Meat Science 93 (2013) 614–620

Contents lists available at SciVerse ScienceDirect

Meat Science

journal homepage: www.elsevier.com/locate/meatsci

Relationship between flavour deterioration and the volatile compound profile of semi-ripened sausage

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ARTICLE INFO

Article history:
Received 10 July 2012
Received in revised form 18 October 2012
Accepted 10 November 2012

Keywords:
Salami
Flavour
Odour
Acceptability
Volatile compounds
Shelf life

ABSTRACT

This study provides data on the relationship between flavour deterioration and the volatile compound profile of semi-ripened pork salami kept under retail conditions for up to 150 days. The flavour of salami deteriorated for 120 days, resulting in rancidity and a loss of acceptability. TBARS increased from 0.16 to 0.57 MDA/kg. The flavour changes during the shelf life of salami were monitored from changes in the volatile profile. The retailing time influenced ($p<0.05$) the level of 27 of the 30 headspace volatiles determined by SPME–GC/MS. Flavour deterioration was associated with the loss and/or degradation of volatiles resulting from spices and microbial activities, and the formation of volatiles from lipid oxidation. The levels of 2-heptenal and methyl esters of heptanoic, pentanoic and hexanoic acids were the best discriminators of storage time, and therefore seem to be promising as marker compounds of flavour deterioration and acceptability.

1. Introduction

Dry-cured fermented sausages, such as salami, are stable for long periods of time at retail due to their low water activity and the use of preservatives, colourings, flavourings, antioxidants and acidifying cultures. The shelf life of salami is mainly limited by the sensory deterioration that accompanies oxidation phenomena, since pathogenic or spoilage bacteria have difficulties to proliferate in dry-cured sausages (Ordóñez, Hierro, Bruna, & de la Hoz, 1999). Previous studies reported that flavour deterioration precedes other signs of sensory spoilage in whole semi-ripened salami pieces kept at retail. As storage time increases, a gradual alteration of flavour takes place in the salami, causing loss of acceptability (Lee, Lee, Son, Choi, & Lee, 2009; Rubio et al., 2008; Summo, Caponio, & Pasqualone, 2006). Rancidity has been identified as the main cause of flavour deterioration in dry-cured sausage (Morrissey, Sheehy, Galvin, Kerry, & Buckley, 1998), while the possible formation of other off-flavours, such as mouldy, acid, putrid or pungent traits, seems to play a minor role in the loss of eating quality (Bedia, 2012). In contrast, the red-purplish colour of dry-cured meat due to nitrous-myoglobin formation is very stable, although a certain discolouration has been reported in vacuum-packed salami slices at retail (Rubio et al., 2008; Zanardi, Dorigoni, Badiani, & Chizzolini, 2002).

The chemical pathways of flavour deterioration are complex and involve, on the one hand, the formation of compounds responsible for off-flavours and, on the other hand, the degradation of flavouring compounds from the mature meat seasoned with curing agents, pepper and other minor spices. Flavour will therefore correspond to the interaction between these two antagonist groups of aromatic compounds. Flavour changes during the storage of salami may be monitored through the volatile profile (Marco, Navarro, & Flores, 2008; Misharina, Andreenkov, & Vashchuk, 2001; Summo, Caponio, Pasqualone, & Gomes, 2011). The volatile compounds of sausage give an indication of the chemical and metabolic process that occurs during the display period. Several groups of volatile compounds have been reported in salami, such as aldehydes, ketones, alcohols, esters, alkanes and terpenes, among others. These volatiles can be grouped according to their possible origin, into volatiles from spices (terpenes and aliphatic sulphur compounds), lipid autooxidation (aldehydes, hydrocarbons, alcohols and ketones), microbial esterification (e.g. propyl acetate and ethyl propanoate), carbohydrate fermentation (e.g. 1,3-butanediol and phenyl acetaldehyde), amino acid catabolism (e.g. 2-methylbutanal, 2-methyl-1-butanol and 2,3-butanediol) and other origins (Andrade, Cordoba, Casado, Córdoba, & Rodríguez, 2010; Lorenzo, Montes, Purriños, & Franco, 2012; Meynier, Novelli, Chizzolini, Zanardi, & Gandemer, 1999; Olesen, Meyer, & Stahnke, 2004; Summo et al., 2011), although several of these volatiles may have more than one origin.

Rancidity in dry-cured sausage has been associated with the formation of aldehydes, ketones and carboxylic acids through lipid autooxidation, and, to a lesser extent, with the production

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http://dx.doi.org/10.1016/j.meatsci.2012.11.006

of free amino acids such as lysine, tyrosine or aspartic acid (Morrissey et al., 1998; Ordóñez et al., 1999). Lipid oxidation largely takes place by reaction with the oxygen occluded in the sausage, depending on fat composition and the balance between pro-oxidant and antioxidant agents. The oxidation reactions of salami can be inhibited by means of several strategies, such as using antioxidants or vacuum or protective gases during mincing, stuffing or packing; however, meat oxidation continues during storage at a rate that is dependent on the temperature and the presence of fluorescent lighting in the display case. Some types of low-size salami are retailed as aerobically packed pieces to preserve their typical mould covering. The pro-oxidizing conditions responsible for flavour deterioration will be not be the same in whole pieces, which are gradually dehydrating and which are less exposed to lighting than sausage slices. The objective of this study was to determine the relationships between flavour deterioration and the volatile profile in a semi-ripened salami retailed as whole pieces. The possibility of monitoring flavour deterioration and shelf life through changes in the volatile profile during storage was also evaluated.

2. Material and methods

2.1. Sausage manufacture and sampling

Three different batches of salami were manufactured by a local company (Elaborados Cárnicos de Lorca, Murcia, Spain) using the following recipe (g/kg): boned pork shoulder (880), water (44), sodium chloride (22), black and white pepper (10), dextrose, lactose and sucrose (20), dextrin (20), potassium nitrate (0.15) and sodium nitrite (0.15), sodium isoascorbate (0.5), sodium citrate (0.3) sodium glutamate (2.5) and Ponceau 4R red (0.2). The commercial mixture of additives and spices was provided by Cargill Texturizing Solutions (Barcelona, Spain). The meat was minced in an atmospheric mincer using a 6 mm plate (Laska GMBH, WW1302, Nu-Meat Technology, Girona, Spain). A commercial starter culture composed of (g per 100 g culture) *Pediococcus pentosaceus* (50), *Staphylococcus carnosus* (25) and *Staphylococcus xylosus* (25) was provided by Degussa Ferment's Aromatization SAS (La Ferté sous Jouarre, France). The lyophilised cultures were rehydrated (15 g in 200 mL chlorine-free water) for 4 h and then sown in the mass at a rate of 6×10^7 CFU/g.

The meat was then mixed with the starter cultures, additives and spices in an AMU102 vacuum mixer (Maquinaria Vall, Miralcamp, Lleida, Spain). The paste was stuffed into the casing on a WF-612 automatic line (Albert Handtmann Mahcinefabrik, Biberach an der Riss, Germany). Swine casing, slightly curved, 40–43 mm calibre and 300–320 mm in length, was used. The casing was previously desalted and washed with chlorinated-free water. The recently stuffed pieces were bathed in mould (*Penicilium chrysogenum* PS5.1, Cargill Texturizing Solutions Cultures SAS, La Ferté Sous Jouarre, France) solution (0.8 g/L water) and hung from steel racks 1.2 m wide, 1.2 m deep and 2.2 m high. The loading density on the trolleys was 19 kg/m^3. The trolleys were placed in an air-drying room (Sabroe S.A., Barcelona, Spain) set at 15 ± 1 °C during the whole drying stage. The relative humidity (RH) was gradually reduced after the first day at ambient humidity to eliminate water through dripping, 6 days at 80 ± 5% RH and 5 days at 70 ± 5% RH. The temperature and RH were verified using a P 650 thermohygrometer (Dostmann Electronic GmbH, Wertheim-Reicholzheim, Germany) with a precision of 0.2 °C and 0.5% RH. The average proximal composition (g per 100 g) of fresh-made sausage (day 0) was: moisture (33.3 ± 1.3), total protein (22.4 ± 0.5), total lipids (32.0 ± 0.6), and ash (5.1 ± 0.2). The average values of pH and water activity of fresh-made sausage were 5.1 ± 0.0 and 0.87 ± 0.02, respectively (Bedia, 2012). To study shelf life, the salamis were packaged in perforated (6 mm diameter) polypropylene BA-85 bags (Plásticos Sierra del Oro, Abarán, Murcia, Spain) and then stored at 10 ± 1 °C and 65 ± 0.2% R.H. for 0, 30, 60, 90, 120 and 150 days in an open display cabinet (Booster Group, Santiago, Chile) continuously illuminated with white fluorescent light (1000 lx), simulating retail display conditions.

2.2. Chemical analysis

Volatile compounds were extracted using solid-phase microextraction (SPME). A SPME device (Supelco, Bellefonte, PA, USA) containing a fused-silica fibre (10 mm length) coated with a 50/30 μm layer of DVD/CAR/PDMS was used. The fibre was conditioned prior to analysis by heating it in a gas chromatograph injection port at 270 °C for 60 min. Extraction was performed at 35 °C for 30 min. Before extraction, samples were equilibrated for 15 min at the temperature used for extraction. Once sampling was finished, the fibre was withdrawn into the needle and transferred to the injection port of the gas chromatograph–mass spectrometer (GC–MS) system. Volatiles were analyzed in duplicate in all the dry-cured sausages. Analyses were performed on a Hewlett-Packard 6890N Series GC gas chromatograph fitted with a HP 5973N mass spectrometer and a MSD Chemstation (Hewlett-Packard, Palo Alto, CA, USA). A split/splitless injection port, held at 260 °C, was used to thermally desorb the volatiles from the SPME fibre onto the front of the DB-624 capillary column (J&W scientific: 30 m × 0.25 mm id, 1.4 μm film thickness). The injection port was in splitless mode, the split valve opening after 2 min. Helium was used as a carrier gas with a linear velocity of 36 cm/s. The temperature programme was as follows: 40 °C, maintained for 2 min and then raised to 100 °C at 3 °C/min; then from 100 to 180 °C at 5 °C/min, and from 180 to 250 °C at 9 °C/min, with a final holding time of 5 min; total run time 50.8 min. The mass spectra were obtained using a mass selective detector working in electronic impact at 70 eV, with a multiplier voltage of 1953 V and collecting data at a rate of 6.34 scans/s over the range m/z 40–300. Compounds were identified by comparing their mass spectra with those contained in the NIST05 (National Institute of Standards and Technology, Gaithersburg) library and/or by calculation of the retention index relative to a series of standard alkanes (C_5–C_{19}) (for calculating Kovats indexes, Supelco 44585-U, Bellefonte, PA, USA) and matching them with data reported in the literature. The results are reported as relative abundance expressed as total area counts (AU × 10^6).

Lipid oxidation was determined as thiobarbituric acid reactive substances (TBARS) according to Botsoglou et al. (1994). To prepare the standard used, 73.2 mg 1,1,3,3-tetraethoxypropane (TEP) was diluted with 10 mL of 0.1 N HCl, immersed in a boiling water bath for 5 min, and quickly cooled under tap water. A stock solution of malondialdehyde (239 μg MDA/mL) was prepared by transferring the hydrolyzed 1,1,3,3-tetraethoxypropane (TEP) solution into a 100 mL volumetric flask and diluting with water. Working MDA solutions (2.39 μg/mL) were prepared by pipetting a 1 mL aliquot of the stock solution into another 100 mL volumetric flask and diluting to volume with water. Samples (2 g) were transferred to a 50 mL centrifuge tube, and volumes of 5% w/w aqueous trichloroacetic acid (TCA) (8 mL) and 0.8% butylated hydroxytoluene in hexane (5 mL) were successively added. The content of the tube was homogenized with a Silent Crusher for 1 min at high speed (9500 rpm) and centrifuged for 10 min at 3000 rpm. The top hexane layer was discarded. The bottom aqueous layer was made to a 10 mL volume with 5% TCA, and a 2.5 mL aliquot was pipetted into a screw-capped tube to which a volume 1.5 mL of 0.8% aqueous TBA was also added. Following incubation for 30 min at 70 °C, the tube was cooled under tap water; the reaction mixture was submitted to third-derivative spectrophotometry against blank reaction mixture. Aliquots of standard solutions were pipetted into screw-capped tubes and diluted to 2.5 mL volume with 5% TCA. A 1.5 mL volume of 0.8% TBA was added to each tube, and the reaction