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Volatile Components of Dry Cured Iberian Ham

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ABSTRACT

A study was conducted to identify the volatile compounds in aged Iberian hams, processed in the traditional way. The volatiles from aged hams were entrained in cold traps after distillation under high vacuum. The distillate was collected with dichloromethane and analysed by gas-chromatography–mass-spectrometry (GC–MS). Seventy-seven compounds were tentatively identified in the volatile fraction. Alkanes (12), branched alkanes (14), aldehydes (13), and aliphatic alcohols (9) dominated the volatiles. Small amounts of lactones (5), esters (9) and ketones (7) and other miscellaneous compounds were also present. The possible origins of these compounds and their relationship with the characteristic flavour of this product are discussed.

INTRODUCTION

The Iberian pig is a porcine breed of great economic importance in the south-western region of Spain. The Ministry of Agriculture, Fisheries and Food estimated that about 1 million hind legs from Iberian pigs are processed into cured hams each year (MAPA, 1984). Some Iberian hams (Montanchez, Jabugo, Guijuelo) have attained a high degree of consumer acceptance, due to their intense and characteristic flavour. For these hams, pigs are fattened in pastures, with acorn (*Quercus ilex* and *Quercus suber*) as their basic feed until they achieve a final weight of about 140 kg. Its

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processing has two definite steps: salting–postsalting and ripening. During the first period, salting and surface drying is combined with low temperature to reduce the risk of bacterial spoilage. Next, the hams are left to mature up to 14 months under environmental conditions (temperature ranges from 20 to 35°C).

Many investigators have studied the flavour components of fresh meats, but only a few reports dealing with flavour constituents of cured hams are available (Cross & Ziegler, 1965; Lillard & Ayres, 1969). Several authors have shown that the degradation products derived from proteins and lipid, increase during the ageing of Country-style hams (Ockerman *et al.*, 1961), Parma hams (Chizzolini *et al.*, 1984), French hams (Berdagué *et al.*, 1990) and Spanish hams (Flores *et al.*, 1988; Garcia Regueiro & Diaz, 1989; López-Bote *et al.*, 1990) and that these undoubtedly contribute to the flavour of these hams.

According to Piotrowski *et al.* (1970) the flavour compounds and flavour precursors of Country-style hams can be extracted with a mixture of chloroform–methanol to yield the total lipid fractions, indicating that cured ham odour components or precursors were essentially in the lipid phase. Due to the high level of fattening (8–10% of marbling fat), variations in cured Iberian ham flavour are attributed to the lipid composition of fat tissue and also to the degree of lipid breakdown during processing (Flores *et al.*, 1988; López-Bote *et al.*, 1990). Our study was centred on the organic (dichloromethane-soluble) fraction of the volatile compounds.

No systematic work on the flavour components of Iberian hams has been carried out until now. This paper reports an initial characterization of volatile compounds generated during the ripening process of Iberian ham.

MATERIALS AND METHODS

Processing of the hams

The study involved ten cured hams from the Iberian pig. After slaughter the hams were thoroughly rubbed with sea salt containing about 1% of nitrate and then were introduced into a pile of salt at 0–4°C for 15 days. Later, the hams were brushed to free them from salt left on their surface and were kept at 0–4°C for 62 days, and then were transferred to a chamber with increasing temperature and kept for 45 days until the average temperature reached 18°C. After this first period hams were left to mature for 14 months, first in a natural dryer (temperatures up to 30°C) and then in a cellar at a more constant temperature (16–20°C). The samples were taken from the *Biceps femoris* and *Semimembranosus* muscles of aged Iberian hams.

Isolation of volatiles

The samples were frozen and then homogenized with a blade homogenizer and 100 g of this mixture were transferred into a flask for the extraction of volatile compounds. The flask was connected to an ice-trap cooled with liquid nitrogen, according to Dumont & Ada (1976). The pressure was maintained at approximately 10^{-2} mbar for 5 h. After distillation, the traps were carefully washed with distilled water. The eluted fractions were mixed and extracted with 3×5 ml washes of distilled dichloromethane (Normapur-Prolabo). The resulting extract was concentrated with a Kuderna column (120 mm length), until approximately 254 μl, and then 0·5 μl was injected into the gas chromatograph.

Capillary gas-liquid chromatography–mass spectral (GC–MS) analysis

A Nermag R10-10C quadrupole automated GC–MS system directly coupled to a Girdel 31 gas chromatograph equipped with split–splitless injector was used.

Separation was performed with a J and W scientific fused silica capillary column (60 m × 0·32 mm i.d.), coated with SE54 (film thickness 1 μm). The carrier gas was helium (velocity 35 cm/s) and the oven temperature was programmed from 40°C to 240°C, at a rate of 3°C/min. Splitless injection was used, and Kovats indices (Kovats, 1965) were calculated and compared with available literature data. The mass spectra were measured by electron impact at 70 ev.

RESULTS AND DISCUSSION

A typical chromatogram obtained by plotting the total ion current observed during the GC–MS run is given (Fig. 1). In this chromatogram, a large number of individual peaks with molecular weights in the range from 84 to 310 were observed. Seventy-seven of these were identified either tentatively or their identity was confirmed (Table 1).

The list of all the compounds identified in the ham shows the following groups: alkanes (12), branched alkanes (14), aldehydes (13), ketones (7), aliphatic alcohols (9), esters (9), lactones (5) and other miscellaneous compounds.

Among these volatiles, the alkanes and the branched alkanes were present in the largest amounts, with their relative areas constituting 6·82% and 12·31% of the total area respectively. Hydrocarbons were probably derived from the oxidative decomposition of lipids, a reaction catalysed by haem

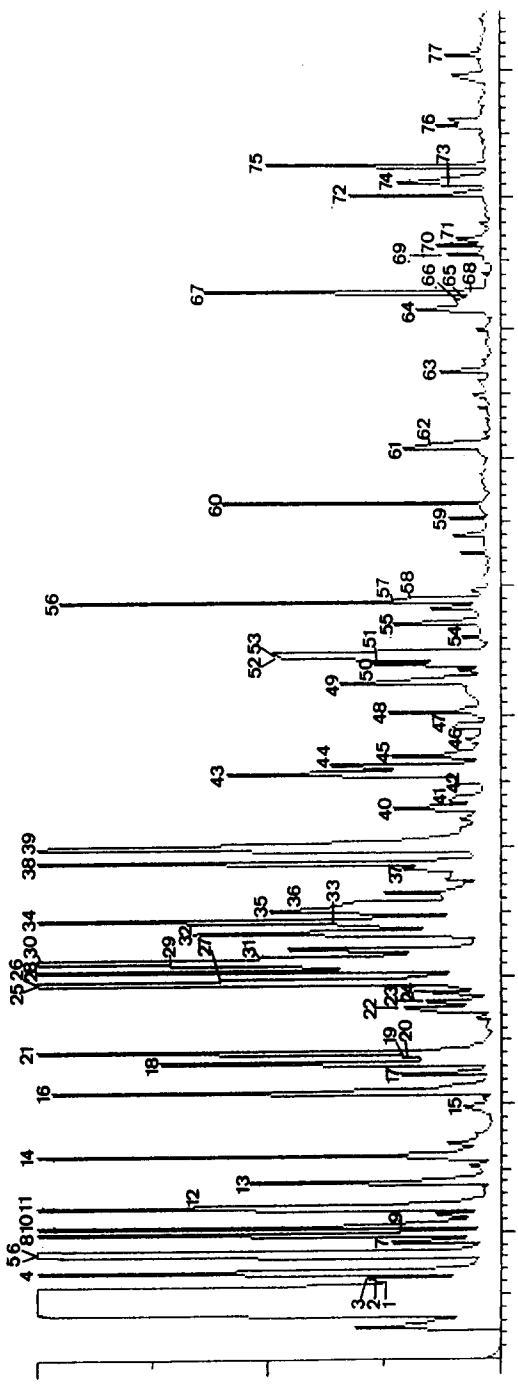

Fig. 1. Gas chromatogram of dry cured ham volatiles. The numbers mark such compounds identified. For more details, see Table 1 and Materials and Methods.

TABLE 1
Volatile Components of Dry Cured Ham 'Jamon Iberico'

No.[a]	*No.*[b]	*Name*	*Kovats index*[c]	*Reliability of ident.*[d]	*Rel. area*[e]	*f*
		Hydrocarbons: n-*alkanes*				
1	30	Decane	1 000	a	5·14	1
2	37	Undecane	1 100	a	0·18	1
3	44	Dodecane	1 200	a	0·20	1
4	50	Tridecane	1 300	a	0·16	1
5	58	Tetradecane	1 400	a	0·24	1
6	59	Pentadecane	1 500	a	0·19	1
7	62	Hexadecane	1 600	a	0·36	1
8	63	Heptadecane	1 700	a	0·14	1
9	66	Octadecane	1 800	a	0·03	1
10	71	Nonadecane	1 900	a	0·08	—
11	76	Heneicosane	2 100	a	0·04	—
12	77	Docosane	2 200	a	0·06	—
		Hydrocarbons: branched alkanes, alcenes				
13	23	Unidentified branched alkane	953	—	0·44	—
14	25	Unidentified branched alkane	976	—	3·15	—
15	28	Unidentified branched alkane	992	—	4·45	
16	32	Unidentified branched alkane	1 030	—	0·78	—
17	33	Unidentified branched alkane	1 039	—	0·91	—
18	36	Unidentified branched alcene	1 056	—	0·78	—
19	41	?Methylundecane	1 171	d	0·07	—
20	42	Unidentified branched alkane	1 185	—	0·09	—
21	46	Unidentified branched alkane	1 215	—	0·49	—
22	47	?Methyldodecane	1 250	d	0·20	—
23	52	Unidentified branched alkane	1 326	—	0·35	—
24	53	Unidentified branched alkane	1 332	—	0·33	—
25	54	Unidentified branched alkane	1 350	—	0·16	—
26	65	Unidentified branched alkane	1 791	—	0·11	—
		Aldehydes: aliphatic aromatics				
27	2	Butanal	—	c	—	1
28	5	3-Methylbutanal	—	c	3·66	1
29	6	2-Methylbutanal	—	c	1·14	1
30	8	Pentanal	—	c	1·08	1
31	14	Hexanal	797	a	17·06	1
32	18	Heptanal	897	a	0·84	1
33	34	Phenylacetaldehyde	1 044	b	1·88	1
34	38	Nonanal	1 107	a	2·77	1
35	40	(E)-2-nonenal	1 160	b	0·24	1
36	45	Decanal	1 205	a	0·33	1
37	49	(E-Z)-2,4-decadienal	1 298	b	0·67	1
38	51	(E-E)-2,4-decadienal	1 320	b	0·50	1
39	67	Hexadecanal	1 808	a	0·52	1

(*continued*)

TABLE 1—*contd.*

No.[a]	*No.*[b]	*Name*	*Kovats index*[c]	*Reliability of ident.*[d]	*Rel. area*[e]	*f*
		Ketones: aliphatics				
40	1	Butan-2,3-dione	—	c	—	1
41	3	Butan-2-one	—	c	—	1
42	7	3-Methylbutan-2-one	—	c	0·25	1
43	9	Pentan-2,3-dione	—	c	0·21	1
44	10	3-Hydroxybutan-2-one	704	c	1·83	1
45	17	Heptan-2-one	886	b	0·29	1
46	27	2-Methyloctan-3-one	990	c	0·16	—
		Aliphatic: alcohols				
47	11	3-Methylbutan-1-ol	729	c	2·24	1
48	12	2-Methylbutan-1-ol	733	b	1·00	—
49	13	Pentan-1-ol	762	b	1·33	1
50	16	Hexan-1-ol	865	b	2·26	1
51	20	2-Butoxyethanol	903	c	0·26	—
52	24	Heptan-1-ol	968	c	0·34	1
53	26	1-Octen-3-ol	979	a	4·40	1
54	39	Phenylethanol	1 119	b	10·27	—
55	70	Tetradecan-1-ol	1 886	c	0·17	—
		Carboxylic acids				
56	68	Pentadecanoic acid	1 814	b	0·06	1
		Esters				
57	15	2-Methylbutanoic acid ethyl ester	846	c	0·11	—
58	29	Hexanoic acid ethyl ester	995	c	0·37	—
59	43	Octanoic acid ethyl ester	1 197	c	0·58	—
60	56	Decanoic acid ethyl ester	1 393	c	0·98	—
61	61	Unidentified branched carboxylic acid alkyl ester	1 589	—	0·25	—
62	64	Hexadecanoic acid ethyl ester	1 783	c	0·15	
63	73	Unidentified branched carboxylic acid alkyl ester	1 976	—	0·04	—
64	74	Unidentified branched carboxylic acid alkyl ester	1 996	—	0·14	—
65	75	Unidentified carboxylic acid alkyl ester	2 025	—	0·33	—
		Lactones				
66	21	γ-Butyrolactone	907	b	2·98	—
67	22	γ-Valerolactone	948	b	0·41	—
68	35	γ-Hexalactone	1 052	b	0·27	—
69	48	γ-Octalactone	1 263	b	0·26	—
70	55	γ-Nonalactone	1 368	b	0·67	—

TABLE 1—*contd.*

No.[a]	*No.*[b]	*Name*	*Kovats index*[c]	*Reliability of ident.*[d]	*Rel. area*[e]	*f*
		Sulphur compounds				
71	19	3-Methylthio propanol	902	c	0·19	—
		Chloride compounds				
72	4	Trichloromethane	—	c	0·66	—
73	57	2-Chloronaphthalene	1 395	a	0·24	—
		Others				
74	31	2-Ethoxyethoxy ethanol	1 002	c	0·29	—
75	60	BHT	1 520	b	0·61	—
76	69	Phthalic acid alkyl ester	1 872	d	0·12	—
77	72	Phthalic acid alkyl ester	1 974	d	0·47	—

[a] Current number of compounds.
[b] Peak number in Fig. 1.
[c] Kovats indices calculated for the DB5 capillary column of the GC–MS system.
[d] The reliability of the identification or structural proposal is indicated by the following symbols:
a; mass spectrum and retention time identical to those of an authentic sample;
b: mass spectrum and Kovats index in agreement with the corresponding literature data;
c: mass spectrum consistent with spectra found in literature;
d: tentative identification by mass spectrum, e.g. position of methyl branching unknown.
[e] Relative percentage of total peak area (solvent excluded).
[f] Compound either identified (1) or not (—) by Shahidi *et al.* (1986).

compounds, such as myoglobin and haemoglobin. The large quantities of branched alkanes found in the aged hams could be potentially interesting because very few branched hydrocarbons have been reported in studies of other cured meat volatiles (Gray & Pearson, 1984; Berdagué *et al.*, 1990). As these molecules are also found in fresh meats (Shahidi *et al.*, 1986), one possible source of them might be the unsaponifiable fraction from the feed of Iberian pigs (acorn and other vegetable products). Anyway, it is believed that saturated and unsaturated hydrocarbons do not play a significant role in the flavour of meat (Min *et al.*, 1979).

The aldehydes content reached high values (30·69% of the total area). Straight chain aldehydes may be formed by breakdown of the hydroperoxides derived from unsaturated fatty acids (Frankel, 1985). Hexanal (17·06%) was the most abundant of the volatile compounds identified in the hams from Iberian pigs. Cross & Ziegler (1965) examined the volatile carbonyls, isolated from both cured and uncured Country-style hams, and found that the uncured ham contained higher levels of hexanal and smaller quantities of branched chain aldehydes. Curing of Iberian hams involves the

addition of salt alone, and in some cases, low quantities of nitrate. Although nitroso compounds seem to retard the formation of several of the higher molecular weight aldehydes, such as hexanal, the high temperature along with the long processing period of Iberian hams, contributed to lipolytic and oxidative degradation of unsaturated fatty acids, which are very abundant in adipose tissue of Iberian pigs (Flores *et al.*, 1988; López-Bote *et al.*, 1990). Other aldehydes found in dry hams probably have different origins such as degradation products of lipids, proteins and reactions between proteins and carbohydrates. The major formation route of branched-chain aldehydes isolated (2-methylbutanal, 3-methylbutanal and phenylacetaldehyde) seems to be the oxidative deamination–decarboxylation of amino acids via Strecker-degradation. The free amino acid content increases sharply as a consequence of intense proteolytic breakdown, and also water activity, reaching values near to 0·79 during the maturing of Iberian hams (López-Bote *et al.*, 1990). These changes suggest that Maillard reactions could be the principal vector by which these aroma compounds are formed.

The alcohols accounted for 22·27% of the total relative area. Most of the alcohols identified, such as pentanol, hexanol and heptanol are likely oxidative decomposition products of lipids, whereas the most abundant, phenylethanol, arises from the catabolism of the amino acid phenylalanine. In general, the straight chain primary alcohols have greenish, woody notes and are considered to affect the overall flavour. Phenylethanol is responsible for a floral note, and 1-octen-3-ol, which is found in large amounts in the dry Iberian ham, has a mushroom-like odour. The presence of branched alcohols (2-methylbutan-1-ol, 3-methylbutan-1-ol), which are highly volatile, was also noted.

A large number of esters were found, but, due to their great structural variability, it was very difficult to identify them using GC–MS. Shahidi *et al.* (1986) suggested that the esters probably arise as a consequence of esterification of the various alcohols and carboxylic acids. Esters are generally associated with fruity flavours.

The lactones identified are formed in the lipid portion by the lactonization of hydroxy fatty acids, which are normal constituents of triglycerides, and also by the oxidation of oleic acid and unsaturated aldehydes. The flavour properties of these lactones are buttery, oily, fatty and fruity (Baines & Mloztiewicz, 1984).

The large amount of olfactory volatiles found in Iberian hams suggests intense proteolytic and lipolytic breakdown during maturation. This was expected, because the Iberian hams are aged at higher temperatures and processed for longer times than other cured hams.

The distillate collected in the cold traps had an aroma reminiscent of Iberian ham. Once the volatile compounds present in the extract have been

identified, the question still remains, which of them are important to the flavour of Iberian hams, and which are superfluous.

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