VOLATILE COMPOUNDS DURING RIPENING IN ITALIAN DRIED SAUSAGE

L.O. Sunesen [a,*], V. Dorigoni [b], E. Zanardi [b], L. Stahnke [a]

[a] Department of Biotechnology, Technical University of Denmark, Building 221, DK-2800 Lyngby, DENMARK
[b] Istituto di Scienza e Tecnologia Degli Alimenti, Universitá di Parma,Via del Taglio 8, 43100 Parma, ITALY
* Corresponding author. Tel.: + 45 45 25 29 58, fax: + 45 45 88 49 22, E-mail: los@ibt.dtu.dk

Background

In dried sausages volatiles mainly derive from added seasoning, lipid autooxidation and microbial metabolism of lipids, proteins and carbohydrates. Therefore the sort and amount of volatiles are dependent on the type of meat, fat, salts and ingredients and the applied methods of cutting, stuffing, fermenting and ripening. In short, all choices during sausage production will directly or indirectly influence the profile of volatiles in the end product.

Also in sausages, the drawback of fundamental research is the uncertainty of its relevance in practice. The many and constantly changing parameters documented in sausages during fermentation and ripening may be understood individually and to some extent interactions can be predicted, but a comprehensive understanding of evolution of volatiles is still lacking. Studies of changes occurring over time can be of interest in both analysis of market products and fundamental research of sausage production. Several investigations of this kind have been published, and the area was recently reviewed (*Ordonez, Hierro, Bruna, & Hoz, 1999*). But the evolution of volatiles during processing of real sausages has only attracted little research. Studies have only been published on Chorizo (*Mateo & Zumalacárregui, 1996*) and French sausages (*Croizet, Denoyer, Tran, & Berdagué, 1992*).

Objectives

The purpose of the present work was to increase the knowledge of evolution of volatiles. Hereby evidence of changes occurring in real sausages is provided which in it self gives rise to new discussions of e.g. origins, but can also serve as yardstick when evaluating the degree of relevance of studies of model sausages or microorganisms in petri dishes.

Methods

Mould covered dried sausages from a commercial Northern Italian standard production were studied. The sausages consisted of 72 % meat from pig shoulders, 28 % streaky bacon, skimmed milk powder, nitrate, nitrite, ascorbic acid, spices including whole black pepper, white powdered pepper, garlic and the starter cultures *Lactobacillus curvatus* and *Micrococcus varians* (LM1, BITEC, Stuttgart). *Penicillium nalgiovense* (PNT1, Lacto Labo, France) was applied on the surface. Sausages were collected from the same batch at day 0, 4, 11, 18, 28 and 39 (finished sausages). Additionally, sausages from this batch were kept in standard cardboard packaging at 8 °C until day 50, corresponding to the normal time of distribution to retailers. Samples were stored at – 30 °C until analysis.

For studying differences in water content and pH between the core and edge of sausages, the outer 7 mm and a 20 mm in a diameter central tube were analysed separately.

Volatiles were extracted by a purge-and-trap method. A slurry of 60 g of minced sausage and 50 g of saline solution (100 g NaCl/l water) were divided into three purge flasks, and equilibrated for 30 min. at 42 °C in a water bath and finally purged at 42 °C for 30 min. The extracted volatiles were trapped onto 225 mg of Tenax TA (Chrompack, Denmark) in a stainless steel tube. For each day of sampling two samples from each sausage were analysed in triplicates. Five µl of a 1 % octane in methanol solution was used in triplicate at each day of analysis as external standard. Tenax tubes were thermally desorbed in a thermal desorber (ATD 400, Perkin Elmer, Denmark). Compounds were separated in a gas chromatograph (Hewlett-Packard, 5890, Denmark) equipped with a low polar DB1701 column (J & W Scientific, USA, length 30 m, internal diameter 0,25 mm, thickness of the phase1 µm). Characteristic ions were selected for each compound and used for quantification in octane equivalents.

Results and discussion

As shown in Table 1, core pH fell from initial 6.2 to 5.1 during processing, while pH in the sausage edge fell to 5.5 at day 39 and then rose slightly again. The higher pH level in the sausage edge was probably caused by fungal lactate catabolism and ammonia production.

A total of 68 volatile compounds were collected, identified and quantified by dynamic headspace sampling and GC/MS. The compounds belonged to classes of terpenes (12), aromatic hydrocarbons (10), alcohols (9), aldehydes (9), sulphur compounds (8), ketones (8), miscellaneous (8) and alkanes (4).

Pepper compounds were quantitatively the largest group of volatiles. They accounted for between 51 % and 81 % of the total count in ng octane equivalents, which is equivalent to other studies (*Meynier, Novelli, Chizzolini, Zanardi, & Gandemer, 1998*), (*Viallon, Berdagué, Montel, Talon, Martin, Kondjoyan, & Denoyer, 1996*). Large covariance was found between all pepper compounds, which support their common origin. All garlic compound concentrations increased during ripening. The most abundant compound allyl methylsulfide raised the first 11 days after which no large change occurred. The compounds ascribed to garlic are qualitatively in striking accordance with the aliphatic sulphur compounds found in an another Italian dry sausage (type Milano) (*Meynier et al., 1998*).

Volatile lipid oxidation products made up between 3 % and 18 % of the total amount of volatiles. The percentage of oxidation products was low when compared with similar studies (*Meynier et al., 1998; Viallon et al., 1996*). Generally concentrations of oxidation compounds rose successively through the ripening period, but samplings from day 39 were more oxidised than expected from the other samplings. Many aldehydes are products of lipid autooxidation, concentrations of aldehydes were on this ground expected and found to rise during ripening. These rises included marked fluctuations, but were generally in the order of a doubling. In

our study hexanal, which has a green odour (*Stahnke, 1994*), was at all times the most abundant aldehyde. Decanal was only detected after 28 days of processing, again indicating that oxidation intensifies toward the end of maturing. The most abundant alcohol 1-octen-3-ol, stemming from autooxidation, also increased during ripening. Its noteworthy, that 1-propanol and 2-heptanol, were not present in mince, but both compounds were found after fermentation. Propanol was earlier shown to be characteristic to this sausage when compared to three other European sausages (*Stahnke, Sunesen, & Smedt, 1999*). Propanol may arise from carbohydrate metabolism via propanal (*Halvarson, 1973*). Methyl ketones are products of microbial β-oxidation of saturated fatty acids followed by β-keto acid decarboxylation, (*Okumura & Kinsella, 1985*). Their amount increased markedly especially towards the end of ripening. As 4-heptanone was found only after 39 and 50 days of ripening and to our knowledge has not been ascribe to lipid autooxidation, this compound most likely originated alone from fungal β-oxidation of fatty acids.

Isoleucine and leucine are precursors of the important aroma compounds 2- and 3-methylbutanal and their corresponding alcohols and acids. Likewise phenylalanine is precursor for benzeneacetaldehyde. The four volatiles ascribed to amino acid catabolism in this study, all increased in concentration during ripening and also increased in relative abundance of the total amounts of volatiles.

Benzeneacetaldehyde increased impressively both during fermentation and ripening, moving from no presence to being the second most abundant, only topped by limonene. Benzeneacetaldehyde was lately thought to characterize this sausage when compared to three other sausages and to impart a hyacinth odour (*Stahnke, Sunesen, & Smedt, 1999*).

In Figure 1 the development during storage of three groups of volatile compounds are compared. Continuously n-aldehydes increased, but the concentrations were markedly higher at day 39 than at the other days of sampling and probably should be disregarded. The increases from day 28 to 39 are from 20-fold (pentanal) to 2-fold (octanal). Methylketones also increased during ripening especially toward the end of ripening. Increases in 2-heptanone and 2-nonanone concentrations were the main reason for the rise in methylketones. Surface moulds probably caused this late rise. Volatile products from amino acid catabolism increased mostly, primarily because of benzeneacetaldehyde, but the other catabolic products also increased successively.

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Table 1. pH and water content during sausage ripening

	pH		Water content (%)	
Day	Core [a]	Edge [b]	Core	Edge
0 (no starter)		n.d.		n.d.
0		6,2		60
4	5,6	5,6	57	54
11	5,2	5,5	55	44
18	5,5	5,8	51	38
28	5,1	5,6	51	32
39	5,1	5,5	43	30
50	5,1	5,6	41	29

[a] A 20 mm diameter tube. [b] The outer 7 mm..
n.d. = not determined.

Figure 1. Development of selected groups of volatile compounds during storage