PHOSPHOLIPID CHANGES DURING FREEZING OF PORK TREATED BY DIFFERENT MECHANICAL AND HEAT PROCEDURES

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INTRODUCTION

PHOSPHOLIPIDS, due to their composition, are very liable to oxidative changes and the appearance of warmed over, stale and rancid flavor in meat is attributed to them. Changes of phospholipid content during meat storage have been examined to a small extent (Awad et al., 1968; Hood and Allen, 1971; Jakubov et al., 1975; Krzywicki, 1965; Krzywicki and Ratcliff, 1967) and in the available literature we have not found data on the changes of phospholipids and neutral lipids during storage of meat treated by different mechanical and heat procedures. For that reason, in our previous works (Djordjević et al. 1978; Djordjević et al., 1979) we examined the changes of total lipids, phospholipids and neutral lipids caused by mechanical and heat treatments and during cooling. The aim of the present study was to follow these changes during freezing of meat treated by different mechanical and heat procedures, being of importance for industrial practice and culinary art.

MATERIALS AND METHODS

M. LONGISSIMUS dorsi of domestic white meaty pigs (females, about 6 months old, 75-85 kg in dressed weight, deriving from the same farm and fed in the same way) was used for the examinations. After cooling of sides at 2-4°C for 24 hours, from longissimus dorsi muscles of approximately the same pH value, the section covering the last two thoracic and the first three lumbar vertebrae was taken. The samples were freed of visible fatty and connective tissues. Two ways of mechanical treatment were applied: intensive grinding, namely preparation of homogenates, and cutting into pieces (meat slices as thick as vertebrae were devided by two cross cuts into four parts. On that occasion, 20% NaCl-water solution was added or injected in the quantity of 10%.

The following heat treatments were applied: pasteurization (200 g cans - at 80°C for about 30 minutes, till the obtainment of 70°C in the can content center), sterilization (200 g cans - 118°C/30 minutes, maximum temperature in the can content center - 115°C) and roasting (muscle pieces, being on the surface rubbed in with sodium chloride in the quantity of 1% on meat weight, were roasted in dish-shaped aluminium foils in drying oven at 180-200°C till the obtainment of 65-70°C in the meat center).

Raw meat and treated samples were examined immediately after mechanical and heat treatments and after storage for 30, 60, 90, 120, 150 and 180 days at - 18°C, packed in aluminium foil. The surface layer, 8 mm in width, and the central part of roasted meat slices were separately analysed. Frozen samples were analysed after being kept at 2 - 3°C for 16 hours. From each experimental group, there were analysed six samples in the above mentioned periods. The same procedures as those described in the previous work (Djordjević et al.,1978) were used for the determination of phospholipid content, peroxide value, TBA number and the content of free fatty acids in total lipids, phospholipids and neutral lipids.

Mean value, standard deviation and variance coefficient were determined. Influence of mechanical and heat treatments on the changes of lipids, namely phospholipids during storage of samples at -18°C, were examined by t-test analysis of differences (Snedecor and Cochran, 1967).

RESULTS AND DISCUSSION

THE PHOSPHOLIPID content decreased constantly in all samples during storage at -18°C (Table 1), being always lower in homogenates than in meat pieces. In our previous work, significantly lower phospholipid content was established in raw homogenates than in raw meat pieces at the end, namely on the 15th day of their storage

Changes of phospholipid content in samples during storage at $-18^{o}C$, dependent on the way of mechanical and heat treatments

Table 1.

Treatment	Days of storage						
	0	30	60	90	120	150	180
Mechanical treatment				$\bar{x}$			
a. Homogenate	0.552	0.520	0.490	0.462	0.440	0.423	0.416
b. Meat pieces	0.557	0.527	0.497	0.470	0.449	0.432	0.422
Heat treatment							
1. Pasteurization							
a_1 Homogenate	0.530	0.499	0.468	0.442	0.421	0.405	0.393
b_1 Meat pieces	0.543	0.514	0.481	0.457	0.437	0.418	0.405
2. Sterilization							
a_2 Homogenate	0.524	0.494	0.467	0.439	0.415	0.399	0.396
b_2 Meat pieces	0.536	0.505	0.476	0.453	0.426	0.413	0.398
3. Roasting							
c_1 Surface layer	0.598	0.558	0.521	0.491	0.467	0.449	0.439
c_2 Central part	0.610	0.570	0.534	0.503	0.477	0.459	0.448

Treatments	Differences $\lvert d\bar{x} \rvert$						$\lvert d\bar{x}_{\%M/DM} \rvert$
	30	60	90	120	150	180	180
a :b	0.007	0.007	0.008	0.009	0.009	0.006	0.56
a_1:b_1	0.015·	0.013	0.015	0.016	0.013	0.012	2.09·
a_2:b_2	0.011	0.009	0.014·	0.011·	0.014··	0.002	0.44
a_1:a_2	0.005	0.001	0.003	0.006	0.006	0.003	0.45
b_1:b_2	0.009	0.005	0.004	0.011	0.005	0.007	1.20
a_1:a	0.021··	0.022··	0.020·	0.019·	0.018·	0.023··	3.86···
a_2:a	0.026··	0.023·	0.023··	0.025··	0.024··	0.020···	3.41···
b_1:b	0.013	0.016·	0.013	0.012	0.014	0.017·	2.33·
b_2:b	0.022··	0.021··	0.017··	0.023··	0.019··	0.024···	3.53···
c_1:b	0.031···	0.024··	0.021··	0.018·	0.017·	0.017	6.56···
c_2:b	0.043···	0.037···	0.033···	0.028···	0.027···	0.026··	4.49···
c_1:c_2	0.012·	0.013·	0.012	0.010	0.010	0.009	2.07
c_1:b_1	0.044···	0.040···	0.034··	0.030··	0.031···	0.034·	4.23··
c_1:b_2	0.053···	0.045···	0.038···	0.041···	0.036···	0.041··	3.03·
c_2:b_1	0.056···	0.053···	0.046···	0.040···	0.041···	0.043···	2.16
c_2:b_2	0.065···	0.058···	0.050···	0.051···	0.046···	0.050···	0.96

$\bar{x}$ - mean value of phospholipid content, %

$\lvert d\bar{x} \rvert$ - absolute value of the difference of phospholipid content

$\lvert d\bar{x}_{\%M/DM} \rvert$ - absolute value of the difference of phospholipid percentage in sample in relation to its quantity in raw meat (M), expressed on dry matter basis (DM)

·$p < 0.05$ ··$p < 0.01$ ···$p < 0.001$

at $2-3^{o}C$, regardless of the expression way - directly or on dry basis (Djordjević et al., 1979). In the case of frozen-stored samples these differences were not significant neither at the end nor in any of the examined periods of storage. This is possible due to the decrease in phospholipid extractability from frozen samples, established by Fishwick (1968) in chicken meat. The consequence of this is probably the decrease - in closely equal percentages - in phospholipid content in meat pieces and in homogenates at the end of storage at $-18^{o}C$.

In all examined periods of storage at $-18^{o}C$, pasteurized and sterilized samples had significantly lower phospholipid content than raw samples being mechanically treated in the same way, whereas there were nor significant differences between equally mechanically treated pasteurized and sterilized samples. Almost the same was observed regarding the content of free fatty acids. After storage at $2-3^{o}C$, the decrease of phospholipid content was more pronounced in the surface layer than in the central part of roasted meat slices (Djordjević et al., 1979), whereas at the end of storage at $-18^{o}C$ - calculated on dry basis - this decrease was markedly higher in the central part. However, differences in the percentage of phospholipid contents between surface layers and central parts of roasted meat slices, in relation to the quantity in raw, namely fresh meat, were not significant.

Considerably higher peroxide values and TBA numbers in raw homogenates than in meat pieces are, in our opinion, the result of the exposure of a larger surface to the oxygen influence and the increased possibility of the oxygen incorporation into meat during grinding. These factors influenced the increase of oxidation during grinding and a relatively rapid oxidation of meat during storage. More pronounced oxidative changes in heat treated samples than in raw meat samples being also mechanically treated, could be explained by the fact that heat denaturation of protein in the lipoproteins results in the phospholipid being more susceptible to oxidation by ferric haem pigment and other pro-oxidants (Yamauchi, 1972) as well as by better diffusion of oxygen within heat treated tissue (Keskinel et al., 1964).

Higher oxidative changes in pasteurized than in equally mechanically treated sterilized samples, registered immediately after heat treatments, were also observed during storage in frozen state. Differences in peroxide

Changes of peroxide value[1], TBA number[2] and free fatty acids[3] in samples during storage at -18°C, dependent on the way of mechanical and heat treatments[4]

Table 2.

Treatments	Differences $\|d\bar{x}\|$																	
	Peroxide value						TBA number						Free fatty acids					
	30	60	90	120	150	180	30	60	90	120	150	180	30	60	90	120	150	180
a :b	3.28	2.44	3.03	2.08	2.14	1.72	3.68	1.32	7.69	12.60	13.70	14.35	1.32	1.25	0.53	0.41	1.01	0.98
a_1:b_1	1.26	1.80	2.91	2.03	2.70	3.28	2.49	6.87	13.83	11.83	13.46	12.34	0.94	1.27	0.52	0.65	0.94	0.94
a_2:b_2	1.15	3.86	3.43	1.83	1.08	5.76	2.89	7.13	9.44	11.28	9.58	9.96	0.37	0.08	0.45	0.99	0.84	0.74
a_1:a_2	1.23	0.63	1.76	3.82	0.32	3.08	0.24	0.34	5.82	5.05	7.62	3.89	0.07	0.18	0.28	0.23	0.04	0.02
b_1:b_2	1.12	2.69	2.28	0.04	1.94	0.60	0.16	0.60	1.43	4.50	3.74	1.51	0.64	1.01	0.35	0.11	0.14	0.22
a_1:a	2.96	2.58	2.52	3.40	2.60	2.46	1.25	5.17	6.64	4.64	4.55	1.33	0.32	0.11	0.09	0.37	0.84	1.33
a_2:a	1.73	1.95	0.76	0.42	2.92	5.54	1.49	4.83	0.82	0.41	3.07	2.56	0.39	0.07	0.19	0.14	0.76	1.31
b_1:b	4.98	3.22	2.64	3.45	2.04	0.90	2.44	0.38	0.50	5.41	4.79	3.34	0.70	0.09	0.08	0.61	0.77	1.29
b_2:b	3.86	0.53	0.36	3.49	3.98	1.50	2.28	0.98	0.93	0.91	1.05	1.83	1.34	1.10	0.27	0.72	0.63	1.07
c_1:b	4.43	5.95	5.54	4.35	4.04	2.65	4.56	4.85	7.18	9.57	7.49	10.16	1.82	1.10	0.84	0.44	0.42	0.14
c_2:b	3.98	2.52	4.41	4.74	3.34	2.41	3.01	4.35	6.80	7.80	7.74	8.01	1.36	0.76	0.19	0.26	0.26	0.58
c_1:c_2	0.45	3.43	1.13	0.39	0.70	0.24	1.55	0.50	0.38	1.77	0.25	2.15	0.46	0.34	0.65	0.70	0.68	0.44
c_1:b_1	0.55	2.73	2.90	0.90	2.00	1.75	2.12	5.23	6.68	4.16	2.70	6.82	1.12	1.01	0.92	1.05	1.19	1.15
c_1:b_2	0.57	5.42	5.18	0.86	6.06	1.15	2.28	5.83	8.11	8.66	6.44	8.33	0.48	0.00	0.57	1.16	1.05	0.93
c_2:b_1	1.00	0.70	1.77	1.29	1.30	1.51	0.57	4.73	6.30	2.39	2.95	4.67	0.66	0.67	0.27	0.35	0.51	0.71
c_2:b_2	0.12	1.99	4.05	1.25	0.64	0.91	0.73	5.33	7.73	6.89	6.69	6.18	0.02	0.34	0.08	0.46	0.37	0.49

1) meq peroxide oxygen/1000 g of lipids 2) mg malonaldehyde/1000 g of lipids 3) % oleic acid in 100 g of lipids

4) letters a, b, a_1, b_1, a_2, b_2, c_1 and c_2 denote the same mechanical and heat treatments as in table 1.

$^{\cdot}P < 0.05$ $^{\cdot\cdot}P < 0.01$ $^{\cdot\cdot\cdot}P < 0.001$

Contribution of phospholipids (%) in lipid oxidation and hydrolysis during storage of samples at - 18°C

Table 3.

Days of storage	Homogenate						Meat pieces						Roasted meat			
	Raw		Pasteurized		Sterilized		Raw		Pasteurized		Sterilized		Surface layer		Central part	
	$\bar{x}$	C_v	$\bar{x}$	C_v	$\bar{x}$	C_v	$\bar{x}$	C_v	$\bar{x}$	C_v	$\bar{x}$	C_v	$\bar{x}$	C_v	$\bar{x}$	C_v
I. Peroxide value																
30	85.31	5.14	83.11	6.39	83.05	6.48	82.31	8.79	80.14	7.96	80.11	9.48	88.95	7.05	86.28	8.89
60	84.98	4.10	78.13	9.92	79.11	7.57	79.35	8.96	78.33	8.42	81.82	8.08	84.93	5.34	82.11	12.62
90	81.11	5.07	81.12	6.60	82.36	8.17	80.59	7.42	78.04	8.04	76.35	10.04	79.35	10.54	75.91	7.48
120	79.10	4.29	76.38	5.89	75.35	7.46	78.56	6.35	74.60	8.96	75.11	9.89	76.28	11.53	79.38	9.91
150	80.19	4.84	74.05	7.73	71.38	7.97	75.12	8.40	76.12	12.25	77.46	9.73	76.44	8.94	72.17	14.96
180	75.36	4.69	71.35	11.82	72.95	8.24	79.78	8.25	72.65	10.33	73.21	5.89	72.68	7.45	74.02	9.99
II. TBA number																
30	90.38	3.19	92.75	3.64	90.41	3.02	89.10	4.72	90.84	3.54	91.35	3.20	93.10	2.98	92.09	4.17
60	88.89	5.03	89.11	3.77	90.62	3.75	88.39	4.55	88.44	4.93	89.41	3.74	91.39	2.64	90.17	3.48
90	86.73	4.41	91.04	3.26	89.17	4.59	88.75	4.30	88.02	3.48	90.71	3.24	92.03	3.29	89.43	5.91
120	87.10	4.70	90.11	2.99	87.43	5.92	87.95	3.22	90.11	3.14	89.35	5.35	90.77	3.77	91.33	4.09
150	84.47	4.69	86.39	4.55	88.98	4.46	80.04	14.35	87.32	3.05	87.62	5.49	88.96	3.63	88.30	5.38
180	84.92	6.44	86.44	6.67	86.03	4.44	84.92	4.38	85.64	8.53	86.15	8.70	87.34	5.94	89.25	3.66
III. Free fatty acids																
30	65.66	7.99	65.31	9.10	66.22	9.02	66.55	10.76	65.31	9.10	65.34	13.39	64.90	13.60	67.92	6.45
60	67.11	8.40	67.07	5.77	67.12	6.98	64.52	15.25	67.07	5.77	68.35	4.01	68.38	6.53	67.97	10.47
90	66.78	13.90	68.47	6.47	68.08	4.94	66.92	10.66	68.47	6.47	69.15	6.28	66.65	8.33	69.37	5.02
120	68.91	7.04	71.12	3.99	70.35	4.35	67.14	4.98	71.12	3.99	68.12	3.66	70.62	3.87	71.98	3.93
150	71.49	3.69	72.11	4.67	69.22	5.60	72.59	2.95	72.11	4.67	71.91	4.63	69.78	7.15	71.96	4.32
180	72.95	9.18	70.29	3.38	70.11	12.58	71.14	3.15	70.29	3.38	71.87	2.56	72.70	7.69	70.93	6.42

$\bar{x}$ - mean value

C_v - variance coefficient

values and TBA numbers between equally mechanically treated pasteurized and sterilized samples were significant in almost all examined periods of freezing. These differences were higher during storage of samples in frozen state than during cooling, being more pronounced in the case of homogenates. The highest oxidation degree was observed in pasteurized and then in sterilized homogenates, being of the similar intensity in the surface layer of roasted meat slices. The central part of roasted meat slices shows oxidation to somewhat higher extent than pasteurized meat pieces. During storage of heat treated samples at -18°C, the lowest oxidation was observed in sterilised meat pieces, being somewhat higher than in raw pieces. The rancidity of frozen samples, according to sensory evaluation, was more intensive than shown by peroxide values and TBA numbers. The differences between taste panel observations and chemical indices are probably due to the reduced extractability of phospholipids from frozen meat (Fishwick, 1968), the malonaldehyde loss in the reactions with meat constituents and in the formation of carbonyl addition products at low temperatures (Kwon et al., 1965; Witte et al., 1970). According to Buttkus (1967), the rate of reaction between α-amino acids of myosin and malonaldehyde is greater at -20°C than at 0°C.

From the results presented in Table 3, it can be seen that 71.35 - 86.28% of peroxide value and 80.04 - 92.75% of TBA number originate from phospholipid changes, whereas the rest, i.e. 13.73 - 28.65%, namely 7.25 - 9.96%, originate from the changes of neutral lipids. Higher contribution of phospholipids to oxidative changes in the initial phase of storage and in frozen state is probably due to their liability to oxidation and their higher quantity at the begining of storage. From the total content of free fatty acids, 64.52 - 72.59% are free fatty acids from phospholipids and 27.41 - 35.48% from neutral lipids. The tendency of the increase of phospholipid contribution to these changes during storage in frozen state, can be explained by their decomposition.

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