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Food Chemistry 64 (1999) 461–465

Food Chemistry

Characterization of the headspace volatile compounds of selected Spanish dry fermented sausages

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Received 10 October 1997; received in revised form 16 February 1998; accepted 16 February 1998

Abstract

The volatile profile of three different Spanish dry fermented sausages ('salchichón', 'fuet' and 'chorizo') was studied using dynamic capillary gas–liquid chromatography/mass spectrometry (GC–MS) headspace analysis. Complex mixtures of esters, ketones, alcohols, aldehydes and terpenes characterized retail samples of each of these products. Esters were dominant components of the volatile compounds from one type of salchichón (salchichón 2), terpenes of the other type (salchichón 1) and of one type of fuet (fuet 2). Common to both types of fuet was a number of ketones and alcohols. 'Chorizo' had similar high numbers of esters as 'salchichón 2' but also had three sulphur-containing compounds which are known components of garlic and are used as an ingredient in chorizo.

1. Introduction

The production of dry fermented sausages is a major industry in Spain. Their annual production amounts to about 170000 metric tonnes, accounting for 18% of total meat products (MAPA, 1992). Many different varieties are made, with different geographical regions having distinct formulations. The most widely consumed types of dry fermented sausages throughout Spain are 'salchichón', 'chorizo' and 'fuet'.

'Salchichón' is a product manufactured from a mixture of chopped pork and/or beef, lard, curing agents (salt, nitrate, nitrite, sugar and ascorbates) and spices, of which the most usual is whole or ground black pepper (*Piper nigrum*). The product, after mixing and casing, is subjected to fermentation (20–24°C, 48 h, relative humidity 90–95%) and ripening (12–15°C) for about 1 to 8 months. This product has a minimum diameter of 20 mm although usually its diameter is greater than 30 mm. 'Fuet' is a similar product, with a diameter between 20 and 40 mm but it is fermented and ripened at 14–15°C and 80–85% relative humidity usually for a total time of 15–20 days. 'Chorizo' has a similar composition and diameter to 'salchichón', the major differences being the replacement of black pepper with garlic (*Allium sativum*) and paprika from the red pepper (*Capsicum annuum*). The ripening period may vary from about 15 days to several months.

Several papers dealing with microbiological changes (Sanz et al., 1988; Selgas et al., 1988; García et al., 1992) and biochemical aspects of protein (Lois et al., 1987; Astiasarán et al., 1990) and lipid (Lois et al., 1987; Lizárraga et al., 1989; Domínguez & Zumalacárregui, 1991; Chasco et al., 1992, 1993) breakdown during the ripening of Spanish dry fermented sausages have been published. However, less information is available about the volatile substances associated with these products, with just two studies dealing exclusively with aldehydes (Chasco et al., 1992; Chasco, 1993) 'chorizo' volatiles extracted using the Likens–Nickerson technique (Mateo and Zumalacárregui, 1996). The objectives of the present work were to characterize the main volatile compounds present in the above mentioned dry fermented sausage varieties and to establish a classification of dry fermented sausages based on the volatile pattern and source.

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0308-8146/99/$—see front matter
PII: S0308-8146(98)00066-1

2. Materials and methods

2.1. Samples

Five different samples, one brand of 'chorizo' and one each of two brands of 'salchichón' and 'fuet'(salchichón 1 and 2, fuet 1 and 2) were purchased from retail shops at different periods of the year. The estimated ripening times were, according to the information on the labels, more than 2 months for the 'chorizo' and 'salchichón 2' and less than 1 month for 'salchichón 1' and 'fuets 1 and 2'. In 'salchichón 2' and 'fuet 1', whole black pepper corns were visible on slicing, but there were not seen in 'fuet 2' and 'salchichón 1' in which, it was assumed, ground black pepper had been used. The 'chorizo' and both 'salchichones' had diameters of between 40 and 60 mm, the 'fuets' had diameters of about 25 mm.

2.2. Analytical procedure

The sausage samples were thinly sliced and casing material, and any obvious pepper corns, were removed. Of the remaining material, 25 g was coarsely ground and placed in a conical flask (500 ml), which was then fitted with a Dreschel bottle gassing head. The flask and contents were equilibrated at room temperature for 30 min with the gassing inlet sealed and the outlet fitted with a glass-lined stainless steel capillary trap (PST 20, SGE) packed with Tenax GC adsorbent polymer. The flask and contents were placed in a thermostatically controlled water bath at 29°C and volatiles were swept onto the Tenax trap using a helium flow of 20 ml min^{-1} for 30 min. For analysis, compounds were desorbed by heating at 250°C for 5 min in a Unijector assembly (SGE) and injecting on to a 50 m×0.3 mm fused silica capillary column (CpWax57CB, Chrompack), and cryofocused by immersing 15 cm of the column adjacent to the heater in a solid CO_2/acetone bath (–96°C). The bath was then removed and chromatography achieved by holding at 60°C for 5 min followed by a programmed rise to 190°C at 4°C min^{-1}. The column was fitted in the oven of a Carlo Erba model 4130 gas chromatograph with the oulet of the column fitting directly into the source of a Finnigan 4000 mass spectrometer, which was coupled to an Incos 2100 data system operating in the continuous scan mode. Compounds were identified by comparing their gas chromatography retention times and mass spectra with those of authentic compounds supplied by Polyscience and Fluka or, if the latter were not available, by comparing mass spectra with library spectra (Heller & Milne, 1978).

The total ion current (TIC) registered in the mass spectrometer for individual compounds was used as a semi-quantitative measure of the amount of the compound in the sample. Prior to each batch of samples being analysed, a series of injections of 2 ng ethyl hexanoate was made into the GC-MS under the conditions described and the TIC peak areas calculated. The multiplier voltage was adjusted so that the TIC area was ±10% of that obtained at the outset of the work. The TIC areas of the reported compounds were calculated using the data system and normalized to this value to enable comparisons to be made.

Results are the mean of three different samples from each type of dry fermented sausage.

3. Results and discussion

About 70 compounds comprising various mixtures of esters, ketones, alcohols, aldehydes, terpenes and sulphur-containing compounds were detected for each type of sausage (Table 1). Although there were some differences between each type of sausage, each type had a consistent pattern of volatiles allowing their differentiation. To facilitate comparisons between sausage types, average TICs for each compound in the different sausage types were used (Fig. 1).

To understand the formation of flavour in dry fermented sausages it is important to identity the origin of the volatile compounds. The flavour characteristics of dry sausages are thought to result from a combination of microbial activities, autooxidation processes and spices, whose relative importance varies from product to product. Several compounds (ethanol, 3-hydroxy-2-butanone, 2,3-butanedione and 2,3-butanediol) may be formed by fermentative microorganisms via glycolysis (Kandler, 1983). Likewise, the methyl-branched aldehydes may be produced by microorganisms, from the corresponding branched chain amino acids, i.e. L-leucine, L-valine and L-isoleucine, yielding 3-methyl butanal, 2-methyl propanal and 2-methyl butanal, respectively (Hinrichsen & Andersen, 1994). An alternative source could be Strecker-type degradation of the same amino acids. Ethyl esters are formed enzymatically from ethanol and carboxylic acids. The ability of microorganisms to form these compounds is well known (Hosono et al., 1974) and the importance of microorganisms for the production of ethyl esters in fermented sausages has been demonstrated (Stahnke, 1994). However, this action seems to need a relatively long ripening time, as may be deduced from Fig. 1, in which the esters were only detected in 'salchichón 2' and 'chorizo', which had ripening times longer than 2 months. A similar conclusion may be deduced for ester formation in Parma dry ham where microorganisms seem to be important for flavour development (Chizzolini et al., 1993; Hinrichsen & Pedersen, 1995). An increase in the ester levels was clearly observed after about 200 days of ripening (Hinrichsen & Pedersen, 1995). On the other hand, many of the identified aldehydes (Belitz & Grosch, 1987) and ketones (Berdagué et al., 1991; Stahnke,

Table 1
Volatile compounds detected in selected Spanish dry fermented sausagaes

No.	Compound	% of total ion current[a]					Previous identification[c]
		ID[b]	Chorizo	Salchichón 1	Salchichón 2	Fuet 1	Fuet 2	
1	Ethyl acetate	RT/MS	0.32	0.00	0.55	0.01	0.01	2, 3, 4, 5
2	Ethyl propanoate	RT/MS	1.26	0.00	0.74	0.01	0.01	2, 4, 5
3	Ethyl *n*-butanoate	RT/MS	28.88	0.39	16.92	0.01	0.01	2, 4, 5
4	Ethyl *n*-pentanoate	RT/MS	0.16	0.00	1.39	0.01	0.01	4, 5
5	Ethyl *n*-hexanoate	RT/MS	4.18	0.00	5.45	0.01	0.01	2, 5
6	Ethyl *n*-heptanoate	RT/MS	0.01	0.00	0.46	0.01	0.01	2
7	Ethyl *n*-octanoate	RT/MS	1.50	0.05	1.11	0.01	0.11	2, 4
8	Ethyl 2-methylpropanoate	MS	1.26	0.05	4.25	0.01	0.28	
9	Ethyl 2-methylbutanoate	RT/MS	1.66	0.00	2.50	0.01	0.28	4, 5
10	Ethyl 3-methylbutanoate	MS	7.26	0.05	8.32	0.28	1.02	4, 5
11	Ethyl lactate	RT/MS	9.00	0.00	9.06	0.01	0.01	
12	Isobutyl ethanoate	RT/MS	0.01	0.00	0.65	0.01	0.01	4
13	Isobutyl propanoate	RT/MS	0.01	0.68	2.13	0.42	0.23	
14	Unidentified ester	MS	0.01	0.00	0.18	0.01	0.01	
15	Isopentyl ethanoate	RT/MS	0.01	0.00	1.76	0.01	0.85	
16	Hexyl ethanoate	RT/MS	0.01	0.00	0.28	0.01	0.01	
17	2-Heptanone	RT/MS	1.50	0.00	1.20	8.28	5.43	1, 2, 3, 4
18	2-Octanone	RT/MS	0.01	0.05	0.01	0.28	0.01	1, 3
19	2-Nonanone	RT/MS	0.24	0.00	0.01	2.81	0.85	1, 4
20	3-Octanone	RT/MS	0.01	0.05	0.01	0.28	0.01	
21	4-Methyl-2-pentanone	RT/MS	0.01	0.00	0.01	0.28	0.23	1, 4
22	6-Methyl-5-hepten-2-one	RT/MS	0.01	0.15	0.46	0.42	0.23	3
23	2,3-Butanedione	RT/MS	0.79	0.10	0.92	2.95	1.36	3, 4, 5
24	2,3-Pentanedione	RT/MS	0.01	0.05	0.01	0.01	0.11	4
25	3-Hydroxy-2-butanone	RT/MS	1.26	0.10	1.85	30.44	17.94	2, 3, 4
26	2,3-Butanediol	RT/MS	0.01	0.00	1.39	10.80	3.62	2, 3, 4, 5
27	1,2-Butanediol	RT/MS	0.01	0.05	0.37	11.50	1.02	
28	*n*-Butanol	RT/MS	0.01	0.00	0.74	0.28	0.01	4
29	*n*-Pentanol	RT/MS	0.32	0.00	1.85	0.28	0.01	2, 3
30	*n*-Hexanol	RT/MS	5.52	0.24	6.75	0.56	0.28	2, 4
31	*n*-Heptanol	RT/MS	0.01	0.05	1.66	0.01	0.01	2
32	*n*-Octanol	RT/MS	0.01	0.05	0.55	0.14	0.01	
33	2-Methylpropanol	RT/MS	3.79	0.39	2.22	1.68	0.91	4, 5
34	2-Methylbutanol	RT/MS	0.63	0.10	1.39	1.12	0.01	
35	3-Methylbutanol	RT/MS	4.10	1.70	8.97	12.49	8.49	1, 2, 3, 4, 5
36	2-Butanol	RT/MS	0.01	0.00	0.01	0.98	0.23	4, 5
37	2-Ethylhexanol	RT/MS	0.01	0.00	0.46	0.14	0.01	
38	2-Octen-1-ol	MS	0.01	0.19	0.01	0.56	0.51	
39	1-Octen-3-ol	RT/MS	0.71	0.00	1.02	0.01	0.01	1, 2, 3, 4
40	3-Hexenol	RT/MS	6.63	0.00	0.01	0.01	0.01	
41	*n*-Pentanal	RT/MS	1.50	0.73	1.20	0.56	1.58	3, 4
42	*n*-Hexanal	RT/MS	1.26	12.71	3.24	2.10	3.79	1, 2, 3, 4, 5
43	*n*-Nonanal	RT/MS	0.01	0.00	0.37	0.01	0.01	1, 2, 3, 4
44	3-Methylbutanal	RT/MS	0.01	0.29	0.09	2.24	0.40	2, 3, 4, 5
45	2-Heptenal	RT/MS	0.01	0.29	0.18	0.01	0.06	2
46	Benzaldehyde	RT/MS	0.01	0.00	0.65	0.14	0.01	1, 5
47	Alpha-pinene	RT/MS	2.21	1.75	4.81	2.53	0.68	1, 2, 4
48	Beta-pinene	RT/MS	0.32	2.72	0.01	1.68	1.58	1, 2
49	3-Carene	RT/MS	0.01	5.05	0.01	0.01	4.30	1, 2
50	Unidentified terpene	MS	0.47	0.00	0.18	1.40	2.38	
51	Sabinene	RT/MS	0.08	16.98	0.01	0.28	0.01	1
52	Myrcene	RT/MS	0.01	14.07	0.09	0.01	13.13	1, 2
53	Alpha-phellandrene	RT/MS	0.01	3.11	0.01	0.01	1.81	1, 2
54	Unidentified terpene	MS	0.39	0.39	0.01	0.28	0.17	
55	Limonene	RT/MS	0.01	31.79	0.92	0.56	24.45	1, 2, 3
56	*p*-Cymene	RT/MS	0.01	1.65	0.28	0.28	0.01	4
57	Unidentified terpene	MS	0.01	0.19	0.01	0.01	0.34	
58	Unidentified terpene	MS	0.09	1.55	0.01	0.56	0.62	
59	Unidentified terpene	MS	0.01	2.14	0.28	0.01	0.57	
60	3,3′-Thiobis-1-propene	MS	3.95	0.00	0.01	0.01	0.01	2
61	Methyl-2-propenyl disulfide	MS	1.89	0.00	0.01	0.01	0.01	2, 5
62	Di-2-propenyl disulfide	RT/MS	6.63	0.00	0.01	0.01	0.01	2

[a] Percentage of total ion current. Each value is the mean of three different samples.
[b] RT/MS, identified by comparison with retention time and mass spectra of authentic reference substances; MS, identified by comparing mass spectra with library spectra (Heller and Milne, 1978).
[c] Previously identified in: 1, Berger et al. (1990); 2, Croizet et al. (1992); 3, Berdagué et al. (1993); 4, Stahnke (1994); 5, Mateo and Zumalacárregui (1996).

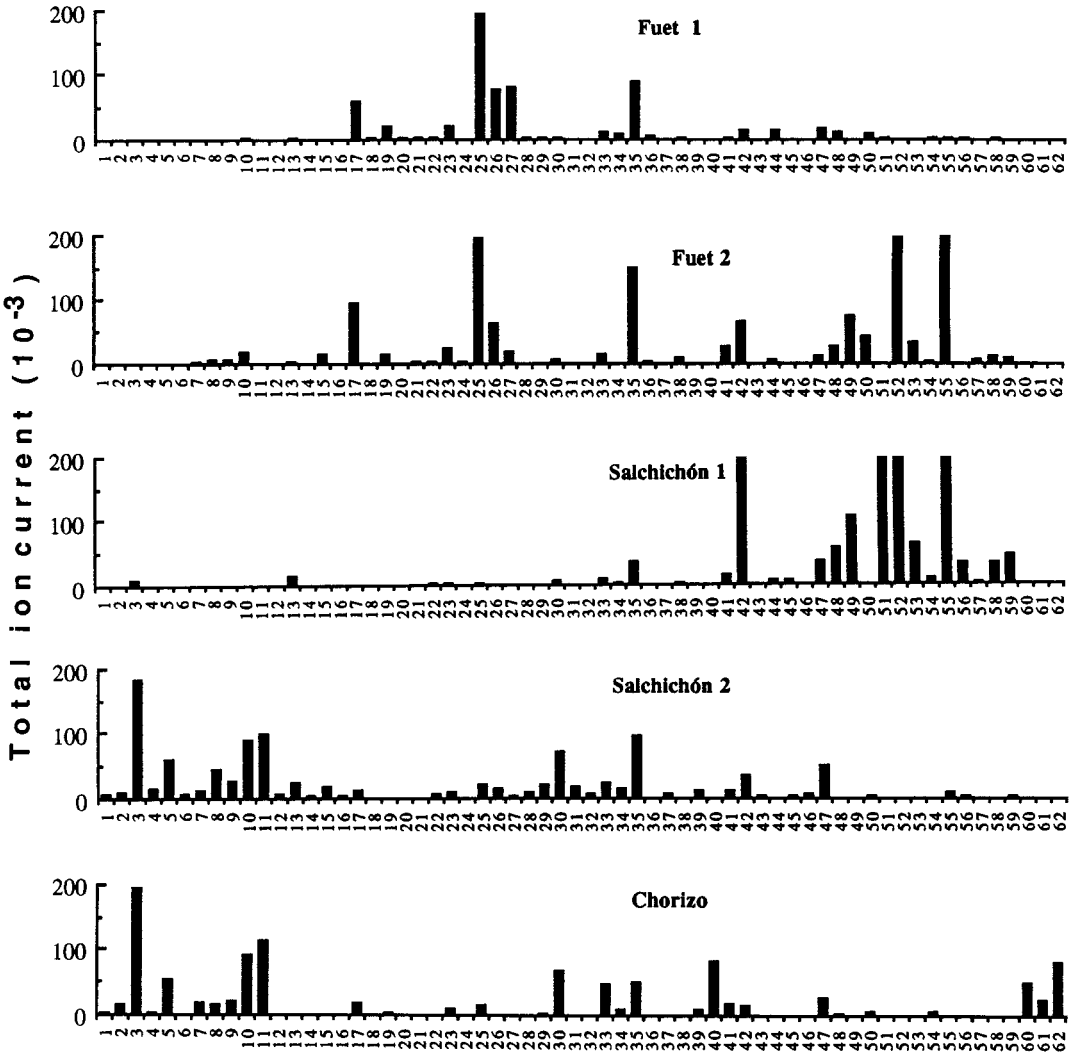

Fig. 1. Volatile profile of Spanish dry fermented sausage. Substance number corresponds with that of Table 1. Compounds 1–16, esters; 17–25, ketones; 26–40, alcohols; 41–46, aldehydes; 47–59, terpenes; 60–62 sulphur derivatives of propene. The following compounds achieved values over 200×10^3 total ion current: number 25 in fuet 1 (217); numbers 25, 52 and 55 in fuet 2 (317, 232 and 439, respectively); numbers 42, 51, 52 and 55 in salchichón 1 (262, 350, 290 and 655, respectively); number 3 in chorizo (366). Results are the mean of three different samples.

1994) can be formed by well-established pathways of oxidation of unsaturated lipid fatty acids. In addition, some of the ketones, and the corresponding secondary alcohols, may have originated from microbial β-oxidation of free fatty acids with subsequent deacylation to the β-keto acids, decarboxylation to the methyl ketone and reduction to secondary alcohols (Dartey & Kinsella, 1971). However, this pathway may be minor because it is characteristic of moulds, which are only present on the dry sausage surface. Finally, several of the identified volatile compounds, such as the terpenes, are well-established components of spices and the sulphur-containing compounds of garlic. The 3-hexenol exclusively detected in the 'chorizo' is possibly derived from paprika, of which it is one of the more abundant volatiles (Wu & Liou, 1986).

The most important feature of the volatile profiles shown in Fig. 1 is the possibility of grouping the different samples by ingredients used in their manufacture, ripening times and product diameter. The main difference between 'fuets 1 and 2' was in the levels of terpenes that dominated in 'fuet 2' and coincided with the use of ground black pepper rather than whole pepper corns as in 'fuet 1'. Furthermore, both 'fuets' presented a similar profile of ketones, alcohols and aldehydes and a lack of esters and sulphur-containing compounds. This pattern suggested that lipid autooxidation could be the main pathway for the generation of volatile compounds. This might be linked in 'fuet' to the thin diameter of the product, which would allow free diffusion of atmospheric oxygen throughout the sausage mass. 'Salchichónes 1 and 2' differed from the 'fuets' in the

absence, or low concentrations, of ketones and aldehydes, with the exception of hexanal. 'Salchichónes 1 and 2' had very different volatile patterns, with esters being the dominant volatile compounds of 'salchichón 2' and terpenes of 'salchichón 1'. The longer ripening time for 'salchichón 2' (2 months compared to 1 month for 'salchichón 1') is consistent with a higher level of the microbial activities, thought to be a major source of the esters, while the use of whole black pepper corns in 'salchichón 2' rather than the ground pepper used in 'salchichón 1' could account for the lower levels of terpene in the former.

The long ripening time for 'chorizo' may also be the explanation for its high content of esters, similar to 'salchichón 2'. The characteristic inclusion of garlic in 'chorizo' is the probable explanation for the presence of the three sulphur derivatives of propene (Table 1, peaks 60, 61 and 62). The well-established strong sensory properties of these compounds probably over-ride those of all of the other volatile compounds detected and give the product its characteristic flavour.

Acknowledgements

The authors gratefully acknowledge the financial support of the Comisión Interministerial de Ciencia y Tecnología (Projects ALI92-0461 and ALI96-0928). E. M. Hierro was the beneficiary of a predoctoral scholarship of the Universidad Complutense de Madrid.

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