for 15 days. This postsalting period was completed by raising the temperature to 12 °C at a rate of 1 °C each 3 days and a relative humidity of 70%, until 95 days. Then, they were taken to a dryer at temperatures varying from 7 to 26 °C and a relative humidity ranging from 80% to 12% for 231 days. Next, the hams were left to mature during 689 days in a cellar at temperatures ranging from 7 to 25 °C and 16–82% relative humidity. The environmental conditions (temperature and relative humidity) were recorded continuously throughout the whole period of maturing.

A sample of each ham (about 1 g) was taken across of subcutaneous adipose tissue covering the biceps femoris muscle, without touching it, using a cylindrical stainless steel tool specially designed (Narváez-Rivas et al., 2007, 2008, 2013a), about once a month since the animal was slaughtered (raw sample) until the dry-cured process was finished (cured ham). Samples were stored at −25 °C until analysis was carried out the next day. Before analysis, the samples of subcutaneous fat coming from both hams of each animal were mixed and minced in order to increase the interface between this and the stripping gas during the concentration step.

2.3. Isolation and concentration of volatile compounds

The volatile compounds were isolated from 0.5 g of minced sample by the dynamic headspace technique and adsorbed on a Tenax trap, using a Purge and Trap (P&T) Concentrator apparatus, Tekmar velocity XPT (Thousand Oaks, CA, USA), based on the method described by Narváez-Rivas, Vicario, Alcalde, and León-Camacho (2010). The purge conditions were as follows: sample temperature, 45 °C; Tenax trap temperature, 35 °C; purge gas flow, 350 mL min^{-1} of nitrogen; purge time: 14 min.

After the purge time, the volatile compounds were desorbed by heating, the Tenax trap at 225 °C for 1 min, and sending the purge gas through a transfer line (kept at 150 °C) into the chromatograph injector.

2.4. Gas chromatography/mass spectrometry (GC/MS) analysis

The GC-ion-trap-MS analyses (Narváez-Rivas, Vicario, Alcalde, & León-Camacho, 2010) were performed using a Varian 3800 gas chromatograph coupled to a Saturno 2000 ion trap mass spectrometer (Varian, Palo Alto, CA, USA). The system was equipped with a 1079 injector operating in full scan mode from 50 to 600 amu at 1 scan/s for identification purpose. The column used was a Supelcowax-10 (SUPELCO, Bellefonte, PA, USA) fused silica capillary column (60 m