OLUTION OF INTRAMUSCULAR LIPIDS DURING PROCESSING OF DRY-CURED HAM

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MMARY

The quantitative and qualitative evolutions of intramuscular lipids were studied during the processing of "french type" dry-cured s. The amounts and the fatty acid composition of glycerides, phospholipids and free fatty acids (FFA) were determined in the *Biceps oris* muscle at different times in the course of processing. Lipolysis occured and continued during the whole processing time, as shown by increase (80 %) in FFA level. This phenomenon seemed to affect chiefly the phospholipids, since this fraction decreased dramatically (70 during processing. By contrast, the amounts of glycerides, which represented 86-88 % of the intramuscular lipids, did not change ificantly. This indicated that glycerides were little hydrolyzed. No significant change was found in the composition of any fraction. This ervation indicated that probably the fatty acids underwent little oxidation.

TRODUCTION

A lot of biochemical changes occur in the dry-cured ham during processing. These changes are of great importance for the quality of product. For instance, lipids are the precursors of numerous volatile compounds. While numerous works were undertaken in Italy and n about changes in lipids of both fat and lean tissues (*i.e.* CANTONI *et al.*, 1971, 1976 ; FLORES *et al.*, 1985, 1987 ; MELGAR *et al.*, 0), such research has not been performed so far, to our knowledge, on "french type" dry-cured ham. Raw material and technology differ m one country to another, so the results obtained on italian and spanish products may not be valid for french ham. For this reason, we ied the changes affecting the muscle lipids during processing of dry-cured hams according to a process usually used in France.

ATERIAL and METHODS

The 60 hams from 30 pigs were taken 24 h after slaughter. They originated from the same batch of pigs and weighed 9 to 10 kg. ty hams were analyzed at the initial time, while the 30 symetric ones were dry-salted and seasoned, following a process commonly used in nch plants. Groups of 10 hams were taken at 2, 6 and 9 months after the begenning of processing. The *Biceps femoris* muscle was oved from each ham, and the following analyses were performed : i/ total lipid extraction according to the method of BLIGH & DYER 59), ii/ separation of total lipids into neutral and polar lipids as described by JUANEDA & ROCQUELIN (1985), iii/ separation of free y acids (FFA) from the neutral lipids as described by GANDEMER *et al.* (1991). Methylation of each lipid fraction was performed ording to the method of MORRISON & SMITH (1964). Gas liquid chromatography of methyl esters was carried out using a Dani 500 omatograph, equipped with a split-splitless injector and a flame-ionization detector paired with a CR3A integrator (Shimadzu). A capillary umn (30 m length ; 0,32 mm internal diameter) coated with a polyethylene glycol stationary phase (0,25 mm thickness) (Econo-Cap ech) was used. Temperature of the column was programmed as follows : 2 min at 140 °C, 5 °C / min still 200 °C, 15 min at 200 °C, perature of the injector and the detector was 250 °C, head pressure of carrier gas (hydrogen) was 0,5 bar, and split flow rate was 40 ml / n. Identification of fatty acids was performed by comparison of their retention times with those of known fatty acids. Neutral lipids were antified by weighing, phospholipids by phosphorus measurement, methyl esters by internal standardization with heptadecanoïc acid. ycerides were defined as the neutral lipids minus the FFA. The amounts of fatty acids were expressed relative to the dry matter without salt M).

ESULTS

ANTITATIVE EVOLUTION OF THE LIPID FRACTIONS :

The fatty acids of each lipid fraction were grouped into 3 classes : saturated, monounsaturated and polyunsaturated. The quantitative olution of the 3 lipid fractions is represented figure 1. Changes affecting each class of fatty acids in the 3 lipid fractions are represented in ble 1. The glycerides were the most important fraction : they contained 86 to 88 % of the total fatty acids. The amount of fatty acids of this

fraction did not vary significantly during the processing. The levels of fatty acids of phospholipids and FFA varied very significantly (P < 0,001) with time : phospholipids decreased regularly during the seasoning, while FFA increased. At the beginning, 12 % of fatty acids belonged to the phospholipids, while 2 % were FFA ; at the end, only 3 % of the fatty acids belonged to the phospholipids, and 9 % to FFA.

Similar evolutions were observed for the different classes of fatty acids within fractions. No significant change was observed in fatty acid class of the glyceride fraction. By contrast, quantities of saturated, monounsaturated and polyunsaturated fatty acids decreased significantly in the phospholipid fraction : they varied respectively from 3,03 to 1,09 mg / g DM (P < 0,001), from 2,18 to 0,75 mg / g DM (P < 0,001) and from 5,04 to 1,65 mg / g DM (P < 0,01). These evolutions were of the same order in every class, since 61 % of the saturated fatty acids, 62 % of the monounsaturated fatty acids and 66 % of the polyunsaturated fatty acids disappeared during the 9 months. In the FFA fraction, quantities of each class increased very significantly (P < 0,001) : the saturated fatty acids vary from 0,43 to 2,97 mg / g DM, monounsaturated fatty acids from 0,47 to 2,38 mg / g DM, and the polyunsaturated fatty acids from 0,97 to 4,03 mg / g DM. These variations represented increases of 85, 80 and 75 % respectively during the period of 9 months.

COMPOSITION OF THE LIPID FRACTIONS :

The fatty acid compositions of the 3 lipid fractions are represented in Table 2.

Glycerides : the monounsaturated fatty acids were the most abundant (58 % of the total fatty acids), followed by saturated (37 %) and polyunsaturated (5 %). Oleic acid was the most abundant acid (52 %), followed by palmitic acid (25 %). Only 5 different polyunsaturated fatty acids were found, long chain fatty acids (> 20 carbons) and fatty acids with more than 4 double-bounds being absent. Only few significant changes in composition were observed throughout the process (14:0 and 20:4).

Phospholipids : the polyunsaturated fatty acids were the most abundant (49 % of the total fatty acids), followed by saturated (30 %) and monounsaturated representing 21 % of the fatty acids. Linoleic acid was the most abundant fatty acid (32 %) ; palmitic and oleic acids represented 21 and 20 % respectively. The high quantity of arachidonic acid (11 %) and the diversity of polyunsaturated fatty acids must be noticed ; long chain and fatty acids with more than 4 double-bounds were present. Composition in fatty acids did not vary significantly throughout the process.

FFA : the composition of the FFA was very close to that of the phospholipids. At the beginning, the FFA contained less saturated fatty acids than the phospholipids (24 % vs 30 %), but these proportions changed from 2 months after begenning (34 % vs 31 %). The monounsaturated fatty acids were a little more abundant in FFA than in phospholipids (26 % vs 21 %), and did not vary significantly during the processing. The polyunsaturated fatty acids changed at the opposite of the saturated fatty acids : at the same level as in the phospholipids at the beginning (50 % vs 49 %), they decreased from the second month in the FFA. These changes in FFA composition were significant only between 0 and 2 months.

DISCUSSION

Proportions of the 3 lipid fractions observed here in raw ham differed from those reported by FLORES *et al.* (1985) : these authors noticed greater amounts of FFA. By contrast, in dry-cured ham, our results were very close to those of FLORES *et al.* (1985). The increase in FFA amounts indicates that some lipolysis occurs throughout the process. The decrease in phospholipids and the similarity between the compositions of the phospholipids and FFA indicates that lipolysis affects mostly the phospholipids. This was previously observed by FLORES *et al.* (1985). The parallelism between the evolutions of the 3 lipid classes (saturated, monounsaturated, polyunsaturated) in both FFA and phospholipids indicates that the lipolysis is probably not specific for the type of fatty acid. This agrees with the data of the literature (OOSTERBAAN & JANSZ, 1965 ; THOMPSON, 1970). Our results about the composition of the glycerides and phospholipids are in agreement with those of GANDEMER *et al.* (1985), LESEIGNEUR-MEYNIER (1991) and FLORES *et al.* (1987) concerning raw ham, and with FLORES *et al.* (1987) concerning dry-cured ham. By contrast, our results concerning the composition of the FFA differ from those of FLORES *et al.* (1987), MELGAR *et al.* (1990) and ASTIASARAN *et al.* (1991) : we found much more polyunsaturated than they did. It is known that oxidation of the fatty acids preferentially affects the double-bounds (FRANKEL, 1984). As a consequence, the most unsaturated fatty acids are the most liable to be oxidized. The absence of significant changes in the composition of any fraction during the process shows that this phenomenon was quantitatively low.

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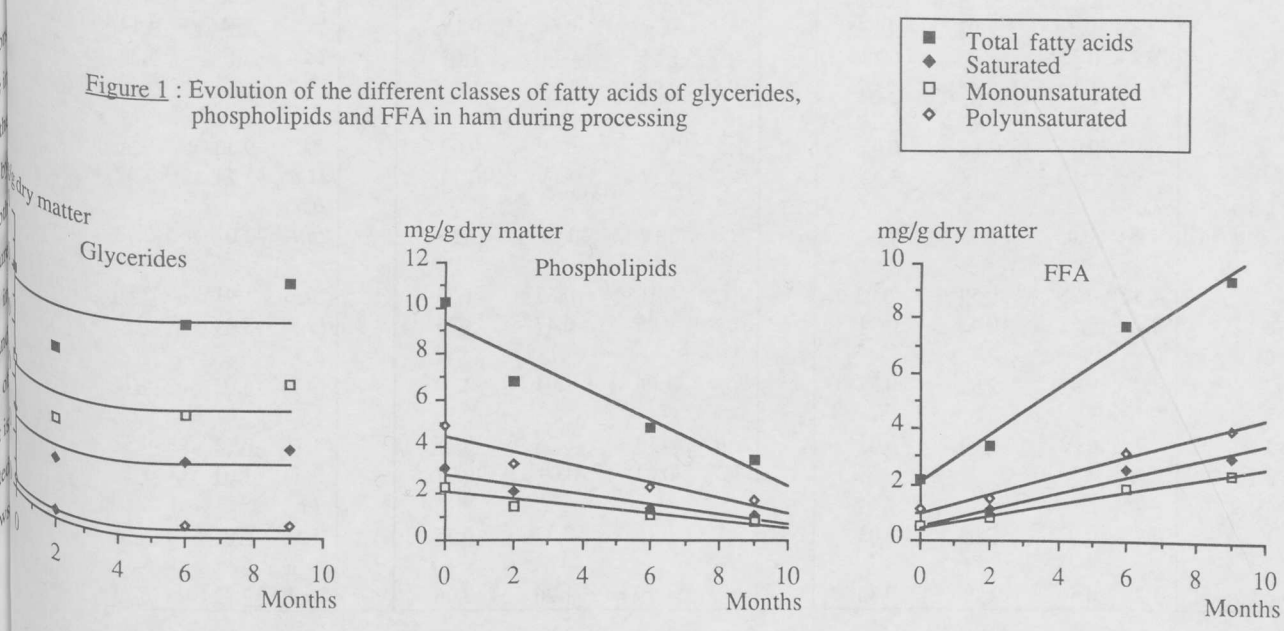

Figure 1 : Evolution of the different classes of fatty acids of glycerides, phospholipids and FFA in ham during processing

Months	0	2	6	9	Time effect
GLYCERIDES :					
Saturated	28,5	-2,27	-0,57	-1,54	
Monounsaturated	44,7	-3,03	2,78	1,21	
Polyunsaturated	3,8	0,10	0,94	0,28	
Total	77,0	-5,20	3,16	-0,05	
PHOSPHOLIPIDS :					
Saturated	3,03	-0,87 a	-1,88 b	-1,74 b	***
Monounsaturated	2,18	-0,65 a	-1,35 b	-1,22 b	***
Polyunsaturated	5,04	-1,61 a	-3,22 b	-3,21 b	**
Total	10,3	-3,1 a	-6,5 b	-6,2 b	***
FREE FATTY ACIDS :					
Saturated	0,43	0,69 b	2,24 a	2,51 a	***
Monounsaturated	0,47	0,32 b	1,52 a	1,90 a	***
Polyunsaturated	0,97	0,60 b	2,53 a	2,90 a	***
Total	1,87	1,61 b	6,29 a	7,30 a	***

Table 1 :
Changes in the quantities of fatty acids in ham during processing
The first column indicates the levels before processing (0 time)
The other columns indicate the differences between values at given times and 0 time
Underlined values indicate a significant change
Values with different indices (a, b) are significantly different at 5 % level of probability
*** : P < 0,001 ; ** : P < 0,01

Table 2 :
Changes in the composition of fatty acids in ham during processing
The first column indicates the composition before processing (0 time)
The other columns indicate the differences between values at given times and 0 time
Underlined values indicate a significant change
Values with different indices (a, b) are significantly different at 5 % level of probability
*** : P < 0,001 ; * : P < 0,05
(1) : 17:1, 20:1 ; (2) : 20:2, 20:3 (glycerides) ; 20:2, 20:3, 22:4 (phospholipids and FFA) ; (3) : 20:5, 22:6

	GLYCERIDES					PHOSPHOLIPIDS					FREE FATTY ACIDS			
Months	0	2	6	9	Time effect	0	2	6	9	Time effect	0	2	6	9
14:0	1,6	-0,08 b	-0,14 b	-0,32 c	***						0,5	-0,03	-0,07	0,05
16:0	24,8	-0,31	-2,03	-1,84		21,2	-0,54	-0,66	0,19		16,2	7,94 a	4,14 b	2,96 b
18:0	10,7	0,34	-0,32	0,13		8,3	1,55	1,24	1,64		6,8	2,01 b	5,38 a	5,55 a
Saturated	37,1	-0,05	-2,48	-2,02		29,5	0,98	0,58	1,82		23,6	9,92	9,46	8,55
16:1	4,4	0,04	0,17	0,05		1,2	-0,41	-0,09	0,00		2,7	-0,30 ab	-0,46 b	0,00 ab
18:1	52,4	-0,68	1,18	1,32		19,7	0,27	0,24	0,73		22,8	-1,74 ab	-2,52 b	1,71 a
Others (1)	1,0					0,7					0,6			1,76 a
Monounsaturated	57,8	-0,45	1,43	1,66		21,4	0,19	0,68	1,23		26,1	-2,01 ab	-2,73 b	
18:2n-6	4,6	0,25	0,59	-0,02		32,2	-0,15	-0,65	-1,23		29,3	-1,91	-2,66	-4,35
20:4n-6	0,1	0,22 ab	0,42 a	0,34 ab	*	10,8	-0,75	-0,47	-1,35		12,5	-3,34 ab	-1,53 a	-2,33 a
Others (2)	0,0					3,0					2,9			-7,22
N-6	4,8	0,47	1,01	0,32		46,0	-1,06	-1,04	-2,50		44,7	-6,02	-4,72	
18:3n-3	0,4	0,02	0,04	0,03		1,0	-0,19	-0,25	-0,31		1,3	-0,18 a	-0,32 b	-0,36 b
22:5n-3						1,3	-0,04	0,09	-0,07		2,6	-1,04	-1,23	-1,46
Others (3)						0,8					1,6			1,28
N-3	0,4	0,02	0,04	0,03		3,1	-0,13	-0,22	-0,55		5,5	1,40	1,37	
Polyunsaturated	5,2	0,50	1,05	0,36		49,1	-1,19	-1,26	-3,06		50,2	-7,32	-6,73	-10,31