VOLATILE COMPOUNDS OF DRY CURED HAM : IDENTIFICATION AND SENSORY CHARACTERISATION BY SNIFFING

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SUMMARY

The volatile components of dry cured ham were extracted by Dynamic Headspace and analyzed by Gas-Chromatography-Mass-Spectrometry (GC-MS). The structure of the more volatile molecules was identified by GC-MS and measure of Kovats indices. More than 60 compounds were identified including a number of aldehydes, ketones, alcools, esters, aromatics and heterocycles. These compounds come from the catabolism of the main constituent parts of the meat (glucids, lipids and protids) during the curing of the hams, from the pig feed or technological processes. Flavor tests showed the existence of several aromatic molecules of which some, still unidentified today, had the characteristic odor of dry cured products.

INTRODUCTION

Dry cured ham is a non-smoked product manufactured following two basic principles: stabilisation through a drop in water activity and elaboration of the flavour through maturation. The different steps in the manufacturing processes are described in detail by FRENTZ (1982). Very little research has been carried out on the flavour of dry cured ham. They mainly concern the American works of OCKERMAN et al. (1964) and LILLARD and AYRES (1969) on "Country Style hams", the Italian works of GIOLITTI et al.(1971) on "Italian and Parma Type" hams, the Spanish research of GARCIA et al.(1991) into "Iberian hams" or the French works of BERDAGUE et al.(1991) and BERDAGUE and GARCIA (1990). These authors have shown the presence of carbonyl compounds (alkanals, alk-2-enals, alk-2,4-dienals and ketones), alcohols, fatty acids and sulphurous molecules or various alkans (GARCIA et al.,1991). The aim of this study is to extend and update the identification of the more volatile compounds of dry cured ham and to carry out flavour tests to determine the molecules that are responsible for its aroma. It constitutes a preliminary stage leading to more technological research into the flavour of dry cured ham.

MATERIAL AND METHODS

Materials: for the purpose of this study we used 36 dry unsmoked cured hams manufactured from pigs belonging to 4 different genotypes (BERDAGUE et al., to be published). The hams were ripened during 9 months. All analyses were carried out on muscle *Biceps-Femoris*.

Isolation of volatiles : The volatile constituents from hams were isolated by a dynamic headspace method using a DELSI (platine DCI) apparatus. Before extraction by helium, hams were deep frozen and ground in a domestic blender. Immediately after this operation, 40 grams of ham were placed in a flask to extract the volatile compounds that were trapped on TENAX-GC. Details of the extraction conditions allowing the coupling of the headspace system with a gas chromatograph HP 5890 SII and a mass spectrometer HP 5971A will be published soon.

Capillary gas-liquid chromatography-mass spectrometry (GC-MS) analysis : after thermal desorbtion of the trap, volatile components were directly injected for identification into the GC-MS system. Separation was performed with a DB5 SUPELCO fused silica capillary column (60 m x 0,32 mm i.d., film thickness 1 µ). Carrier gas was helium (velocity : 35 cm sec^{-1}) and the oven was programmed from 35 to 180 °C at a rate of 3°C min^{-1}. The mass spectra was measured by electron impact at 70 eV. KOVATS indices were calculated after TRANCHANT (1982).

Flavor tests : the sensory characteristics of the differents compounds chromatographed were measured by olfactory tests directely at the exit of the chromatographic column. In order to obtain a direct comparison with the mass spectrometry results, chromatographic separation was carried out under the same conditions as for the GC-MS coupling. The KOVATS indices corresponding to each odor were calculated. Three assessors took part in the flavour tests.

RESULTS AND DISCUSSION

A list of the molecules identified in the 36 hams with their chromatographed quantities are listed in Table 1. The more representative chemical families are the aliphatic compounds : 10 aldehydes, 10 ketones, 9 alcohols, 11 alkans and alkens, 5 esters and 1 ether. The 11 cyclic compounds are : 6 aromatic hydrocarbons, 3 furans, 2 terpenoids and 1 pyrazine.

Among the non-branched aliphatic compounds, the series of aldehydes (from pentanal to decanal), methyl-ketones (from propanone to 2-octanone), alcohols (pentanol and hexanol) or alkans (from pentane to decane) are typical products of lipid oxidation (LOURY, 1972; PAQUETTE et al., 1985). The methyl-branched aliphatic compounds may be of various origins (HERTZ et CHANG 1970) but the most probable is that of the catabolism of branched amino-acids such as valine, leucine or isoleucine. Indeed BERGER et al.(1990) have shown that several of the compounds identified here can be produced by acid hydrolysis of the delipidated salami meat. Phenyl-2-ethanol or phenylacetaldehyde and dimethyldisulfide are potential degradation products from the phenylalanine and the cystine. Terpenoids and xylenes come from the insaponifiable fraction of the food. The same is true for toluene, with another possible origin from catabolism of the phenylalanine.

Results of the flavor tests show a wide variety of odors. In Figure 1 only the descriptors corresponding to a wide consensus and intense perception of the assessors have been presented. Among odors noted, those of dairy products (butter, cheese...), heavy odors (rancid, soap, plastic...), certain piquant, irritating odors and odors of mushroom, musty and salting products were perceived by the assessors as being an important component in the aroma of the ham. On the other hand fruity, floral, herbaceous and green notes were not seen to correspond clearly to the olfactive characteristics of the hams. In a general way, the association between an odor and a chromatographic peak should be considered with precaution because of frequent coelution between a high peak which has been identified

by GC-MS and a small non identified but very olfactive one. However, molecules such as 2,3-butanedione (butter), hexanal (rancid, green), nonanal (very rancid), 2-heptanone (blue cheese) and 1-octen-3-ol (mushroom) which have very intense odors during sniffing, should contribute significantly to the flavor of the hams.

CONCLUSION

The extraction of the more volatile compounds of dry ham has led to the identification of various molecules whose blend is responsible for the odor of the product. Flavor tests have shown up the existence of molecules with intense olfactive characteristics. These compounds correspond to several typical components of the aroma of dry ham. This study is a preliminary research on the biochemical origins of these compounds. More technological studies linked to the main technological factors, are being considered for the future so that the flavor of dry cured products can be better understood and controlled.

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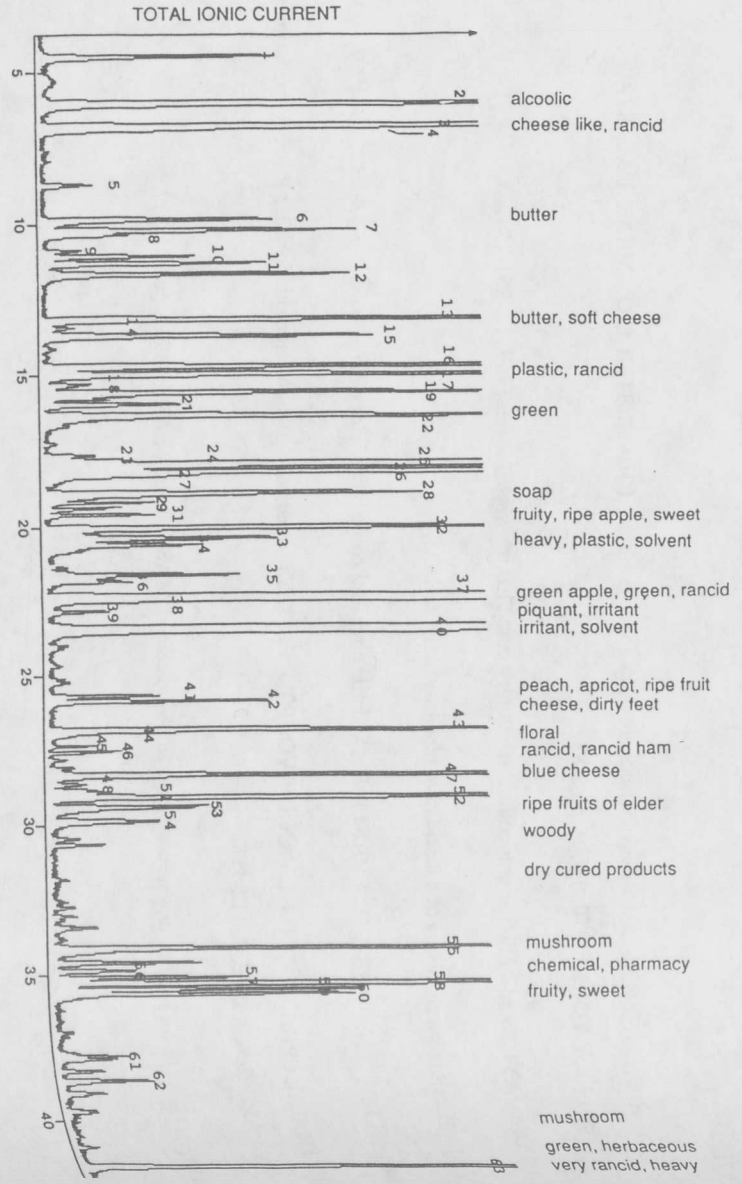

FIGURE 1 : Typical gas chromatogram obtained from the hams and predominant odors during the sniffing tests. The numbers mark such compounds identified in table I.

Peak n°	Chemical name	Kovats Index	Reliability of identification	Extracted quantities
1	carbon dioxide	-	c	-
2	ethanol	-	a	120.9 ± 73.2
3	2-propanone	-	c	442.0 ± 95.7
4	pentane	500	a	16.2 ± 24.5
5	2-methyl-propanal	552	b	<1
6	2,3-butanedione	585	b	10.8 ± 9.5
7	hexane	600	a	15.1 ± 5.8
8	2-butanone	602	b	156.2 ± 100.6
9	alkyl-butanoate	609	d	37.9 ± 31.7
10	acetic acid,ethyl ester	613	b	16.0 ± 6.1
11	trichlorométhane	618	a	contaminant
12	2-methylpropan-1-ol	624	b	56.4 ± 25.7
13	3-methylbutanal	651	b	58.3 ± 18.9
14	unknown 1 (MW=86)	656	-	<1
15	2-methylbutanal	662	b	39.2 ± 14.6
16	3 pentanone	680	b	30.0 ± 12.5
17	2-pentanone	685	b	81.0 ± 36.5
18	?-heptene	690	d	<1
19	pentanal	695	b	24.2 ± 11.1
20	n-heptane	700	a	<1
21	2-ethylfuran	702	b	4.2 ± 2.3
22	3-hydroxybutan-2-one	708	b	31.6 ± 12.8
23	unknown 2 (MW=86)	728	b	3.1 ± 2.5
24	3-methyl 3-buten-1-ol	730	c	2.4 ± 1.2
25	3-methylbutanol	733	b	74.1 ± 50.9
26	unknown 3	736	-	25.7 ± 14.5
27	methyl-branched alkane (MW=100)	738	d	<1
28	dimethyl-disulfide	747	d	10.2 ± 7.6
29	3-méthyl-2-pentanone	752	d	<1
30	2-methylbutanol	754	d	<1
31	butanoic acid, ethyl-ester	757	d	13.2 ± 13.3
32	1-pentanol	765	b	32.5 ± 19.6
33	methyl-benzene	769	a	5.9 ± 2.1
34	unknown 4	772	-	7.3 ± 4.1
35	2-hexanone	788	b	12.3 ± 7.7
36	unidentified alkane	791	d	<1
37	hexanal	798	a	66.5 ± 29.9
38	octane	800	a	<1
39	?-octene	806	d	<1
40	tetrachloroéthene	815	b	contaminant
41	butanoic acid, alkyl ester (MW=130)	849	d	10.0 ± 6.6
42	butanoic acid, alkyl ester (MW=130)	852	d	17.0 ± 16.4
43	hexan-1-ol	866	b	10.2 ± 3.2
44	p.xylène	867	c	<1
45	m-xylène	874	c	<1
46	unknown 5 (MW=106)	877	-	1.8 ± 0.8
47	2-heptanone	889	b	12.0 ± 4.0
48	butyl-furan	892	b	<1
49	unidentified terpenoid	896	d	<1
50	o-xylene	898	c	<1
51	nonane	900	a	<1
52	heptanal	902	a	5.9 ± 1.3
53	2-butoxy, ethanol	905	c	3.1 ± 0.9
54	2,6-dimethyl-pyrazine	913	c	2.9 ± 1.9
55	1-octen-3-ol	981	a	1.9 ± 0.5
56	2-octanone	990	b	<1
57	2-pentyl-furan	994	d	<1
58	2,2,4,6,6-pentamethylheptane	997	d	contaminant
59	decane	1000	a	1.4 ± 0.9
60	octanal	1003	a	3.8 ± 0.9
61	limonène	1030	d	5.5 ± 5.3
62	benzene-acetaldehyde	1051	b	variable
63	nonanal	1105	b	9.2 ± 2.1
64	phenyl-2-ethanol	1121	b	1.8 ± 1.2
65	decanal	1205	b	2.9 ± 0.9

Table 1 : Volatile components identified by headspace analysis of dry cured ham. KOVATS indices are calculated for the DB5 capillary column of the GC-MS system. The reliability of the identification or structural proposal is indicated by the following symbols : a = mass spectrum and retention time identical to with those of an authentic sample ; b = mass spectrum and Kovats index in agreement with the corresponding literature data ; c = mass spectrum consistant with spectra found in literature ; d = tentative of identification by mass spectrum. Chromatographied quantities are expressed in nanograms of external standard dodecane.