TRACING OF THE CHANGES IN VOLATILE MONOCARBONYLS AND LIPID OXIDATION PRODUCTS IN PORK DURING THE MANUFACTURE OF CANNED HAM

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MEAT and meat product flavour is an important index of their quality (1). Many authors (2-6) consider that the basic flavour of meat is related to water-soluble precursors in meat and is developed on its heat treatment.

Carbonyl and sulfur-containing compounds are among the most diverse classes of chamical compounds which are present in all the isolates and concentrates of basic meat flavour. They are predominating also among the compounds forming the flavour complex in closed systems subjected to heat treatment where conditions are created for the development of an off-flavour (7).

Hams are products of a typical flavour, which is formed in the course of their manufacture, during curing, ageing, and heat treatment. The technological operations mentioned above create optimum conditions for the change of water-soluble flavour precursors, as well as of the lipids considered by many authors responsible for the characteristic meat flavour (1, 8, 10).

The objective of the present work was to follow the changes in volatile monocarbonyls and lipid oxidation products in pork during the manufacture of pasteurized and sterilized canned hams.

MATERIALS AND METHODS

FOUR samples were analysed in each of two parallel experiments: from the raw material for the "Roussé" ham, raw meat, uncured, I; cured meat, II; and further, model cans of the "Roussé" ham, pasteurized (III), and sterilized (IV).

The meat was prepared from pork hams. Pasteurization was performed at a temperature of 78°C until reaching 69-70°C in the centre of the cans of meat, and for sterilization, the F-value was equal to 6-7. The meat and the contents of the cans were analysed in the following manner:

I. Volatile monocarbonyls from the water-soluble flavour precursors isolated from lean muscle (Im, IIm, IIIm, and IVm) were determined using adsorption and thin layer chromatography by the modified method of Langner's (11).
II. Adipose tissue was treated under the mildest conditions possible (12) to obtain a fat uninfluenced by the experiment (If, IIf, IIIf, IVf), which was analysed for:
1. Volatile monocarbonyls by Schwartz's method (13);
2. Hydrolysis and oxidation products (acid number and peroxide value) /14/;
3. Lipid autooxidation products by the method of Parr and Swoboda (15).

The amount of volatile monocarbonyls isolated from lean muscle was determined by the absorption of the acetone solutions of their derivatives with 2,4-dinitrophenylhydrazine (2,4-DNPH) in the UV region of a Carl Zeiss VSU-2P spectrophotometer.

An automatic Mußem type collector (hungary) was used for the quantitative determination of volatile monocarbonyls from adipose tissue.

All the reagents used were analytical grade, high purity ones.

RESULTS AND DISCUSSION

Table 1 shows the levels of the hydrazones of the monocarbonyls, isolated from the experimental material, estimated as mM of propionaldehyde hydrazone per 100 g of product.

The least square method of variation statistics was used.

The first two columns of the table show the experimental values of the monocarbonyls isolated and identified by the modified method of Langner's from lean muscle and, after Schwartz et al. (13), from the fat. The subfractions of monocarbonyl derivatives were eluated from the absorption column (magnesium oxide-cellit) with eluating mixtures of an increasing polarity. The absorption of 125 fractions of 5 ml each was measured in the UV range by Parks's method (17).

The chromatograph in Figure 1 shows the separation of the four basic subfractions of the monocarbonyl derivatives isolated from the adipose tissue of the experimental material. As can be seen from the chromatograph, the subfractions of the monocarbonyl derivatives isolated from

the uncured uncooked and the cured uncooked meats are considerably lower, compared to the ones obtained from the pasteurized or the sterilized product. That correlates well with the experimental values of the ketone and the aldehyde subfractions indicated in Table 1 (columns III and IV). On the other hand, the difference is obvious between the total monocarbonyls isolated

Table 1.

Sample	Experiment I				Experiment II			
	Total monocarbonyls, mM/100 g[a]				Total monocarbonyls, mM/100 g[a]			
	Lean Muscle	Adipose Tissue	Ketone Subfraction	Aldehyde Subfraction	Lean Muscle	Adipose Tissue	Ketone Subfraction	Aldehyde Subfraction
I	1.21	1.01	0.50	0.20	1.19	0.95	0.49	0.20
II	1.38	1.12	0.60	0.25	1.30	1.12	0.60	0.25
III	1.40	1.21	0.85	0.32	1.41	1.22	0.80	0.30
IV	1.59	1.30	0.90	0.34	1.55	1.30	0.85	0.34

[a] Mean value of four trials.

from lean muscle and the ones isolated from adipose tissue in both the raw material (cured and uncured), and the products of pasteurization or sterilization. Our experimental data confirm the view of some authors (16), according to which the precursors of the basic meat flavour are among the water-soluble meat components, and fat depots are rather the solvent, than the source of carbonyl compounds.

Fig. 1, obtained by measuring, in the UV region, the absorbance of the subfractions of the monocarbonyl derivatives (17), indicates clearly that the ketone subfraction (peak I), followed by acetone (peak II) are in a relatively large quantity, exceeding nearly twice that of the aldehyde subfraction (peak III between fractions 55 and 70).

The hydrazones of 2-enals appear between fractions 75 and 90 (peak IV), and those of the 2,4-dienals appear, on eluation usinf pure chloroform, between fractions 90 and 100. The analytical procedure used by us for plotting Fig. 1, allows to eluate and separate both the non-polar subfractions of the monocarbonyl derivatives (ketones, aldehydes), and the more polar, unsaturated subfractions of the 2-enals and the 2,4-dienals.

Our experience indicates that the differences in the monocarbonyls isolated from the pasteurized or the sterilized product are not large, but are considerably higher on comparison to cured uncooked, or uncured uncooked raw material. From Table 1 it becomes obvious that the share of the ketone subfraction is greater than that of the aldehyde one, and at that, the former is more variable in both the raw material and the canned product.

The qualitative characterizing of the two basic subfractions of the monocarbonyl derivatives (the ketone and the aldehyde ones) was performed by thin layer chromatography on DC-Kieselgel, impregnated with PEG-400, in a benzene-hexane developing system. The individual compounds were compared in R_f-value to corresponding chemically pure reference substances. The ketone subfraction was found to contain: acetone, butanone, methyl-hexyl ketone, methyl-octyl ketone, and the aldehyde subfraction, acetaldehyde, propionaldehyde, and octanal.

Along with changes in monocarbonyls, changes were followed also in the lipids, extracted from the experimental samples under the mildest conditions possible (12). Lipid changes were characterized by measuring the absorbance of total conjugated oxidised products (COP_V) and the oxodiene value (OV) in the UV region by the method of Parr and Swoboda (15), which can detect the initial stage of fat autooxidation. Those changes were compared to hydrolytic and oxidative deterioration determined using the traditional titrimetric methods of acid number and peroxide value estimation (14). The data from the analyses are incorporated in Table 2.

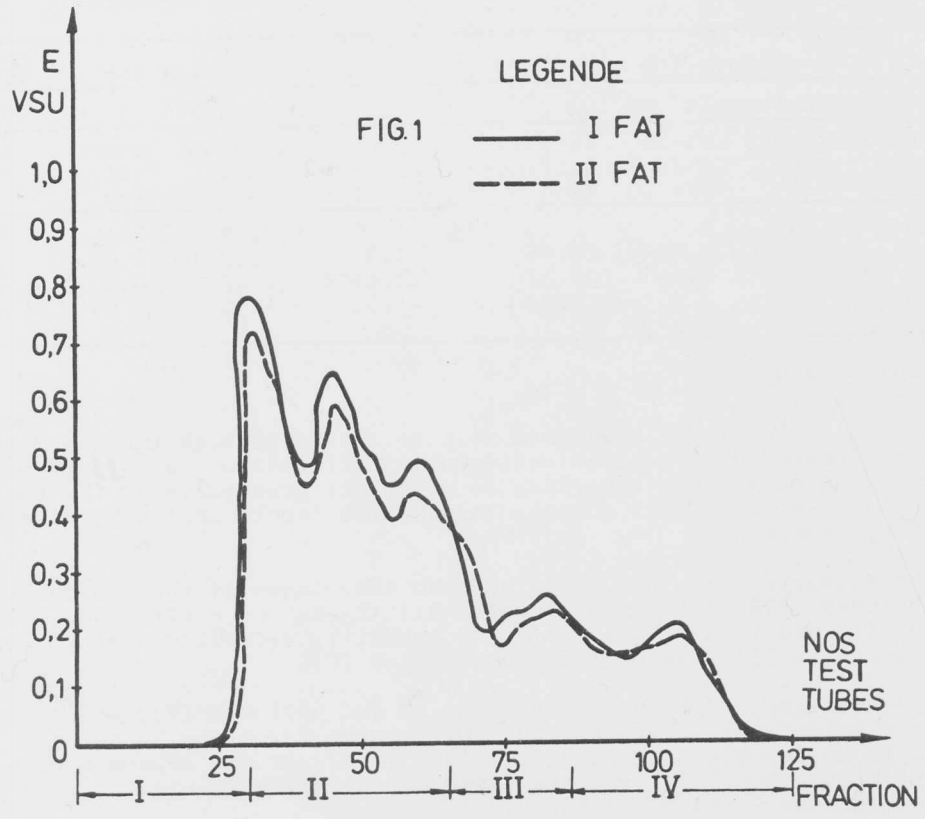
Table 2.

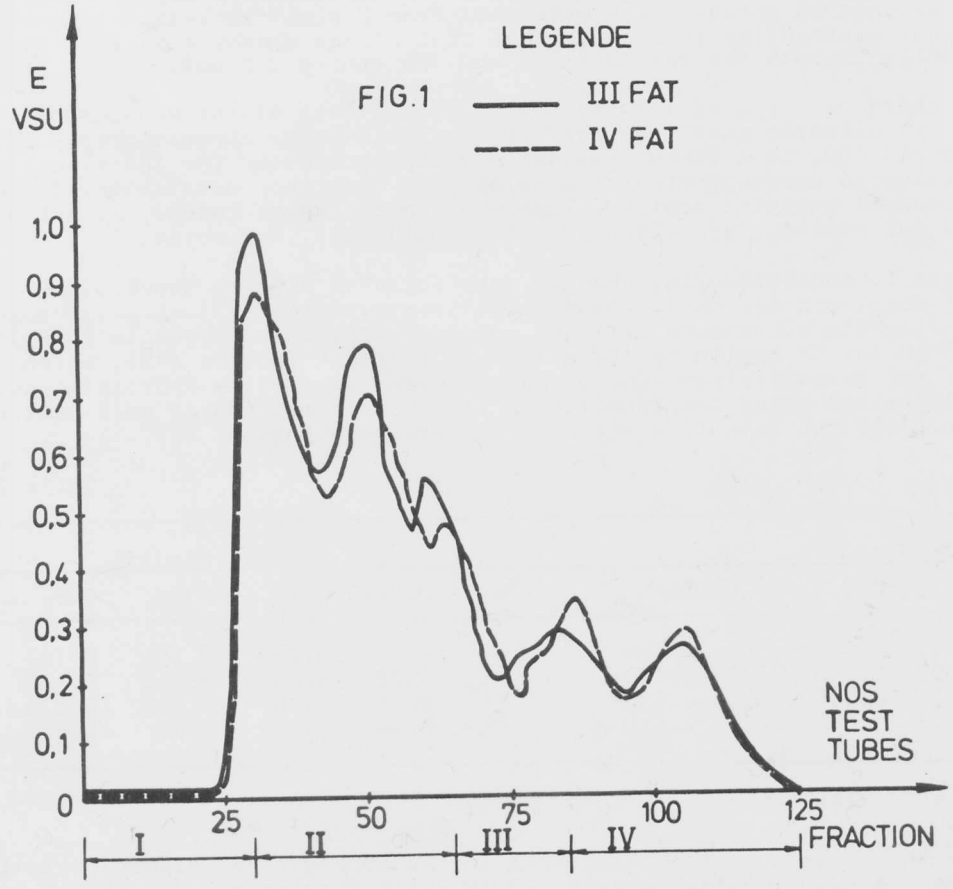
Sample	Experiment I[a]					Experiment II[a]				
	ANo,°	PV,°	O.V.	COP_V	COP_R	ANo,°	P.V.,°	O.V.	COP_V	COP_R
I	0.59	0.01	0.025	0.360	0.100	0.50	0.01	0.030	0.350	0.100
II	0.83	0.02	0.030	0.370	0.140	0.80	0.02	0.030	0.360	0.140
III	1.04	0.04	0.060	1.07	0.530	0.95	0.04	0.065	1.05	0.530
IV	1.15	0.04	0.080	1.25	0.610	1.05	0.06	0.070	1.10	0.610

[a] Mean value of 4 trials.

Table 2 reflects the changes in the absorbance in the UV region of alcohol solutions of the fat isolated from the experimental material (12), which changes are due to the appearance and the disappearance of chromophore groups as a result of the analytical procedure (15). This

method gives an estimation not only of the hydroperoxides formed on lipid oxidation, which can be determined by the traditional titrimetric method (14), but also of the secondary oxidation products: hydroxy and carbonyl compounds called conjugated oxidized product (COP_V), which cannot be detected by titration using sodium thiosulphate, since they do not release





iodine. COP_V is some three times higher in the canned meats, compared to that determined in the raw material. The same regularity is also observed in the COP_R column, which is an unmeasured quantity obtained from the experimentally determined ratio of polyene oxidation products to diene ones. By the experimentally determined oxodiene values (OV), one can judge about a growth of unsaturated carbonyls in the experimental samples subjected to heat treatment, when compared to the ones obtained from the uncured uncooked or the cured uncooked pork. From Fig. 1 it is obvious, that peaks IV and V, indicating the subfraction of 2-enals and 2,4-dienals, correlate well with the experimental values for OV, COP_V, and COP_R, shown in Table 2.

CONCLUSIONS:

1. The total monocarbonyl hydrazones isolated from lean muscle from the experimental material, are higher than those isolated from the adipose tissue.
2. The monocarbonyl derivatives obtained from the canned products are considerably higher than those isolated from the uncured or the cured uncooked raw material.
3. The ketone fraction of the monocarbonyls is richer and more variable than the aldehyde one.
4. The unsaturated fractions of the monocarbonyls are approximately two times higher in the canned products, compared to the raw material.
5. The total conjugated oxidised product, determined in canned product lipids, is 3 times higher than that in the raw material.

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