Volatile hydrocarbon profile of Iberian dry-cured hams. A possible tool for authentication of hams according to the fattening diet

Narváez-Rivas M., Gallardo E., Vicario I.M., Alcalde M.J., León-Camacho M.

in

De Pedro E.J. (ed.), Cabezas A.B. (ed.).
7th International Symposium on the Mediterranean Pig

Zaragoza : CIHEAM
Options Méditerranéennes : Série A. Séminaires Méditerranéens; n. 101

2012
pages 527-531

Volatile hydrocarbon profile of Iberian dry-cured hams. A possible tool for authentication of hams according to the fattening diet

M. Narváez-Rivas*, E. Gallardo*, I.M. Vicario, M.J. Alcalde*** and M. León-Camacho***

*Food Characterization and Quality Department, Instituto de la Grasa (CSIC),
Avda. Padre García Tejero, 4, 41012 Seville (Spain)
**Department of Food Science and Nutrition, Faculty of Pharmacy, University of Seville (Spain)
***Agroforestry Science Department, University of Seville (Spain)

Abstract. The aims of this work were to carry out a comprehensive study of the volatile hydrocarbons of 34 Iberian dry-cured hams and to evaluate the efficiency of these compounds for discriminating hams according to the fattening system: "Montanera" (B) and "Cebo" (C). The samples of hams were obtained by mincing the semimembranosus and semitendinosus muscles from slices of dry-cured ham. The analyses were carried out by gas chromatography-mass spectrometry with a polar capillary column and after a previous extraction by Purge and Trap method. Forty-three volatile hydrocarbons were identified, 26 of them for the first time in Iberian dry-cured ham. Only five compounds showed significant differences between the two types of hams. Among the 33 volatile hydrocarbons, 22 of them allowed a complete discrimination of the two groups of hams according the fattening system.

Keywords. Iberian pig – Slice ham – Volatile hydrocarbons – GC-MS.

Profil en hydrocarbures volatils chez des jambons ibériques. Un instrument éventuel pour vérifier l'authentification des jambons en fonction de la diète

Résumé. *L'objectif de ce travail est de mener une étude concernant les hydrocarbures volatils sur 34 jambons ibériques et d'évaluer l'efficience de ces composés en vue de différencier les jambons en fonction du système d'alimentation: "Montanera" (B) et "Cebo" (C). Les échantillons de jambons ont été obtenus sur des tranches de jambon, plus précisément des mélanges des muscles* Semimembranosus *et* Semitendinosus*. L'analyse a été réalisée par GC-MS avec une colonne polaire après extraction par une méthode de "purge and trap". Quarante-trois hydrocarbures volatils ont été identifiés, parmi lesquels 26 l'ont été pour la première fois chez des jambons ibériques séchés. Seuls cinq composés ont montré des différences significatives entre les deux types de jambons. Sur les 33 hydrocarbures volatils, 22 ont permis que les deux groupes de jambons étudiés se différencient complètement concernant leur système d'alimentation.*

Mots-clés. *Porc Ibérique – Tranche de jambon – Hydrocarbures volatils – GC-MS.*

I – Introduction

Several authors (López *et al*., 1992) have identified a large number of volatile compounds such as aldehydes, ketones, aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, carboxylic acids, esters and lactones in the Iberian dry-cured hams. It has been postulated that these compounds arise from numerous chemical or enzymatic reactions such as lipolysis, chemical or enzymatic oxidation, proteolysis, Strecker degradation and Maillard reactions (Toldrá *et al*., 2000). Most of these studies on volatile compounds have been carried out with the aim of characterizing them or describe their contribution to the flavour of dry-cured hams. Only an attempt to explore the utility of these compounds as classifying factor for the fattening diet has been carried out, but in loins not in hams. The aims of this work were to carry out an exhaustive study of the volatile compound fraction of 34 Iberian ham samples and to explore the utility of

these compounds, mainly short chain hydrocarbons, as discriminating factors for the fattening diet system.

II – Experimental design

1. Ham samples

A total of 34 samples of dry-cured hams from castrated male 14-month-old pure Iberian pigs and processed in an industry for 24 months were used: 23 corresponding to animals of "Montanera" and 12 corresponding to animals of "Cebo". Slices were cut parallel to the femur and to different depths form each ham. Each slice contained semimembranosus and semitendinosus muscles were trimmer by removing the adipose tissue.

2. Methods

The volatile hydrocarbons were analysed by the dynamic headspace technique and adsorbed on a Tenax trap, using a Purge and Trap Concentrator apparatus Tekmar velocity XPT (Thousand Oaks, CA, USA), based on the method described by Sabio *et al*. (1998), one of the most useful analytical methods to determine volatile compounds. After, the volatile compounds were desorbed by heating, the Tenax trap at 225ºC for 1 min, and sent throw of transfer line (dept at 150 ºC) into the chromatograph injector. The GC-ion-trap-MS analyses were performed using a Varian 3800 gas chromatograph coupled to a Saturno 2000 ion trap mass spectrometer (Varian, Palo Alto, CA, USA).The identification and quantification of the volatile hydrocarbons was done comparing the spectra with those from NIST (National Institute of Standars and Technology) and WILEY libraries and verified by standards.

III – Results and discussion

1. Volatile hydrocarbons profile of ham

A total of 43 volatile hydrocarbons have been identified by GC-MS (Fig. 1). The different hydrocarbons identified in the volatile fraction from "Montanera" and "Cebo" samples are shown in Table 2. Together with mean values, standard deviation (S.D.), maximum and minimum values.

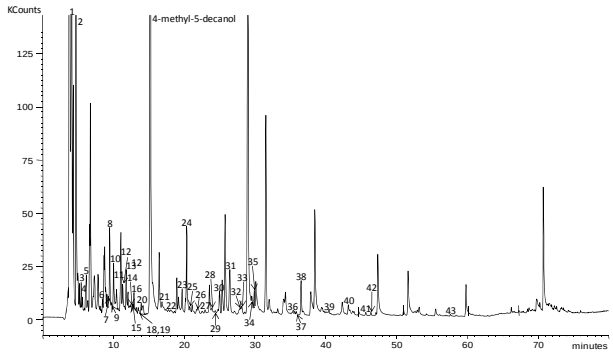

Fig. 1. Chromatograms of the volatile compounds profile of Iberian ham slice samples.

In the group of linear and branched hydrocarbons, 2,4-dimethyl-heptane, 2-octene, 2,2,5,5-tetramethyl-hexane, 2,25-trimethyl-hexane, 2,3,5,8-tetramethyl-decane, 4-methyl-1-decene, 2,4,6-trimethyl-heptane, diisoamilene, 7-methyl-pentadecene, 2,2,3-trimethyl-nonane, 5-(1-

methyl-propyl)-nonane and 3-methyl-5-undecene are observed for the first time in the volatile fraction of Iberian ham.

Table 1. Volatile hydrocarbons profile of Iberian dry-cured ham samples

No.	Volatile hydrocarbons	*"Montanera"*				*"Cebo"*			
		mean	**SD**	**max**	**min**	**mean**	**SD**	**max**	**min**
	n-alkanes								
5	Nonane	0.36	0.28	0.91	0.00	0.25	0.15	0.45	0.05
8	Dodecane[a]	2.65	3.42	10.10	0.00	0.40	0.28	0.89	0.00
	Branched alkanes								
1	3-methyl-hexane	4.64	4.90	23.46	0.56	4.17	1.14	5.93	2.37
2	2,4-dimethyl-heptane[a]	4.65	3.11	11.85	0.89	7.04	3.53	14.28	0.86
7	2,2,5,5-tetramethyl-hexane[b]	0.12	0.28	1.12	0.00	0.48	0.42	1.15	0.00
9	2,2,5-trimethyl-hexane	0.84	1.14	3.20	0.00	0.21	0.25	0.70	0.00
10	2,3,5,8-tetramethyl-decane	1.78	1.74	5.38	0.05	0.98	0.94	2.67	0.00
14	2,4,6-trimethyl-heptane[a]	0.60	0.54	1.77	0.00	0.23	0.19	0.54	0.02
16	7-methyl-pentadecane	0.53	0.59	1.83	0.00	0.38	0.47	1.28	0.00
17	2,2,3-trimethyl-nonane	0.31	0.41	1.51	0.00	0.25	0.35	0.98	0.00
18	5-(1-methyl-propyl)-nonane	0.15	0.17	0.52	0.00	0.10	0.14	0.39	0.00
21	2,6-dimethyl-undecane	0.11	0.12	0.41	0.00	0.05	0.08	0.24	0.00
	n-alkenes								
4	2-octene[a]	0.21	0.14	0.49	0.00	0.11	0.08	0.25	0.01
	Branched alkenes								
12	4-methyl-1-decene	1.64	1.58	4.83	0.06	0.90	0.66	2.30	0.10
26	3-methyl-5-undecene	0.12	0.18	0.58	0.00	0.14	0.19	0.68	0.00
27	4-methyl-1-undecene	0.18	0.21	0.93	0.00	0.26	0.30	1.08	0.03
	Cyclic								
3	1,2-diethyl-cyclobutane	0.17	0.10	0.41	0.00	0.35	0.56	2.06	0.05
6	Butyl cyclopentane	0.16	0.20	0.93	0.00	0.15	0.23	0.87	0.00
20	Heptyl-cyclohexane	0.12	0.26	1.16	0.00	0.29	0.35	0.97	0.00
22	1-ethyl-1-methyl-cyclohexane	0.08	0.16	0.73	0.00	0.10	0.14	0.46	0.00
29	Octyl-cyclohexane	0.06	0.15	0.64	0.00	0.18	0.31	0.99	0.00
37	2-ethenyl-cyclohexane	0.03	0.07	0.29	0.00	0.02	0.02	0.05	0.00
39	Butenyl cyclohexene	0.03	0.04	0.17	0.00	0.02	0.03	0.09	0.00
43	*cis*-1,2,3,4-tetramethyl-cyclopentane	0.14	0.30	1.25	0.00	0.07	0.12	0.31	0.00
	Terpenic								
31	Limonene	0.49	1.14	5.41	0.00	1.12	1.39	4.09	0.03
11	4-carene	0.88	0.95	2.59	0.00	0.36	0.27	1.00	0.06
19	Germacrane B[a]	0.35	0.30	1.05	0.00	0.11	0.13	0.31	0.00
	Aromatic								
13	Methyl-benzene	2.10	3.07	13.42	0.34	0.43	0.23	0.96	0.14
15	Diisoamilene	0.34	0.41	1.67	0.00	0.24	0.22	0.67	0.00
23	p-xylene	0.30	0.20	0.79	0.00	0.30	0.25	0.76	0.05
24	m-xylene	0.61	0.72	3.15	0.00	0.37	0.32	1.15	0.00
25	Decahydro-*cis*-naphtalene	0.31	0.50	2.08	0.00	0.04	0.06	0.18	0.00
28	2-methyl-decahydronaphtalene	0.10	0.19	0.70	0.00	0.08	0.23	0.81	0.00
30	o-xylene	0.14	0.16	0.60	0.00	0.33	0.38	1.16	0.00
32	Propyl-benzene	0.11	0.15	0.73	0.00	0.09	0.14	0.40	0.00

Table 1. Volatile hydrocarbons profile of Iberian dry-cured ham samples (cont.).

No.	Volatile hydrocarbons	*"Montanera"*				*"Cebo"*			
		mean	SD	max	min	mean	SD	max	min
33	Decahydro-*trans*-naphtalene	0.05	0.08	0.24	0.00	0.11	0.15	0.37	0.00
34	1,3,5-trimethyl-benzene	0.03	0.07	0.30	0.00	0.09	0.14	0.43	0.00
35	1-ethyl-4-methyl-benzene	0.05	0.13	0.61	0.00	0.03	0.09	0.30	0.00
36	1-methyl-3-(1-methyl-ethyl)-benzene	0.04	0.09	0.45	0.00	0.07	0.08	0.23	0.00
38	1,2,4-trimethyl-benzene	0.15	0.20	1.00	0.00	0.12	0.08	0.30	0.05
40	1,2,3-trimethyl-benzene	0.11	0.31	1.50	0.00	0.02	0.02	0.07	0.00
41	4-ethyl-1,2-dimethyl-benzene	0.02	0.04	0.16	0.00	0.00	0.01	0.04	0.00
42	2-ethyl-1,3-dimethyl-benzene	0.01	0.02	0.07	0.00	0.00	0.01	0.04	0.00

[a] For p< 0.05; [b] For p< 0.01.

All cyclic hydrocarbons except limonene: 1,2-diethyl-cyclobutane, butyl-cyclopentane, germacrane B, heptyl-cyclohexane, 1-ethyl-1-methyl-cyclohexane, octyl-cyclohexane, 2-ethenyl-cyclohexane, butenyl-cyclohexane and *cis*-1,2,3,4-tetramethyl-cyclopentane compounds have been identified for the first time in the present work. On the other hand, in the present study, we have identified the 4-carene, which has not been described previously.
Most of the aromatic hydrocarbons have been previously described by other authors, however, decahydro-*cis*-naphtalene, decahydro-*trans*-naphtalene, 2-methyl-decahydronaphtalene and 2-ethyl-1,3-dimethyl-benzene have been described for the fist time in this work. Besides, (1-methyl-propyl)-benzene, 1-propenyl-benzene and 1-methyl-4-(1-methyl-ethenyl)-benzene compounds were detected and they have not been described at the literature previously.
A PCA was performed (Fig. 2) where it shows a fair separation between "Montanera" (B) and "Cebo" (C) samples. To achieve a better separation of the groups according to fattening diets a linear discriminant analysis (LDA) was carried out. Fig. 3 shows the case discrimination, grouped by fattening diet, according to the first canonical variable or square roots obtained from the classification function. A complete separation between the two groups can be observed.

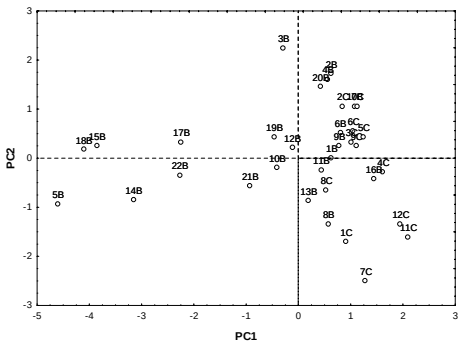

Fig. 2. Principal Component Analysis (PCA).

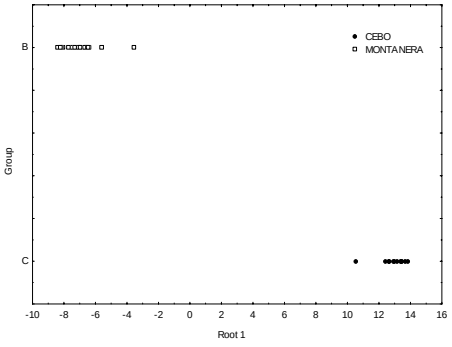

Fig. 3. Linear Discriminant Analysis (LNA).

Acknowledgments

The authors are grateful to the Designation o Origin "Los Pedroches" for the collaboration and given help. This study was supported by projects PET 2007-0015 and P08-AGR-03498.

References

Sabio E., Vidal-Aragón M.C., Bernalte M. J. and Gata J. L., 1998. Volatile compouns present in six types of dry-cured ham from south european countries. In: *Food Chem.*, 61: 493-503.

López, M.O., de la Hoz, L., Cambero, M.I., Gallardo, E., Reglero G. and Ordóñez, J.A., 1992. Volatile compounds of dry hams from Iberian pigs. In: *Meat Science*, 31: 267-277.

Toldrá, F., Aristoy, M-C. and Flores M.. 2000. Contribution of muscle aminopeptidases to flavor development in dry-cured ham. In: *Food Res. Int.*, 33: 181-185.