AROMA VOLATILE MOLECULES OF MORTADELLA

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Key words: mortadella, aroma, volatiles

INTRODUCTION

Mortadella is a popular Italian pork product, the name of which comes from "mortar", once used to mash and mix all lean and fat remains of the slaughtered pig. In recent years, though, there have been moves towards a standardization of what has been called "Mortadella Bologna" and which is intended to be a top quality product (UNI, 1994). The research which has been undertaken was aimed at identifying the volatile molecules responsible for mortadella flavour since no investigation has been specifically conducted on such a product.

MATERIALS AND METHODS

Samples of 13 different commercial brands were bought from local commercial premises. The samples were characterized for proximate composition and NaCl content (AOAC, 1990), pH, residual nitrites (Slack, 1987), hydroxyproline (ISO standard method 3496), peroxide value (AOAC, 1990) and Thiobarbituric Reactive Substances (TBARS) (Tarladgis et al., 1960).
Volatiles were extracted and concentrated by Dynamic Headspace Volatile Concentration, separated, identified and quantified by Gas Chromatography and Gas Chromatography/Mass Spectrometry. The compounds were identified by comparison with available libraries (NBS, NIST, TNO), by comparison with standard molecules and by matching with retention indices of the literature. Odor port assessment (Sniffing test, i.e. Gas Chromatographic Effluent Sniffing) was performed on a Hewlett Packard 5890A gas chromatograph equipped with a FID detector and a sniffing port. The end of the column was fitted to a glass-3way connection (0.32 mm i.d.), splitting the effluent 1:1. Sniffing analysis was carried out by eight members of a trained panel who smelled the effluent for 10 min. specifying odor characteristics.

RESULTS AND DISCUSSION

Proximate composition and the other chemical parameters were rather variable, but variation in the contents of the substances determined is in line with what is known from the literature. Water content varied from less than 50% up to nearly 57%; proteins levels from just under 13% to nearly 18%; total fat from about 23% to almost 35%. Wide variations have been observed for pH values, from less than 5.00 to well above 6.00. Residual nitrites were always very low. Hydroxyproline, considered to be an index of the quality of the raw materials, was between 1.5 and 4.0%. General oxidation level, as assessed by peroxide value and TBA, was very limited.
Gas liquid chromatographic analysis has made possible the separation of a set of volatile molecules varying from 92 to 144 in the different mortadella brands and about 90 of such molecules have been identified. As a consequence of the variability observed among different brands, variability probably linked with the technology and the ingredients used, only the molecules constantly observed in at least half the samples have been considered. Such molecules have been classified according to their chemical structure and origin(Tab. 1). In this way 15 hydrocarbons, 3 ketones, 9 alcohols, 12 aldehydes, 1 ester, 3 chlorides, 32 terpenes, 5 sulfur compounds, 2 furans and 1 organic acid have been observed in most samples. The total amount of identified volatile compounds has resulted to be 8253.16 ng/g of sample on average.
Aliphatic and aromatic hydrocarbons make up, respectively, 2.74 and 1.73 % of volatiles. Alkanes and aromatic hydrocarbons have a high olfactory threshold limit and, therefore, contribute to a very limited level to global aroma formation.
Ketones make up 1.83 % of the total volatiles identified and are all of the aliphatic type. They are mainly originated from fatty acids oxidation. The molecules belonging to the 2-alkanones group have specific odours, like for instance the 2-heptanone which has a spicy odour. Like hydrocarbons, ketones have a high perception limit and cannot, therefore, be very important for flavour in meat products.
Alcohols, about 6.5% of the total, are in general the degradation products of lipid hydroperoxides and appear to be very important for flavour. Alcohols of the linear saturated type have an olfactory threshold extremely high and can be neglected. On the other hand, the unsaturated ones, deriving from the oxidative degradation of polyunsatured fatty acids, such as linoleic acid, have a low perception threshold and are among the most important flavour compounds of meat products. A typical example of the latter group is 1-octen-3-ol, a molecule with mushy odour, found in all samples.
Aldehydes, mostly of the aliphatic type, are the second most important group of volatiles identified as they make up 13.49% of the total. Most of them are produced from oxidative degradation of long chain fatty acids. Some aldehydes can be produced from non fatty substrates. This is the case of branched chains molecules, such as 3-methyl-butanal and 2-methyl-butanal, which derive from combined deamination and oxidative decarboxilation reactions of leucine and isoleucine, respectively (Mottram, 1991). Phenylacetaldehyde is a product of phenylalanine catabolism (Bedarguè et al., 1991).
Only one molecule belonging to the esters has been identified and at a very low concentration (<0.5%). A similar case is that of organic acids; butanoic acid being the only compound of this group.
The three molecules belonging to the class of chlorides can be interpreted as residues of pesticides stored in fatty tissues, impurities of laboratory reagents or the result of release phenomena from packing materials at some stage of the production chain.
The biggest group, both for the number of molecules and for its relative incidence (nearly 70% of total), is made up by terpenes. Such compounds are produced by plants by joining at least two molecules with 5 carbon atoms.The 32 different molecules identified include, among others, limonene, over 23% of the entire group, α-pinene, β-pinene, sabinene, safrole, eugenol and carvone. Limonene is found in many essential oils of spices but is particularly abundant in nutmeg, where α- and β-pinene, sabinene and safrole can also be found. Essential oil of cloves is rich in eugenol. Carvone, besides cloves, is present in black pepper. Five compounds have not been identified but from mass spectrometry data can be classified as monoterpenes.

A significant group is the one made by sulphur compounds, nearly 4% of total volatiles. All of them, with the exception of 1,3-dithiane, which has an heterocyclic structure, have a linear chain. Non heterocyclic sulphur compounds play a fundamental role in meat flavour. Such molecules have a very low olfactory perception threshold and minute amounts can have significant effects. Some molecules have a direct effect for their typical meaty flavour, some others bring a simple sulphuric odour (Mottram, 1991). Diallyl disulphide has not been extracted from any type of meat (Shahidi et al., 1986) but it is known to be present in essential oil of garlic and this suggests that the molecule could derive from spices. Indeed, garlic is often added to the mortadella mince.

Finally two molecules belonging to the furan group have been isolated. Their origin is not clear, but carbohydrate degradation in Maillard reactions is the most probable source of furans in meat.

About 95% of the identified volatiles can be linked with known chemical pathways and/or with parent substances.

The biggest share (68%) is taken by molecules released from spices, a fact which is a comment in itself. Lipid oxidation products are the second biggest group with about 15% of total molecules, followed by Maillard products (nearly 9%). There appears to be a strong indication, therefore, that flavour of mortadella is primarily due to the spices used and to a minor extent to the effect of processing technology on raw materials (fats, carbohydrates, amino acids) by way of oxidative and Maillard reactions.

As for the the sniffing test, panel members managed to recognize a great number of odours but only those odours identified by at least half the panel were retained. About half the odours identified can be associated with spices , three or four are aldehydes, one is an alcohol and one is a keton. Three odours could not be associated with a specific molecule (Kovacs index 651, 1165 and 1335) but their strong typical smell suggests that they might be sulphur compounds, such as propyl propanethiosulphonate (K.i. 1348) and propyl methanethiosulphonate (K.i. 1175), which can be found in garlic and onion (Kuo and Ho, 1992). The sniffing test has confirmed the predominat role played by spices in mortadella flavour.

It can be concluded, therefore, that, variations in flavour among different brands and products of various quality levels can be ascribed more to variations in the formulation of ingredients, spices in the first place, than to the effect of processing technology, that is heat induced lipid oxidation and Maillard reactions.

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Acknowledgements: The research has been financed by the Commission of the European Community (AIR2 CT93 1691).

TABLE 1. Volatiles molecules identified in Mortadella ranged according to their most likely origin.

Molecule	ng/g sample (ppb)	Molecule	ng/g sample (ppb)	Molecule	ng/g sample (ppb)
m-cymene	5.78	3,3'-(thiobis)-1-propene	13.29	1-propene-3-methylthio	197.02
p-cymene	144.68	diallyl disulfide	11.27	dimethyl disulfide	99.49
a-thujene	102.72	***Spices***	***5614.68****(68.03)*	1,3-dithiane	6.42
a-pinene	478.30			2-ethyl furane	26.10
camphene	19.25	heptane	8.35	2-furanmethanol	6.77
a-fenchene	17.05	alkane	73.24	***Maillard products***	***723.15****(8.76%)*
terpene not identificate	3.36	1-octene	13.20		
sabinene	644.31	octane	107.95	dodecane	10.46
b-pinene	677.10	nonane	4.75	tridecane	2.83
myrcene	262.20	toluene	51.19	tetradecane	1.76
a-phellandrene	49.20	2-pentanone	84.64	pentadecane	2.30
3-carene	362.85	2-heptanone	22.08	hexadecane	1.07
a-terpinene	549.64	1-penten-3-ol	99.98	p-xylene	20.96
limonene	1297.57	pentanol	31.90	ethylbenzene	51.85
b-phellandrene	78.73	hexanol	13.31	m-xylene	12.22
cineole	12.66	1-octen-3-ol	9.14	styrene	6.47
ocimene	63.78	pentanal	46.64	1,1,1-trichloroethane	55.85
g-terpinene	127.16	hexanal	306.29	trichloroethene	12.83
terpene not identificate	33.31	heptanal	74.89	tetrachloroethene	11.34
terpene not identificate	16.04	2-heptenal	7.80	***Contaminantes***	***189.95****(2.30%)*
terpinolene	87.72	octanal	63.40	*(feed, pesticides, ecc.)*	
b-ocimene	259.14	2-octenal	5.31		
4-carene	4.01	nonanal	250.71	propylacetate	38.23
terpene not identificate	17.39	2-nonenal (E)	2.39	3-methyl-1-butanol	147.67
camphor	7.22	decanal	13.07	2-methyl-1-butanol	179.62
terpene not identificate	62.04	***Lipid oxidation***	***1290.24****(15.63%)*	1,3-butanediol	31.07
a-terpineol	10.73			2,3-butanediol	9.93
carvone	81.53	phenylacetaldehyde	7.46	2-butoxyethanol	19.04
safrole	38.99	3-hydroxy-2-butanone	44.34	butanoic acid	9.59
sesquiterpene	8.82	3-methylbutanal	159.50	***Unknown origin***	***435.15****(5.27%)*
caryophyllene	57.30	2-methylbutanal	176.05		
				Total	***8253.16***