

Carbonyls in Oxidizing Fat.

11. The Effect of the Pro-oxidant Activity of Sodium Chloride on Pork Tissue

SUMMARY—Oxidation of freezer-stored, sodium chloride-cured pork was characterized by a rapid rate and moderately high monocarbonyl/peroxide ratios. Increase in the concentration of NaCl accelerated autoxidation, but did not affect hydroperoxide decomposition to monocarbonyl compounds. High proportions of lean increased autoxidation and the monocarbonyl-peroxide ratios. Sodium nitrite (0.03%) catalyzed autoxidation by reaction with the meat pigment in an apparently independent effect to that exerted by NaCl. Composition of the free monocarbonyl compounds indicated linoleate specificity in peroxide decomposition, although hematin catalysis is nonspecific in its attack on unsaturated fatty acids. Possible direct effects of NaCl did not appear to involve a reactive chloride ion.

INTRODUCTION

THE PRO-OXIDANT EFFECT of NaCl on the triglycerides in meat is one of the most puzzling influences in food science. Observations reported sometimes seem contradictory, and it is possible that a number of factors can operate jointly. Banks (1937) and Lea (1939) suggested that NaCl was not itself a pro-oxidant, but promoted the activity of lipoxidase in meats. However, Banks (1944) and Tappel (1952, 1953) showed that there is no lipoxidase in meat, and it was indicated that the activity promoting autoxidation was due to heme pigments. Separately, the pigments of meat are powerful catalysts of fatty acid and triglyceride autoxidation. However, freezer-stored fresh meat is relatively stable despite the presence of such catalysts.

There is no evidence of a direct specific effect by NaCl on oxidation catalyzed by myoglobin or hemoglobin. Chang *et al.* (1950) found NaCl did not accelerate oxidation being promoted by clear meat extracts or hemoglobin solutions. However, Lea (1939) observed a pro-oxidant effect of NaCl on oxidation caused by expressed meat juice. In this instance, salt may have acted on the tissue cells or fibers in the press fluid.

NaCl has a powerful influence on meat proteins and pigments (Coleman, 1951; Grant, 1956). Gibbons *et al.* (1951) reported that rancidity of bacon sides developed more rapidly as freezer storage temperatures were lowered. Chang *et al.* (1950) observed a direct pro-oxidant effect by 15% or higher NaCl solutions or dry salts where a large surface of contact with lard existed. It was concluded that the freezing process might be similar to a dehydration process. As an example of the effect of physical conditions, Mabrouk *et al.* (1960) found that autoxida-

tion of aqueous emulsions of methyl linoleate were inhibited with increase in dissolved NaCl.

This work was undertaken to determine the monocarbonyl compounds formed by NaCl promoted autoxidation of pork triglycerides. It was also expected that information might be obtained concerning the mechanisms involved in this rancidity problem.

EXPERIMENTAL

PAIRED BACON SIDES were each divided into six segments as described by Gaddis (1952) to give mated samples. Mixtures of ground pork lean and back fat furnished homogenous material for selected studies and experimental setups. After dry curing with analytical grade salts, the bacon segments were sliced (commercial thickness) and stored at 0°F.

Fat for chemical examination was obtained by warming ground experimental samples to 40–50°F and immediately pressing and filtering through cheesecloth. The resulting clear fat or lard was used for monocarbonyl and peroxide determinations. The purpose of this study was to examine the intermuscular fat or triglycerides. If oxidation of polar lipids has occurred, volatile breakdown products might be expected to have diffused into the fat. This procedure of fat separation was used because solvent extraction necessitates the use of methods of carbonyl isolation which break down hydroperoxides (Gaddis *et al.*, 1965, 1966b). The very mild rendering procedure used causes little change in hydroperoxides and free monocarbonyls.

Free volatile carbonyl compounds were isolated from 10 g samples by the vacuum distillation method of Lea *et al.* (1962) as modified by Gaddis *et al.* (1960) and Gaddis *et al.* (1965). The volatile carbonyls were converted to 2,4-dinitrophenylhydrazone derivatives, and the monocarbonyl hydrazone fraction was separated by chromatography on hydrated alumina as described by Gaddis *et al.* (1959a). Monocarbonyl hydrazones were separated into alkanal-alk-2-enal, and alk-2,4-dienal classes by the method of Gaddis *et al.* (1959b). From this resolution, data enabled the determination of proportions of the classes of monocarbonyl compounds. Each class was separated into individual compounds and the compounds were estimated as described by Ellis *et al.* (1959).

Peroxides were determined by the method of Kenaston *et al.* (1955) and expressed as meq/100 g.

RESULTS AND DISCUSSION

Some characteristics of stored, cured pork

Preliminary experiments indicated that NaCl-cured, freezer-stored pork fatty tissue had much higher monocarbonyl/peroxide ratios than observed in previous oxidation studies with lard. Uncured, freezer-stored pork developed peroxides very slowly. Extensive hydroperoxide breakdown to carbonyl compounds with propagation of autoxidation is a characteristic of hematin catalysis (Tappel, 1955). Zipser *et al.* (1964) have commented on the effect of strong peroxide decomposers on TBA number/peroxide ratios. The degree of spontaneous hydroperoxide breakdown to monocarbonyls would appear of possible value in detecting changes in and judging the type of prooxidant activity involved.

Fat tissue well separated from lean in stored bacon slices (NaCl-cured) showed accelerated oxidation, but fat immediately adjacent to the lean streaks had somewhat greater peroxide values and much higher monocarbonyl values and percentage of alkanal compounds. The data suggested that the NaCl-cured lean had a special effect on tissue fat oxidation.

Paired 2% and 6% NaCl-cured bacon segments from one hog were compared after 0°F storage at intervals up to 139 days. Autoxidation was rapid in the cured samples. Uncured samples showed hardly perceptible oxidation during the 139 days of storage. Although significant differences were evident, oxidation progression was not smooth due to the wide variation in composition of the cuts.

A mixture of ground back fat and lean in 1:1 proportions treated with 2, 4 and 6% NaCl had fairly smooth progression in oxidation when stored at 0°F for 20, 40, 57, 90 and 110 days. Degree of oxidation was directly related to the NaCl content. Effect of NaCl concentration on measurements representative of autoxidative characteristics is shown in Table 1. No consistent differences in monocar-

Table 1. Effect of NaCl concentration on autoxidation characteristics.

1:1 Back fat-lean-mixture 0°	Ratios		
	Monocarbonyl $\mu\text{m}/10\text{ g}$	Monocarbonyl to PV	Enal to dienal
90 Days			
2% NaCl	2.0	0.1	1.0
4% NaCl	2.3	0.2	1.0
6% NaCl	2.9	0.1	0.9
110 Days			
2% NaCl	2.7	0.2	1.1
4% NaCl	2.7	0.1	0.9
6% NaCl	3.4	0.1	1.1

bonyl/peroxide and alk-2-enal/alk-2,4-dienal ratio were found. The former ratio has already been discussed as an indication of degree of peroxide breakdown and type of catalytic activity. This result could be construed to indicate that the acceleration of oxidation due to increase in NaCl was not due to augmented catalytic action. Possibly this might be a clue to the direct effect of NaCl that has been suggested.

In this experiment, individual alkanals C₂, C₃, C₆ and

C₉; alk-2-enals C₇, C₈, C₉, C₁₀ and C₁₁; and alk-2,4-dienals C₇, C₉ and C₁₀ were detected and measured. No important differences due to NaCl concentration were noted. C₈ Alkanal, characteristic of oleate, was not detected. There was an increase in proportion of alkanals with NaCl concentration and degree of autoxidation. Such an increase as oxidation progresses has been commonly noted (Ellis *et al.*, 1959).

Effect of proportion of lean

The influence of amount of lean at constant (4%) NaCl content was examined next. As shown in Table 2, the

Table 2. Effect of proportions of lean on oxidation characteristics and alkanal composition of back fat-lean mixtures stored 90 days at 0°F.

	% Lean			
	10	20	50	70
Monocarboxyls μM 10 g	1.6	1.9	2.3	5.1
Ratio—monocarboxyls to PV's	0.11	0.14	0.16	0.16
Ratio—enals to dienals	1.4	1.1	1.0	1.2
% Alkanals				
C ₂	6	3	5	3
C ₃	8	5	4	tr
C ₆	58	67	72	77
C ₉	5	4	3	tr
Total	77	79	84	80

rate of autoxidation increased sharply with the amount of lean in the mixtures. The monocarbonyl/peroxide ratio tended to increase with the lean. A change in this ratio could mean differences in type of catalytic activity. This catalysis might be due to increase in heme pigments or some other active component in the salt-treated lean. There was a trend toward a decrease in the enal-dienal ratio. This might mean a change in the linoleate hydroperoxide isomers, more breakdown of dienal precursors, or simply a greater rate of oxidation of linoleate (Gaddis *et al.*, 1966b).

Table 2 shows that increase in salted lean concentration changed the quantitative composition of the alkanals. C₆ Alkanal increased nearly 20%, and there were definite decreases in C₃ and C₉ alkanals. However, increases in total alkanals were small. The effect of increased cured lean appeared to consist mostly in a selective action toward greater autoxidation of linoleate or breakdown of linoleate hydroperoxides. This seems significant because oleate is by far the major unsaturated fatty acid in pork fat; linoleate amounts to only 5–10% of the total. Tappel (1955) has emphasized that hematin catalysis is non-specific, and that rates are a function of the unsaturation of the lipid as in simple autoxidation.

Mixtures of the above lean-back fat proportions without NaCl had peroxide values in the region of about 17 after 365 days at 0°F. There was only a very small effect of amount of lean on degree of oxidation. Monocarbonyl/peroxide ratios were much higher than those of the salt-treated samples. There was scarcely an appreciable effect

of concentration of lean on the ratios, which were on about the same level as values found for uncured bacon fat (Table 3). The proportion of alkanals was similar to that usually observed at that level of autoxidation. These data indicate significant differences in oxidation characteristics, presumably due to type of catalysis, between cured and uncured pork tissue triglycerides.

Simple and catalyzed autoxidation

The oxidation of ground back fat containing 6% NaCl was compared with 1:1 back fat-lean portions containing 2% and 6% NaCl when stored at 0°F for 26, 42, 58, 93 and 112 days. Autoxidation progressed smoothly in all three groups of samples. Peroxide formation was rapid in the cured back fat samples. In Table 3, oxidation characteristics are compared with similar data for uncured bacon fat and rendered lard (Gaddis *et al.*, 1966b). Significant differences in degree and type of catalysis seem to be indicated by the wide range in the ratios of the four kinds of samples. Lard, presumably nearly free of catalysts, had a very low proportion of alk-2,4-dienals and a low yield of monocarbonyls.

Uncured bacon tissue triglycerides which contained potential catalysts had a very high conversion of hydroperoxides to monocarbonyls and also a low proportion of alk-2,4-dienals. The previously mentioned unsalted samples containing different levels of lean showed little effect of composition on the ratios.

NaCl had a powerful influence on the amount and rate of autoxidation in the lean-containing samples. The effect of salt on ratios resulted in a lower conversion of hydroperoxides to monocarbonyls and increase in proportion of alk-2,4-dienals. This suggests activation by NaCl of a component in the lean that changed the oxidation characteristics of pork adipose tissue. Production of more dienals may be related to changes in hydroperoxide isomer equilibrium. However, it is most likely due to increased rate of oxidation of linoleate or breakdown of its hydroperoxides or alternatively autoxidation of polyunsaturated fatty acids of the polar lipids. Dienal formation has been considered in earlier publications (Gaddis *et al.*, 1966a), and it is otherwise usually increased by heat effect on the hydroperoxides (Gaddis *et al.*, 1959a).

Differences in individual alkanals were examined (Table 4). The lard, an example of uncatalyzed autoxidation

(Gaddis *et al.*, 1966b), had much lower proportions of C₆ alkanal (linoleate) and higher proportions of C₃ alkanal (linolenate) and C₈ and C₉ alkanals (oleate). C₈ Alkanal was not detected in the cured samples, and C₃, C₈ and C₉ alkanals were not present in the uncured bacon. The cured back fat was intermediate in proportion of C₆ alkanal. The wide differences in C₆ alkanal between lard, cured back fat-lean, and uncured bacon do not appear to agree with Tappel's non-specific effect of heme catalysis (Tappel, 1955).

These results indicate a selective action in the oxidation of linoleic acid, if only triglycerides are involved. However, this could be due partially to a specific linoleate hydroperoxide decomposition to C₆ alkanal by hematin. Hematin catalysis progresses by hydroperoxide decomposition, but its exact effect on the nature of carbonyl products is not known. Analysis of the free monocarbonyl compounds isolated from uncured bacon showed the C₆ alkanal present in 80% proportions. This is considerably higher than that found for cured back fat-lean samples (Table 4).

Significant differences, due to the kind of catalytic activity, are indicated between cured and uncured pork tissue fat. Data showed high ratios for oxidized glycerides of uncured pork (Table 3). This indicated a high degree of linoleate specificity, either in the fatty acid oxidative attack or hydroperoxide decomposition. Salt evidently had the effect of decreasing both ratios. In autoxidized lard there was little specificity in fatty acid attack, and the degree of hydroperoxide conversion to monocarbonyls was low.

The pro-oxidant effect of various salts

In addition to NaCl, other salts have been tested for their pro-oxidant activity. The consensus in the literature appears to indicate wide differences existed, with potassium chloride and sodium sulfate having almost no effect (Banks, 1937; Chang *et al.*, 1949, 1950; Watts *et al.*, 1947). However, one theory for direct oxidative action of NaCl is based on reactivity of the chloride ion (Hills, *et al.*, 1946). If this were the case, all chlorides and halogens should behave similarly, and other salts show no effect. It is well known that a number of salts vary in the degree that they inhibit some of the respiratory enzymes of meat (Grant, 1956). Such an effect seems to agree closely with the reported pro-oxidative action of such salts.

Table 3. Effect of lean and sodium chloride on oxidation constants.

	% NaCl	Monocarbonyl μm/10 g	Ratios..	
			Carbonyl to PV	Enals to dienals
112 Days at 0°F				
Back fat (PV 20)	6	1.4	0.07	1.4
1:1 Back fat-lean (PV 17)	2	2.0	0.12	0.9
1:1 Back fat-lean (PV 27)	6	3.7	0.14	0.8
300 Days at 0°F				
Uncured bacon (PV 33)	0	8.3	0.25	2.0
20°C (Light)				
Lard (PV 29)	0	0.5	0.02	1.7
Lard (PV 58)	0	0.9	0.02	2.3
Lard (PV 119)	0	2.1	0.02	2.3
Lard (PV 256)	0	5.6	0.02	3.2

Table 4. Effect of lean and sodium chloride on alkanal proportions.

	% Total monocarbonyls					Total alkanals
	C ₂	C ₃	C ₄	C ₅	C ₆	
112 Days at 0°F						
Back fat 6% NaCl (PV 20)	7	10	60	3	80
1:1 Back fat-lean 2% (PV 17)	2	4	70	2	78
1:1 Back fat-lean 6% (PV 17)	2	4	77	2	85
Uncured bacon 300 days days at 0°F (PV 33)	2	tr	80	82
20°C (Light)						
Lard (PV 29)	1	17	24	9	12	67
Lard (PV 119)	tr	10	44	8	9	72

In an experiment designed to compare directly the pro-oxidative effect of salts, paired bacon segments were dry-cured with 2% NaCl and equivalent quantities of lithium chloride, sodium nitrate, magnesium chloride, calcium chloride, potassium chloride, sodium sulfate and potassium sulfate. By using paired segments, a direct comparison between each salt and NaCl was obtained. When all of the NaCl was absorbed, some of the other salts were not completely assimilated. Results may therefore be modified in the case of CaCl₂, K₂SO₄ and MgCl₂ by their degree of absorption and distribution. All of the salts, even the sulfates, showed some pro-oxidative action on storage at 0°F for 20, 41 and 65 days.

Table 5 shows the comparative oxidative activity of several of the salts. The influence of KCl was higher than expected from reports in the literature. In the case of LiCl and CaCl₂, monocarbonyl and peroxide comparisons did not correlate. LiCl had higher monocarbonyls and lower peroxide values than NaCl. CaCl₂ was the opposite in these relationships. The explanation would seem to be due to a difference in the degree of peroxide breakdown to monocarbonyls. The lack of similarity in pro-oxidant activity of the chloride salts shows that the Hills *et al.* (1946) theory of chloride ion catalysis as applied to meat is probably incorrect.

The amounts of free individual aldehydes formed by the pro-oxidant activities of NaCl and KCl are shown in Table 6. There was close similarity in the composition of these monocarbonyl compounds; also NaCl- and KCl-cured samples had similar monocarbonyl/peroxide ratios.

Pro-oxidant effect of nitrite

Zipser *et al.* (1964) have reported that nitrite when heated with meat converts the pigments to catalytically inactive ferrous nitric oxide hemochromogen. However, when NaCl was present, acceleration of oxidation occurred when the cooked meat was freezer-stored.

The following experiment was set up to measure the effect of unstabilized nitrite-myoglobin combinations on fat autoxidation. Bacon segments were dry cured separately in a paired setup with 0.03% NaNO₂, 2% NaCl and 0.03% NaNO₂ with 2% NaCl. Storage of the slices was at 0°F for 20, 41 and 65 days. Data on oxidation of these samples are shown in Table 7.

The rate of oxidation promoted by 0.03% NaNO₂ tended to be somewhat higher than that of 2% NaCl. When the curing was done with both 0.03% NaNO₂ and 2% NaCl, the oxidative effect was much higher than with 2% NaCl alone. The two influences appeared additive and were conceivably independent. It may be possible that the two compounds activate different catalytic systems. It seems certain that the NO₂-accelerated oxidation is due to the pigments, in particular myoglobin and hemoglobin (Chang *et al.*, 1949).

The strong pro-oxidant effect of practically trace amounts of NO₂ may appear surprising; yet it is not when the facts are considered. NO₂ used was more than sufficient to combine with all the myoglobin. It is known that nitrite-myoglobin combinations are extremely reactive unless stabilized to the hemochromogen by heat (Walsh *et al.*, 1956; Reith *et al.*, 1967). Zipser *et al.* (1963) have ob-

Table 5. Effect of various salts on oxidation of bacon segment in comparison to NaCl.

Storage at 0°F		% of NaCl values				
		LiCl	NaNO ₂	MgCl ₂	CaCl ₂	KCl
20 Days	Monocarb	107	85	85	67	59
	PV	0	103	0	85	41
41 Days	Monocarb	104	70	56	66	42
	PV	79	72	46	100	40
65 Days	Monocarb	121	70	61	66	75
	PV	81	78	73	119	72

served little effect of nitrite on freezer-stored, cooked meat, but strong pro-oxidant action by NaCl. This appears to further support an independent oxidative mechanism of NaCl.

The effect of NaCl and NaNO₂ on peroxide decomposition and monocarbonyl class relationships is shown in Table 7. There was seemingly little difference in peroxide decomposition. However, large differences were present in the effect of the two additives on the ratio of enal to dienal. The proportion of enal to dienal of the NO₂ samples was high and about the same level as found in autoxidation of lard and uncured bacon (Table 3). The significance of this is not clear, but it must be related to the hydroperoxide isomers present and mechanism of peroxide decomposition.

Individual aldehydes found for the NaCl and NaNO₂ samples are shown in Table 8. Proportions in the alkanal

and enal classes were similar. However, the proportion of C₁₀ alk-2,4-dienal was much larger for the NaCl samples, and this may account for the differences in enal-dienal ratios. Results were similar in a comparison of NaCl and NaNO₂ combined cure with NaCl, although the differences in monocarbonyl/peroxide and enal/dienal ratios were much smaller.

This investigation has demonstrated certain oxidation characteristics of NaCl-accelerated oxidation of freezer-stored pork tissue. The exact mechanism of the pro-oxidant influence of NaCl remains to be determined. Separately, heme compounds are very powerful catalysts of fat autoxidation (Tappel, 1952, 1953, 1955). However, as meat pigments they were relatively inactive or slowly effective in freezer-stored fresh pork.

Oxidation of unsaturated fatty acids by heme compounds has been reported (Tappel *et al.*, 1961) to be non-specific

Table 6. Comparison of free aldehydes in bacon segments oxidized by equivalent amounts of salts.

65 Days at 0°F		Alkanals				
		C ₂	C ₃	C ₆	C ₉	
2% NaCl	{ $\mu M/10$ g	0.06	0.10	1.55	0.11	
	{ % total	2.5%	4.5%	69%	5.0%	
2.55% KCl	{ $\mu M/10$ g	0.04	0.08	1.18	0.77	
	{ % total	2.2%	4.8%	69.4%	4.6%	
		Alk-2-enals				
		C ₇	C ₈	C ₉	C ₁₀	C ₁₁
2% NaCl	{ $\mu M/10$ g	0.08	0.06	0.04	0.04	0.04
	{ % total	3.4%	2.5%	1.6%	1.7%	1.6%
2.55% KCl	{ $\mu M/10$ g	0.07	0.05	0.03	0.02	0.02
	{ % total	4.3%	3.1%	1.8%	1.2%	0.9%
		Alk-2,4-dienals				
		C ₇	C ₉	C ₁₀		
2% NaCl	{ $\mu M/10$ g	0.04	0.04	0.11		
	{ % total	1.8%	0.8%	5.0%		
2.55% KCl	{ $\mu M/10$ g	0.04	0.04	0.06		
	{ % total	2.2%	2.1%	3.4%		

Table 7. Effect of NaNO₂ and NaCl on autoxidation characteristics of stored bacon.

Storage at 0°F	Animal No. 1		Animal No. 2	
	0.03% NaNO ₂	2% NaCl	0.03% NaNO ₂ 2% NaCl	2% NaCl
20 Days				
PV	16	17	37	0
Monocarbons ¹	0.4	0.5	0.6	0.2
41 Days				
PV	22	29	52	28
Monocarbons ¹	0.7	0.6	1.1	0.7
Ratios:				
Monocarbons/PV ²	0.14	0.10	0.09	0.10
Alk-2-enal/alk-2,4-dienal ²	2.6	1.3	2.1	1.1
65 Days				
PV	61	50	68	34
Monocarbons ¹	1.3	0.9	1.4	0.6
Ratios:				
Monocarbons/PV ²	0.10	0.08	0.09	0.07
Alk-2-enal/alk-2,4-dienal ²	2.8	1.4	2.7	1.5

¹ Absorbance in 100 ml CCl₄ of monocarbonyl 2,4-dinitrophenylhydrazones from 10 g fat.

² μM of monocarbonyl per g fat.

Table 8. Comparison of free aldehydes produced by NaCl and NaNO₂.

			Alkanals				
			C ₂	C ₃	C ₆	C ₉	
41 Days	2% NaCl	$\mu\text{M}/10\text{ g}$	0.06	0.21	2.07	1.10	
		%	2.2	7.2	71.2	3.3	
	0.03% NaNO ₂	$\mu\text{M}/10\text{ g}$	0.10	0.18	2.16	0.14	
		%	2.1	6.7	70.2	4.7	
65 Days	2% NaCl	$\mu\text{M}/10\text{ g}$	0.08	0.17	3.14	tr	
		%	2.0	4.3	79.2	tr	
	0.03% NaNO ₂	$\mu\text{M}/10\text{ g}$	0.08	0.52	4.48	tr	
		%	1.4	8.9	76.3	tr	
			Alk-2-enals				
			C ₇	C ₈	C ₉	C ₁₀	C ₁₁
41 Days	2% NaCl	$\mu\text{M}/10\text{ g}$	0.08	0.06	0.05	0.04	0.03
		%	2.6	2.1	1.9	1.3	1.2
	0.03% NaNO ₂	$\mu\text{M}/10\text{ g}$	0.10	0.11	0.07	0.04	0.03
		%	3.1	3.5	2.4	1.3	1.0
65 Days	2% NaCl	$\mu\text{M}/10\text{ g}$	0.08	0.10	0.06	0.07	0.09
		%	2.1	2.5	1.6	1.0	1.4
	0.03% NaNO ₂	$\mu\text{M}/10\text{ g}$	0.17	0.12	0.14	0.07	0.09
		%	2.8	2.0	2.4	1.2	1.6
			Alk-2,4-dienals				
			C ₇	C ₉	C ₁₀		
41 Days	2% NaCl	$\mu\text{M}/10\text{ g}$	0.03	0.05	0.11		
		%	1.2	1.8	3.9		
	0.03% NaNO ₂	$\mu\text{M}/10\text{ g}$	0.04	0.04	0.06		
		%	1.2	1.4	1.9		
65 Days	2% NaCl	$\mu\text{M}/10\text{ g}$	0.05	0.05	0.16		
		%	1.2	1.2	4.0		
	0.03% NaNO ₂	$\mu\text{M}/10\text{ g}$	0.06	0.06	0.09		
		%	1.0	1.0	1.5		

and similar to uncomplicated autoxidation. However, oxidation of freezer-stored, cured and uncured pork tissue fat showed a linoleate specificity in oxidation characteristics and monocarbonyl compounds. The high C₆ alkanal content suggests a lipoxidase-type of selective action, but the existence of such an enzyme in meat has been largely ruled out (Tappel, 1952, 1953). The explanation may be that heme compounds have a specific decomposing action on linoleate hydroperoxide to C₆ alkanal.

Autoxidation in this study has been considered to be taking place in the triglycerides. The possible involvement of polar lipids has not been overlooked. The extremely high polyunsaturated fatty acid content of the polar lipids (Hornstein *et al.*, 1961; Kuchmak *et al.*, 1963; Giam *et al.*, 1965) should be reflected in the composition of the free aldehydes (Gaddis *et al.*, 1961; Ellis *et al.*, 1966). The presence of unusual amounts of C₃ and C₇ alkanals and C₇ alk-2,4-dienal should enable the detection of an influence by oxidizing polar lipids. Furthermore, hydroperoxides have not been observed to accumulate in oxidized phospholipids. This incompletely understood type of autoxidation has been reported only in refrigerated, cooked meats (Younathan *et al.*, 1959; Zipser *et al.*, 1957), and has not been observed in freezer storage.

Nothing is known concerning the separate catalytic effect of heme pigments on the monocarbonyl products of oxidized fat or individual unsaturated fatty acids. A spe-

cific linoleate hydroperoxide to monocarbonyl decomposing action by the heme pigment may well exist. Similarly, knowledge of the independent oxidative influence of NaCl, trace metal ions, and lipoxidases would serve to clarify the mechanisms involved. There should also be advantage in the study under appropriate conditions of the volatile and free carbonyls of oxidized polar lipids.

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