Changes in the Lipid Fraction during the Ripening of "Pure Pork" Salami

L. CERISE, U. BRACCO, I. HORMAN, T. SOZZI, J.J. WUHRMANN

Nestlé Products Technical Assistance Co. Ltd.,
Lausanne, Switzerland

(Manager of the R&D Department, Professor L. Rey)

1. Introduction

During the past years, many studies have been made on different varieties of dry sausages. The economical significance of this very popular food fully justifies the efforts made by scientists to acquire a better knowledge of the phenomena which determine the quality of such products, in order to establish more effective processing controls. Numerous authors have studied the various aspects of the manufacture of the varieties of sausages consumed in their own country. If, in a general way, the phenomena detected are of a certain similarity as regards their aspects, the intensity of any one of the factors perceived varies considerably according to the type of sausage concerned.

We have made a complete study of the properties of the Italian "Varzi" salami, including its physical, biochemical and microbiological aspects. We give here the main results concerning the lipidic fraction relating essentially to the variations in composition due to lipolytic activity and, in particular, the esterase (splitting of fatty acids) and peroxydase activity (formation of hydroperoxides) on the α-methylene carbon of the dienes.

Several authors have published the results of their work in this field, namely CANTONI (1), DUDA (2), GIOLITTI (3) and WAHLROOS (4).

2. Material and Method

Our investigations have been carried out on a "pure pork" variety of salami, manufactured by the conventional Italian process. After stuffing of the sausage meat in natural casing, the salami is maintained at 21° C for 3 days, followed by a ripening for 27 days at 12° C. The initial weight of the piece is about 1500 g, and the loss is of the order of 30 % after 30 days. The analyses have been performed on the initial mixture, as well as after 1, 2, 4, 8, 15 and 30 days.

We have then stored the salami at 15° C for 30 days. The final analysis has been made at the end of that period, namely 60

days after the beginning of processing.

Each sampling has been operated as follows: 5 salami have been selected on which a slice of 50 gr, carefully peeled, has been cut, minced and homogenised. The lipids have been extracted according to the diagram given in Figure 1, with a chloroform-methanol mixture (2:1). This method allows to obtain neutral lipids (free fatty acids, triglycerides, diglycerides and monoglycerides), unsaponifiable constituents and polar lipids (phospholipids in particular).

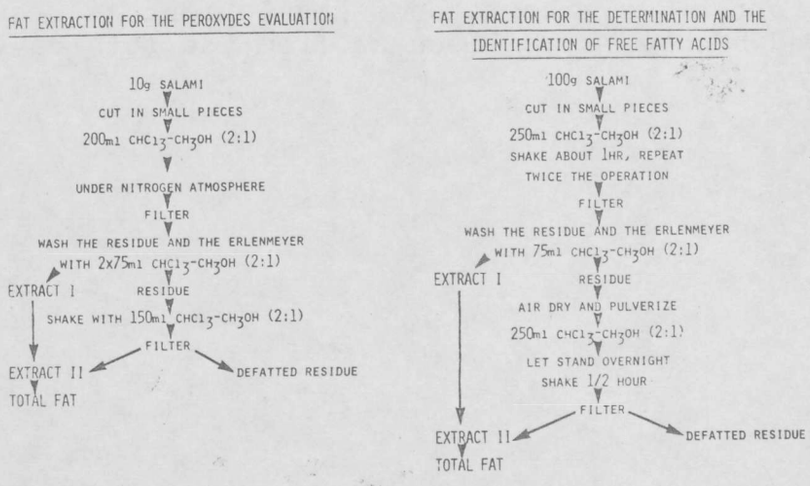

FIG.1 FAT EXTRACTION

The free fatty acids have been determined by titrimetry (5). Their composition has been determined by gas chromatography after separation from the other lipidic constituents by chromatography on a KOH-isopropanol impregnated silicic acid column, as described by McCARTHY (6), then methylation with the methanol-sodium methylate mixture.

The development of the free fatty acids during the process has been followed by gas chromatography on a DEGS polar column with temperature programmed between 100° and 180° C (6° C/min.) and a flame ionisation detector at 300° C.

At the end of the storage period, a more complete identification of the "free fatty acids" fraction has been obtained by coupled gas chromatography and mass spectrometry. We have used a CARBOWAX 20 M column with a temperature between 50° and 190° C (2° C/min.) and an injector temperature of 200° C; the column was coupled with an AEI MS 20 mass spectrometer. Moreover,

we have applied direct injection of the sample on a high resolution AEI MS 9 mass spectrometer; the data were computerized.

The peroxides have been determined by the ferrous salts colorimetric method (7), more sensitive than the iodometric one.

3. Results

3.1. Free fatty acids

Figure 2 shows the evolution of free acidity in gramms of oleic acid per 100 g of fat. It is noted that it increases rapidly up to the second day, and then, after an abrupt decrease on the fourth day, its rate of development is resumed perceptibly and becomes stabilised as from the 15th day.

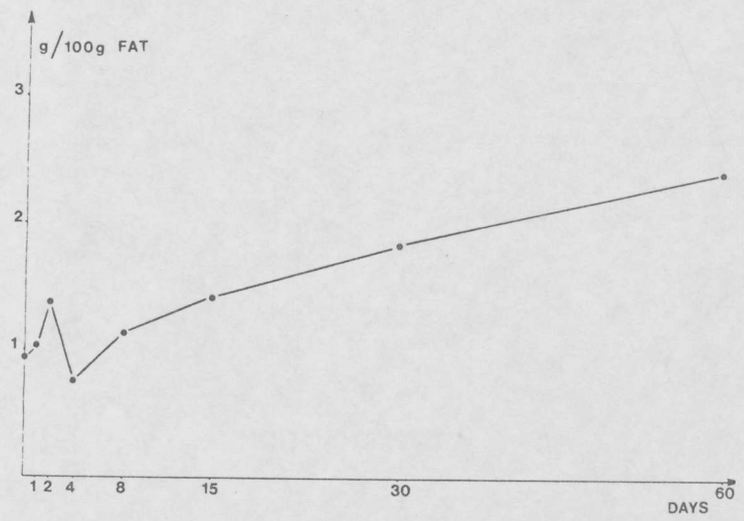

FIG.2 EVOLUTION OF FREE ACIDITY AS OLEIC ACID

According to our experiments with other substrates (milk derivatives), the final value obtained at the end of the storage period, namely 2.25 g of oleic acid per 100 g of fat represents, in our opinion, a maximum value of free acidity compatible with an enzymatic activity (8).

An analysis by GLC of the composition of the "free fatty acids" fraction shows at first significant variations as regards the fatty acids present in higher proportions at the initial stage, namely the oleic and palmitic acids, whereas the stearic and linoleic acids undergo slighter variations (Figure 3). The considerable increase in oleic acid observed during the first 15 days is due to the specificity of the lipolytic attack on the 1 and 3 positions of the triglyceride, which are preferential-

ly occupied by the oleic acid in animal fats. This observation has also been made by WAHLROOS (4). As from the 15th day, the oleic acid content decreases to attain at the end of the storage period 22 % of the total fatty acids. Palmitic acid follows the same evolution but to a somewhat lesser extent.

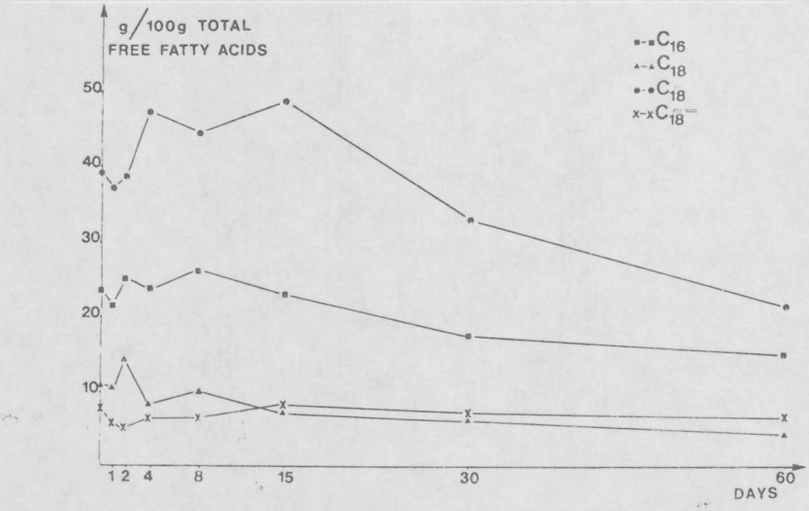

FIG.3 EVOLUTION OF MAIN FREE FATTY ACIDS

As from the 15th day, we have noted the appearance of lipid compounds not present in the initial fat:

- firstly, the short chain fatty acids ($C_{n \leq 10}$) (Figure 4), as previously detected by CANTONI (1). These acids, which arise from the degradation of the fatty acids initially present in the pork fat, represent on the 15th day about 5 % of the total fatty acids,
- secondly, we note the formation of three new compounds indicated as C_x, C_y and C_z (Figure 4). Their proportions increase after the 15th day to attain at the end of the storage period values ranging from 9 to 14 % of the total fatty acids (Figure 5).

Two of these compounds have been identified by mass spectrometry. They are α-butenyl-β-keto-octanoic acid for C_x and α, α'-dimethyl-undecanoic acid or α-ethyl-undecanoic acid for C_y.

The C_z peak has not been definitely identified but, according to the gas chromatography retention time, it could be a methylated derivative of a C_{18} fatty acid.

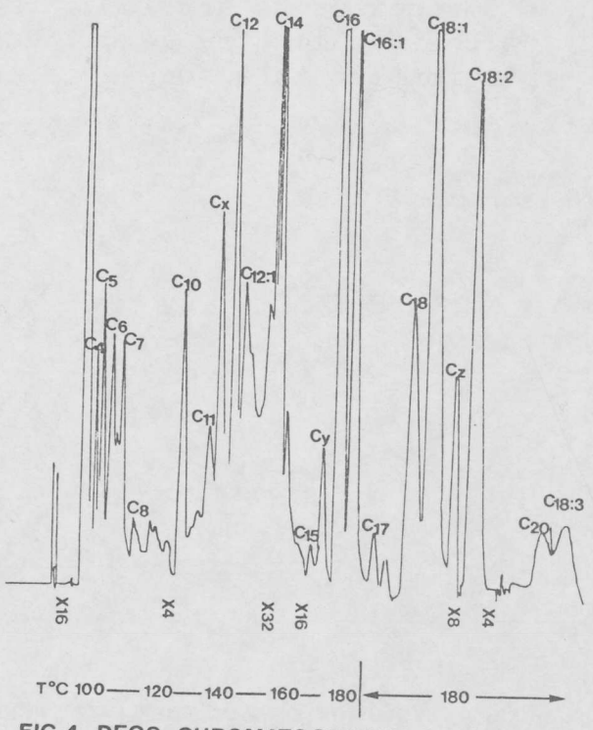

FIG.4 DEGS CHROMATOGRAPHY OF SHORT CHAIN FATTY ACIDS

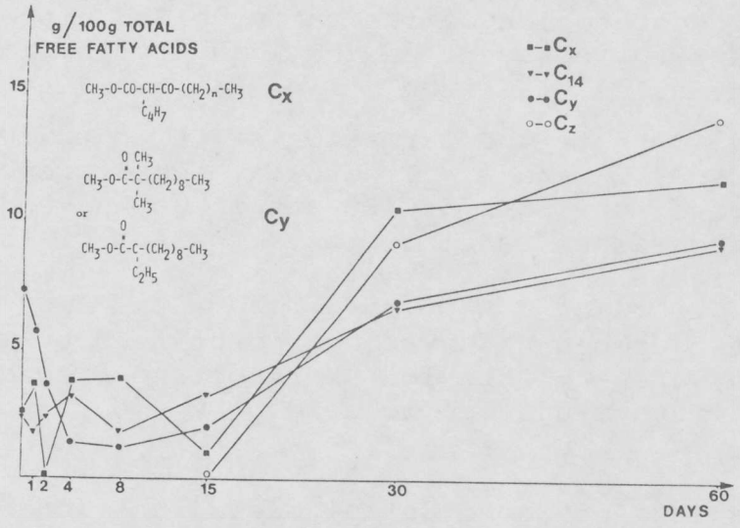

FIG. 5 EVOLUTION OF MINOR FREE FATTY ACIDS

At the end of the storage period, 20 liposoluble compounds have been identified in the "free fatty acids" fraction, in addition to the known acids of pork fat (lauric, myristic, palmitic, stearic, oleic and linoleic acids) and the previously mentioned C_x, C_y and C_z compounds, namely (Figure 6):

- aliphatic compounds with linear and ramified saturated chains of the C_9 to C_{20} series, as well as some of their 2-methyl derivatives,
- aliphatic compounds with di- and trienic unsaturated chains,
- a specific ketonic compounds.

These substances have a certain organoleptic influence, particularly the non volatile ketonic compounds.

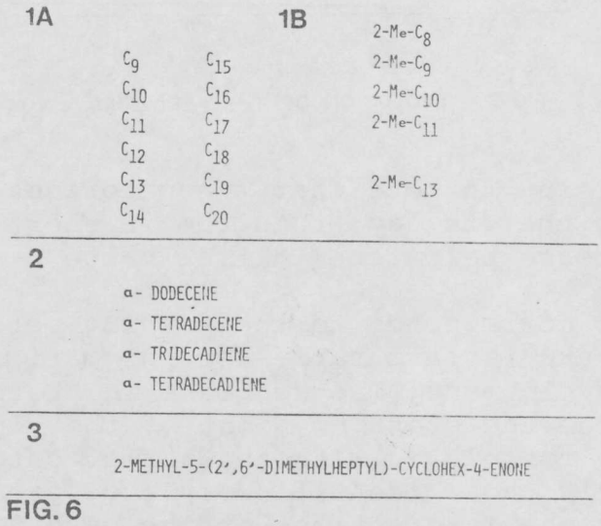

FIG. 6
LIPOSOLUBLE COMPOUNDS IDENTIFIED

LANGNER (9) in fact came to the same conclusion after having also identified some of these compounds. HALVARSON (10) in a comparative study of unsmoked and smoked sausage, had also observed the increase in carbonyls with a chain above 6 carbons in unsmoked sausage only, whereas those with a chain below 5 carbons remained remarkably constant. His theory to the effect that this increase in higher carbonyls arises from the oxidation of unsaturated fatty acids above C_{16} is confirmed herewith.

3.2. Peroxidation

Figure 7 shows the development rate of the peroxides during manufacture.

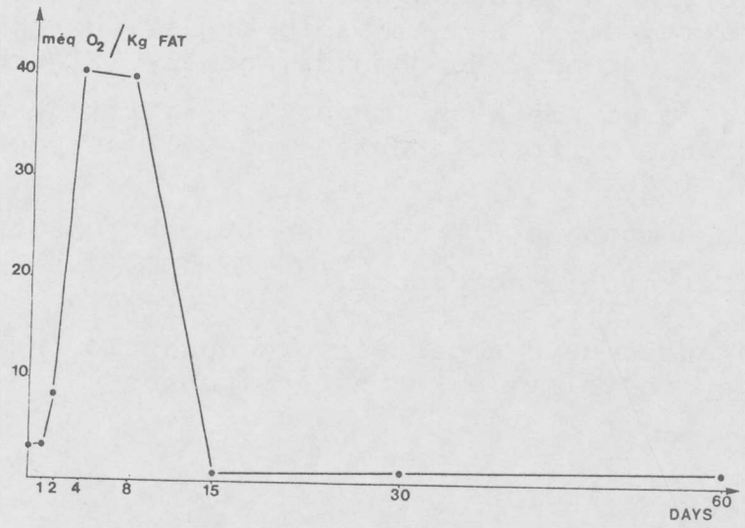

FIG. 7 EVOLUTION OF THE PEROXIDES VALUE

It is surprising to note that the peroxides increase spectacularly up to the 4th day, then remain shortly constant and finally decrease below the initial value.

The increase corresponds to the keeping period at 21° C where the temperature is favourable for enzymatic activities and microbial development. The decrease in the peroxides, which begins as from the starting point of the ripening period (12° C), is to be correlated with the formation of a series of compounds, namely those identified in the "free fatty acids" fraction and the interactions of the peroxides with proteins.

Some of these compounds have a strong influence on the taste and aroma of salami, which develop mainly between the 8th and 15th day of processing, as shown by the organoleptic evaluation of the sausages and their water extracts.

4. Conclusions

There are two distinct evolutionary stages in the lipid fractions during processing.

The first is the formation of enzymatic degradation products such as the free fatty acids, namely oleic acid. It starts on the first day of manufacture and attains a maximum level after 5 days of ripening. During this period, it is noted that there is also a significant increase in the peroxides value.

During the second stage extending over the whole final period of ripening, the products of the lipolytic attack are converted through oxidative reactions into various compounds. Among them, there are short chain fatty acids and higher ramified fatty acids containing carbonyl functions. The formation of the latter is directly related to the decrease in the free fatty acids, in particular oleic acid.

The evaluation of the degree of ripening could not, in our opinion, be made by simple measurement of the peroxides, or by that of the total free acidity, as applied by DAVIDKOVA (11) in the case of meat storage.

However, it seems from our results that the development of oleic acid is closely linked with the degree of ripening, and that the free oleic acid on initial free oleic acid ratio may provide valuable indications during processing.

Acknowledgement

The authors gratefully acknowledge Dr. B. PIOVANO (LOCATELLI SpA, Italy) for the technical assistance and the helpful collaboration in preparing the sample

Bibliography

1. CANTONI C., MOLNAR M.R., RENON P., GIOLITTI G. Industria Conserve, 40, 98 (1965)

2. DUDA Z., Fleischwirtschaft, 9, 974 (1966)

3. GIOLITTI G., Atti Soc. Ital. Sci. Veterinarie, 22, 17 (1968)

4. WAHLROOS O., NIINIVARA F.P., 15th European Meeting of Meat Research Workers (1969)

5. DGF Einheitsmethode C III 2 (1953)

6. Mc CARTHY R.D., J. Lipid Res. 3, 117 (1962)

7. MONNIN J., Mitt. Leb. Unt. u. Hyg., 55/3, 182 (1964)

8. BRACCO U., Nestlé Products Technical Assistance Ltd. Internal Report (1968)

9. LANGNER H.J., HECKEL U., MALEK E., Fleischwirtschaft, 9, 1193 (1970)

10. HALVARSON H., 17th European Meeting of Meat Research Workers (1971)

11. DAVIDKOVA E., HOLASOVA M., JOROUSOVA J., Nahrung 15/6, 611 (1971)