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Volatile compounds in low-acid fermented sausage "espetec" and sliced cooked pork shoulder subjected to high pressure processing. A comparison of dynamic headspace and solid-phase microextraction

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ABSTRACT

Two extraction techniques, dynamic headspace extraction (DHE) and solid-phase microextraction (SPME), were compared to assess the effect of high-pressure treatment (400 MPa, 10 min, 12 °C) on the volatile compounds of low-acid fermented sausage "espetec" and sliced cooked pork shoulder stored at 4 °C. DHE was more efficient at extracting low-boiling compounds such as ethanal, 2,3-butanedione and alcohols, while SPME extracted more efficiently a higher number of chemical families, especially fatty acids. The effect of pressurisation on the volatile fraction of "espetec" was better categorized by DHE, whereas SPME was more appropriate for cooked pork shoulder. The volatile fraction of "espetec" changed slightly after pressurisation, mainly showing a decrease in the levels of lipid-derived compounds, like linear alkanes, aldehydes, or 1-alcohols in pressurised samples. The volatile profile of cooked pork shoulder underwent substantial changes during refrigerated storage, mainly due to microbial metabolism, most of these changes being limited by HPP.

1. Introduction

Low-acid fermented sausages are much appreciated in Mediterranean countries because of their moderate sour taste. The manufacture of these products is based on the use of low temperatures (<12 °C) during ripening, thus avoiding an intense fermentation and a strong acid flavour (Sanz, Vila, Toldrá, & Flores, 1998). During manufacture, low-acid fermented sausages undergo a moderate pH decrease, therefore allowing microbial growth that can affect both shelf-life and safety.

Cooked pork shoulder, very similar to cooked ham, is also an appreciated meat product due to its delicate flavour. High pH and water activity values, as well as the lack of background microbiota competing with spoilage or pathogenic microorganisms, make this product highly perishable (Hugas, Garriga, & Monfort, 2002).

High pressure processing (HPP) is a non-thermal technology capable of inactivating/killing both spoilage and pathogenic microorganisms while retaining the characteristics of minimally processed foods. Within the meat products sector, HPP offers a valuable alternative to thermal pasteurization to be applied after product manufacture (Rastogi, Raghavarao, Balasubramaniam, Niranjan, & Knorr, 2007) thus avoiding post-processing contamination. The effect of HPP on the improvement of shelf-life and microbial safety as well as on the quality of both low-acid fermented sausages and cooked ham has been studied (Aymerich, Jofré, Garriga, & Hugas, 2005; Jofré, Garriga, & Aymerich, 2008; López-Caballero, Carballo, & Jiménez-Colmenero, 1999; Marcos, Aymerich, Monfort, & Garriga, 2008). Non-significant differences for some quality parameters such as lipid oxidation, colour or sensory properties were observed.

Volatile compounds released from foods are closely related to their aroma and can be used for both quality and safety assessment. Different techniques have been employed for the extraction of the volatile fraction of fermented sausages and cooked ham, including simultaneous distillation–extraction, SDE (Baloga, Reineccius, & Miller, 1990; Mateo & Zumalacárregui, 1996), dynamic headspace extraction, DHE, (Edwards, Ordóñez, Dainty, Hierro, & de la Hoz, 1999), or solid-phase microextraction, SPME, (Chiesa, Soncin, Biondi, Cattaneo, & Cantoni, 2006; Marco, Navarro, & Flores, 2004), among others. There is no ideal method for isolating volatile compounds from foods. Furthermore, every method has biases in extracting compounds (Reineccius, 2007), thus leading to different volatile profiles of the same product (Mallia, Fernández-García, & Bosset, 2005). For this reason, comparative studies may be necessary in order to select the technique providing a better understanding of the effect of any treatment on the volatile profile. Comparative studies have been performed in cooked beef extracted by DHE and SPME (Elmore, Papantoniou, & Mottram, 2001), dry-cured ham by SDE and SPME (Garcia-Esteban, Ansorena, Astiasaran, Martin, & Ruiz, 2004), marinated duck by

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DHE, SPME and SDE (Liu, Xu, & Zhou, 2007), goat meat by DHE, SPME and SDE (Madruga, Elmore, Dodson, & Mottram 2009), and pressurised ground beef by DHE and SPME (Rivas-Cañedo, Juez-Ojeda, Nuñez & Fernández-García, 2011a), showing large differences in the final profile depending on the extraction method.

The aim of this study was to compare two headspace extraction techniques, i.e. DHE and SPME, for the assessment of the effect of pressurisation (400 MPa, 10 min) on the volatile profile of "espetec" and cooked pork shoulder. These products have been selected as representatives of fermented meat products and cooked meat products.

2. Materials and methods

2.1. Samples and HPP

Both "espetec" and cooked pork shoulder were purchased at a local supermarket. At the laboratory, the casings were taken off and the sausages were cut into pieces (8-cm long), while the cooked pork shoulder was sliced (4-mm thick). Samples of each product (50 g each) were divided into three batches, wrapped in aluminium foil and vacuum-packed in two multilayer plastic bags (HT 3050, Cryovac Sealed Air Corporation, Milano, Italy). Six samples per product were immediately frozen at −35 °C (control batch). Another six samples per product were subjected the day after packing to HPP at 400 MPa for 10 min at 12 °C (come-up and come-down times were 90 s and 1 s, respectively) in a 100 L capacity discontinuous isostatic press (NC Hyperbaric, Burgos, Spain), held at 4 °C for 3 days and then frozen at −35 °C (pressurised-refrigerated batch). The last six samples per product, which were not HHP-treated, were held at 4 °C for the same period of time and then frozen at −35 °C (unpressurised-refrigerated batch).

2.2. Volatile compound analysis

Before analysis, samples were thawed overnight at 5 °C. Volatile compounds were extracted in triplicate, using DHE and SPME methods previously optimized for each meat product, and analyzed by gas chromatography-mass spectrometry (GC–MS), using a HP-MSD HP 5973 apparatus (Agilent, Palo Alto, USA).

2.2.1. Dynamic headspace extraction (DHE)

Five grams of "espetec" were homogenized in a mechanical grinder (IKA Labortechnik, Staufen, Germany) with 10 g of anhydrous sodium sulphate (Na_2SO_4) and 20 μl of an aqueous solution of 1500 mg/l cyclohexanone as internal standard (IS). Concerning cooked pork shoulder, 10 g of product were homogenized with 20 g of Na_2SO_4 and 20 μl of an aqueous solution of 250 mg/l camphor as IS. In the latter case, camphor was set as IS since cyclohexanone was found to interact with the volatile compounds of cooked pork shoulder. An aliquot of the mixture (3.5 g for "espetec" and 3.0 g for pork shoulder) was subjected to volatile extraction in an automatic dynamic headspace apparatus (Purge and Trap, HP 7695, Agilent), coupled to a GC–MS apparatus for 20 min at 45 °C using helium (45 ml/min) with 10 min of previous equilibration. Volatile compounds were concentrated in a Vocarb 4000™ trap (I trap; Tekmar, Manson, OH) maintained at 35 °C, with 4 min dry purge and directly desorbed during 2 min at 260 °C through a transfer line heated (200 °C) into the GC injection port (220 °C) with a split ratio of 20:1 and 1.4 ml/min helium flow. The Vocarb 4000 trap consists of a combination of 8.5 and 10 cm of Carbopack C/B, respectively, as well as of 6 and 1 cm of Carboxen 1000/1000, respectively.

2.2.2. Solid-phase microextraction (SPME)

Fifteen grams of "espetec" were homogenized with 5 g of Na_2SO_4 and 60 μl of an aqueous solution of 1500 mg/l cyclohexanone. For cooked pork shoulder, 15 g were homogenized with 15 g of Na_2SO_4 and 30 μl of an aqueous solution of 250 mg/l camphor. An aliquot of the mixture (10 g for "espetec" and 12 g of pork shoulder) was subjected to both equilibration and extraction of the volatile compounds (1 h each at 40 °C), as previously described (Rivas-Cañedo et al., 2011a). A 2 cm StableFlex Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) SPME coated fibre (Supelco, Bellefonte, PA, USA) was used for extracting the volatile compounds, followed by a desorption step in the GC port (260 °C, 10 min, splitless mode).

2.2.3. Gas chromatography–mass spectrometry

Chromatographic separation was carried out in a Zebron 100% polyethylene glycol capillary column (60 m long; 0.25 mm i.d; 0.50 μm film thickness; ZB-WAX plus, Phenomenex, Torrance, CA) with 1 ml/min helium flow. The injection port temperature was 220 °C for DHE and 260 °C for SPME analysis to ensure a complete desorption of the volatile compounds from the fibre. The temperature programme and the detection method are described in a previous work (Rivas-Cañedo et al., 2011a). Compound identification was carried out by the injection of commercial standards, by spectra comparison using the Wiley7Nist05 Library (Wiley & Sons Inc., Germany), and/or by calculation of linear retention indexes (LRI) relative to a series of alkanes (C_5–C_{20}). The sums of abundances of up to four characteristic ions per compound were used for semi-quantitative determination. The abundances have been referred to the IS (compound peak area multiplied by 10^3 and divided by the IS peak area).

2.3. Statistical analysis

Statistical analysis was performed with the SPSS Win 12.0 software (SPSS Inc., Chicago, IL). Sums of abundances by chemical families were calculated for each meat product, in order to make the results more manageable and ease comprehension.

Ion abundances of the volatile compounds detected in each product were subjected to analysis of variance (ANOVA) using extraction method and treatment as main effects. In a subsequent step, and due to the highly significant differences observed between extraction methods, the effect of treatment on the volatile profile of each product was studied by means of one-way ANOVA for each extraction method. Tukey's test was used for mean comparison. Statistical significance was assigned at $P < 0.05$.

3. Results

Table 1 lists the compounds detected in the volatile fraction of "espetec" and cooked pork shoulder, ordered by chemical family, together with their chromatographic indices, the ions used for semi-quantification, the method of extraction (ME) and its significance. A total number of 105 compounds were identified in the volatile fraction of "espetec", 76 and 92 of which were respectively extracted by DHE and SPME (Table 1). Sixty-three compounds were extracted by both methods. Concerning pork shoulder, a total number of 72 volatile compounds were detected, 52 of which were extracted by DHE and 65 by SPME. Forty-five compounds were extracted by both methods.

The technique had a significant effect on the extraction efficiency of most volatile compounds, i.e. 93 compounds in "espetec" and 59 compounds in cooked pork shoulder (Table 1). Figs. 1 and 2 show the relative percentages of the main chemical families present in "espetec" and cooked pork shoulder, respectively, remarking