

AN INVESTIGATION OF THE CHEMICAL CHANGES OCCURRING
DURING THE "AGING" OF CURED HAMS

By
W. C. Supplee
"

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TABLE OF CONTENTS

	Page
Introduction	1
Outline of the Experiment	6
Feeding the Animals	7
Slaughtering the Animals	7
Curing the Hams	7
Smoking the Hams	8
Storing the Hams	8
Sampling Hams for Analysis	9
Results of the Analysis	11
Gross Analysis	11
Analysis of the External Fatty Tissue	14
Analysis of the Purified Fat of the Lean Tissue and External Fatty Tissues	18
Analysis of the Lean Tissue	38
Analysis of Hams Produced by Meat Packers ..	53
Summary	58
Supplementary Work	61
Conclusions	64
Bibliography	66

INTRODUCTION

It is the general practice among the farmers of this State to cure enough hams each fall to fill their needs throughout the year. The methods which are in use are fundamentally the same on the various farms, though differences in details, to which great significance are often attached, are the general rule.

The objects of all curing processes are to prevent undesirable decomposition of the meat, and to promote the development of desirable qualities, associated with flavor, aroma, color, etc., which determine the palatability of the product. The general procedure by which these objects are attained is to treat the green meat with various substances which permeate the tissues, rendering it less susceptible to the action of microorganisms and improving the flavor of the meat in one way or another; and finally subjecting the hams to the action of wood smoke, which also has a preservative action and imparts desirable flavors. The principal constituents of curing mixtures are salt, saltpeter, and sugar in some form. To these are added various condimentals according to the preference or habit of the individual.

There are two methods in general use for the application of the curing mixture - the "brine cure", and the "dry cure". The former, as its name implies, consists in submerging the green hams in a brine made up of the desired constituents for two to three days to the pound of meat, and then allowing them to drain in the air preparatory to smoking. In the "dry-cure" method, the curing mixture is rubbed on the surface and the hams stacked in a pile in the smoke house or packed in barrels. The hams are "overhauled", or removed and recoated with curing mixture several times during the curing period. After a total curing of two to four days to the pound, the hams are hung to air-dry the surfaces, and smoked.

The smoking process is carried out in a fairly well-closed room, into which smoke from a slow fire of green wood, (the preference seems to be for hickory), is directed. The smoke treatment is generally given for several hours a day on consecutive or alternate days, until thought to be satisfactory.

After smoking, the hams are usually left hanging in the smoke-house or in an attic until used, though on many farms it is the practice to wrap and sack them previous to storage.

As the hams age in the smoke house, they undergo

some very marked changes. A freshly cured ham is characterized by rather soft, velvety-textured lean of red to pinkish-red color. The external fat layer which blankets the lean meat has a pinkish or pearly white color and is usually rather soft and moist to the touch. The aroma is of a quality which may be described as mild, sweet and "fresh", with varying degrees of "smokiness".

These characteristics undergo changes which become more and more marked, the longer the hams are "aged" or held after curing. The lean meat becomes compact and dry, particularly near the exposed surface. A very general and rather curious change is the appearance of white specks of varying sizes throughout the ham. This is particularly noticeable along the connective tissues which separate the various muscles from one another and the external fatty tissues from the lean, and also along the sheath which covers the bone. Not infrequently, this flecking is found even in the external fat layer.

The fat generally takes on a darker, yellowish or amber color; and loses to some extent its opaqueness, frequently becoming rather crisp and granular, with a somewhat translucent appearance.

The mild, sweet, "fresh cure" aroma gives way to a

peculiar, rather pungent, cheesy one, in which the effect of the smoke seems less pronounced.

All these changes are of a progressive nature and, consequently, the longer a ham has been aged the more preferable it is, providing spoilage does not occur.

Farmers not infrequently save some of their better hams for two, three, and even more years, in order to further improve them; in much the same spirit that liquor connoisseurs keep a few bottles from an unusually good vintage to be further aged for use on special occasions.

It is only reasonable to suppose that the various changes, pointed out above as resulting from the aging process, must be accompanied by alterations in certain of the chemical relationships which existed in the freshly cured hams.

It is a well established fact that all flesh tissues, even when protected from the action of microorganisms, will undergo marked changes at ordinary temperatures, due to the activity of the normally occurring enzymes. The most significant of these autolytic changes are hydrolysis of the proteins into smaller, more soluble fragments and free amino acids, and hydrolysis of the fat into free fatty acids and glycerol. Such changes have no fundamentally deleterious effect on the food value of the meat.

On the other hand, a great variety of changes may occur in meats, as a result of bacterial action, which render it unfit for food; while some of the effects of microorganisms, particularly certain molds, are considered beneficial. A notable example of this is the "ripening" of beef.

Numerous investigations have been carried out on the effect of storage at low temperatures on the chemical and physical makeup of fresh meats. There seems, however, to be practically no information available relating to the effect of aging cured meat at temperatures favorable to enzyme and bacterial action.

As a consequence of this, a rather detailed study of the aging of hams as practiced in this State was begun several years ago at the Maryland Experiment Station.

The project was divided into three phases, with the object of determining how the bacterial flora, chemical composition, and palatability vary as hams are aged.

This thesis contains the results of the chemical work done in connection with this study.

Outline of Experiment

As has been noted, details of the methods which individual farmers employ in curing their hams differ considerably. It was, consequently, necessary to work out a method which was, so far as possible, typical of those used in various localities with the most success.

In raising the pigs for this work, two plans of feeding were employed in order to obtain hams in which the proportions of fat to lean were widely different, there being some question as to the relative desirability of fat hams and lean hams. The pigs were raised at the University of Maryland and taken to the Government Experimental Farm at Beltsville to be slaughtered. The hams were cured and smoked there, and then brought back to the University of Maryland for aging and analysis. When possible, six pigs from the same litter were started on each plan of feeding, thus furnishing enough cured hams so that one ham from an individual could be used for chemical and bacteriological analysis, and the other could be, at the same time, cooked and graded for palatability, at six intervals over a total aging period of two years. The first two hams from each lot were sampled within one month of the termination of the curing process; further samples were taken at intervals of

approximately four months during the first year of aging, and six months during the second year.

The details of each of the operations carried out are described below under their respective headings.

Feeding: The following procedure was carried out in raising the animals used in this work. In the spring and fall, two lots of pigs, usually of at least six pigs each, were put on a ration consisting of corn and fishmeal, supplemented in the summer by pasture, and in the winter by alfalfa hay. One lot was full-fed, the pigs being made to gain as rapidly as possible; the other lot was limited in feeding so as to reach the same average weight as the full-fed in about five months longer time. The average final weight of each hog on the basis of the total lot-weight was 300 pounds.

Slaughtering: The hogs were held off feed, and given only water for 24 hours before slaughtering at the Government Experimental Farm at Beltsville. The carcasses were chilled for 3 days at a temperature of 32-38° F, and then divided into various cuts. The hams were smoothly and evenly trimmed, but not skinned.

Curing: The hams were cured in the following manner:

a mixture of 8 pounds of salt, 2 pounds of granulated sugar and 3 ounces of saltpeter was made up for each 100 pounds of meat. One-half of the mixture was carefully rubbed on all surfaces of the hams, particular attention being given to the bone-ends. The hams were then packed in barrels and put in the refrigerator for 3 days at 32-38° F. One-half of the remaining curing mixture was then rubbed on and the hams repacked, the bottom hams of the first packing being put on the top of the pile. Twelve days following this, the remainder of the mixture was put on and the hams left in the refrigerator until cured, a total of 2 days per pound of meat. The hams were then hung in the refrigerator to "air-cure" for two weeks.

Smoking: Following curing, the hams were washed, allowed to dry, and then smoked two hours a day on alternate days until four smokes had been given; the temperature being kept below 100° F.

Storing: Following smoking, the hams were weighed, wrapped in parchment paper, and put in muslin ham bags. They were then stored in a dry, darkened room at the Maryland Experiment Station.

Sampling the Hams for Chemical Analysis: When a sample was to be taken, the ham was unwrapped, weighed, and lightly wiped with a cloth to remove most of the mold, when this was present.

The ham was then cut in half about one-half inch below and parallel to the aich-bone. Before the bacteriological work was started, both halves of the ham were then separated as carefully as was practicable into skin, external or mechanically separable fat, lean and bone. When it became necessary to take bacteriological samples, the butt half was cut up first, and the hock end dissected after the bacteriological sampling.

As the lean and fat were collected, each piece was put in an empty desiccator to eliminate, so far as possible, moisture loss. Each fraction was then weighed.

The lean was ground in a meat chopper, using a rather fine blade, mixed well, and twice reground and mixed, the meat leaving the grinder being caught in an empty desiccator. In a few cases it was found desirable to grind the lean but once, as some of the new, full-fed hams formed a gummy mass which could not be satisfactorily reground.

The fat was ground once, those portions which would not go through the grinder being removed and cut up finely with scissors.

The fat and the lean were then sampled, 40-60 grams of lean and 20-40 grams of fat being taken.

The lean samples were immediately placed in 250 c.c. Ehrlemeyer flasks and covered with enough 95 percent alcohol to make an approximately 70 percent solution with the water in the tissue. These were then held for one hour at 70° C in a water bath to stop enzyme action, stoppered and stored.

The fat samples were put in desiccators and extracted as soon as possible.

The excess lean was put in one-half gallon jars, covered with ether and stored at 32°-34° F, until extracted for fat. A large sample of the external fat was also mixed and covered with ether in a jar, and placed in the refrigerator.

RESULTS OF THE ANALYSIS OF HAMS HAVING UNDERGONE
DIFFERENT PERIODS OF AGING

In presenting the results of the different phases of the analytical work, it seemed desirable to discuss them, when possible, in the order they were obtained, regardless of their relative significance.

Results of the Gross Analysis

The mechanical separation of the hams into fat, lean, bone and skin might be expected to show some of the general relationships between the full-fed and slow-fed groups, and also any gross changes that aging may bring about in the several fractions within each group.

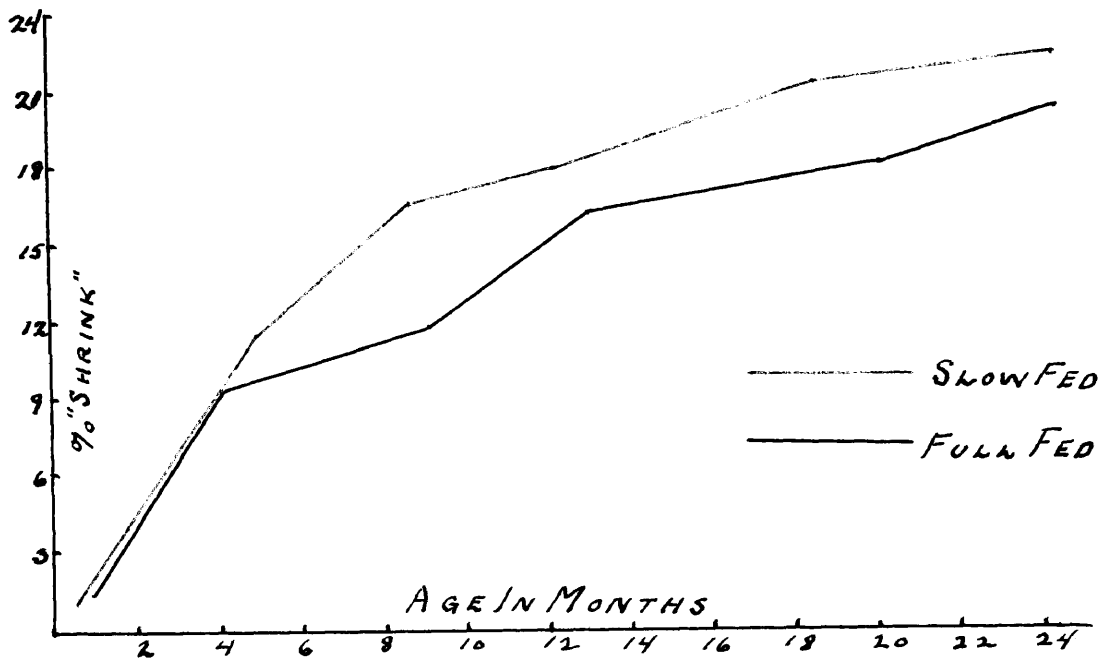
Table I, below, contains the average values for the different fractions in freshly-cured hams. The effect of the two planes of feeding on the type of ham produced is very clearly shown, the slow-fed hams having a greater amount of lean tissue, bone and skin, but less fat.

In Table II, the average percentages of the several fractions are given for slow-fed and full-fed hams of comparable ages, along with the loss in weight, or "shrink", which has occurred during storage.

It can be seen that an extensive loss of weight occurs as the hams age. In Figure I this "shrink" is plotted against the time of aging. The curve obtained shows that loss of weight in the slow-fed groups is somewhat more extensive than in the full-fed, after the first four months of aging. Also, the curves show that in both groups the greater loss occurs during the first year.

FIGURE I.

Percentage "Shrink" in Full and Slow-Fed Hams
After Various Periods of Aging



The figures on the percentages of lean and fat at different ages, given in Table II, seem to show little outside of roughly indicating that shrinkage is due more to losses from the lean than from the fatty tissue. It will be shown later that shrinkage was due to the combined effects of loss of moisture and fat from the lean tissue, and loss of water and possibly some fat from the external layer.

Analysis of the External Fatty Tissue

To determine the effect of aging on the composition of the external fat layer, a number of samples were extracted with ether and the extractable material and the ether-insoluble matter weighed. The difference between the sum of these and the total weight was considered to be water. The results obtained are given in Table III, and are graphed against time of aging in Figure II.

It must be pointed out that these results must be viewed solely for their qualitative significance. Great difficulty was experienced in satisfactorily sampling the semi-liquid mass obtained when the fat-layers were ground. This difficulty was obviated to a large extent, finally, by allowing the mass to solidify in the refrigerator before mixing and sampling. Even though the checks obtained in this

work were not all that could be desired, and the number of samples is not very great in view of the variable nature of the material analyzed, the data plainly shows several interesting points.

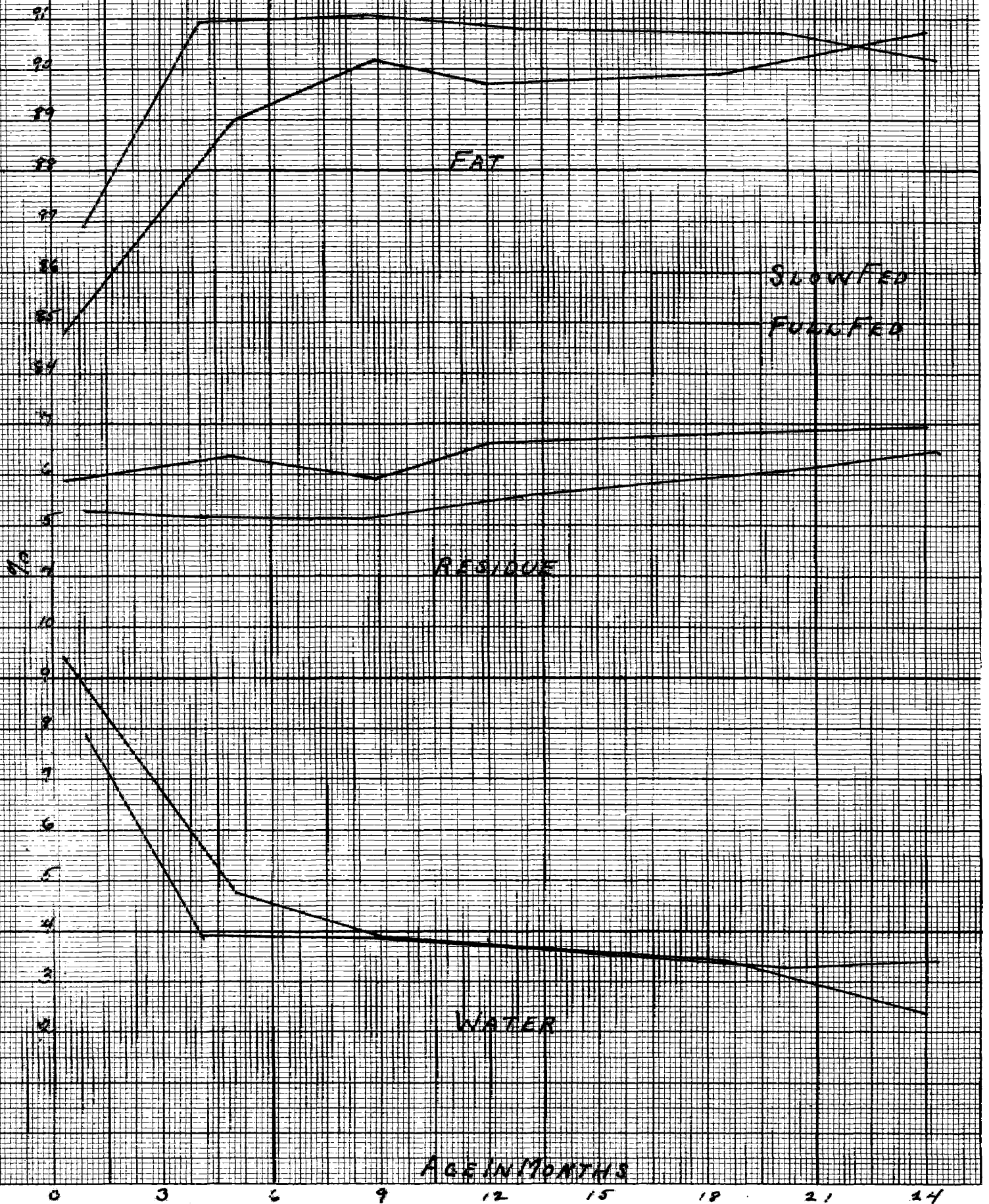
The ether-insoluble material, which may be assumed to be chiefly protein connective tissue, is shown to be distinctly higher in the slow-fed hams, while the fat content is lower.

TABLE III.

Percentage of Fat, Water and Ether-Insoluble Residue in the External Fatty Tissue

FULL-FED				SLOW-FED			
Age in Months	Fat	Water	Residue	Age in Months	Fat	Water	Residue
1.0	86.89	7.84	5.27	0.3	84.75	9.37	5.88
4.1	90.96	3.91	5.14	4.9	88.94	4.72	6.34
8.5	91.05	3.89	5.11	8.8	90.13	3.98	5.89
12.9	90.77	3.64	5.59	12.0	89.69	3.72	6.60
20.0	90.70	3.25	6.05	18.4	89.89	3.37	6.80
24.3	90.16	3.37	6.47	24.0	90.73	2.33	6.94

FIGURE II
PERCENTAGES OF FAT, RESIDUE AND WATER IN THE EXTERNAL FATTY TISSUE



The increase in the fat content shows clearly that there is an extensive loss of moisture from the external fatty-tissue of both groups. In the full-fed hams this loss is very rapid, most of the change occurring during the first four months, while in the slow-fed hams this loss seems somewhat more gradual.

The slight decrease noted in the fat content of the full-fed hams seems to indicate that there was a loss of fat from the fatty tissue during the second year of aging. This indication is strengthened by the fact that the difference between the percentage of ether-insoluble residue of the full-fed and slow-fed tissue decreases during this period.

Changes in the Physical Appearance of The Fat.

There was a noticeable tendency in many of the older hams for the external fatty layer to lose its pinkish color and smooth texture, and to become somewhat crisp and granular and take on an amber translucent appearance.

The discolorations in the fatty layer were undoubtedly due to a large extent to gradual permeation of the fat by the "creosote" bodies absorbed on the surface in the smoking process.

The crisp, rind-like texture seems to be a possible result of a hardening of the connective tissue framework in which the fat is laid down, due to the extensive loss of water which has just been shown to occur in this layer.

The combined effects of moisture loss and hydrolysis of the fat points strongly to the possibility that the translucent appearance which develops in the external fatty layers of some of the hams may be due to disruption of the normal emulsoid state of the fat, and a subsequent "clearing" action of the semiliquid fat on the connective tissues and the skin. Such an action is utilized in histological work, dried tissues being permeated with oils and fats of various kinds in order to produce a continuous phase of uniform density with a consequent reduction of the scattering of light rays.

Analysis of the Purified Fat Extracted From
the Lean and Fatty Tissues

Extraction and Purification of the External Fat - A suitable amount of the ground fatty tissue was heated on the steam bath for about one-half hour at 75° C, and the melted mass strained and squeezed through cheese-cloth. The impure fat-ether mixture thus obtained was evaporated under partial vacuum until most of the ether was removed, filtered while warm through filter paper into a round-bottomed flask, and the heating continued under vacuum until two samples taken one-half hour apart gave checking refractive indices. The fat was then considered to be pure and dry, and if not to be analyzed immediately, was stored in the refrigerator at 32° - 38° F in brown glass bottles.

Extraction and Purification of the Meat Fat - The ground lean was placed in a large Sando extractor and treated with ether until the easily extractable fat was removed. The meat was then removed from the extractor and dried in a current of warm air. After drying, extraction was continued for 8 - 10 hours, the ether driven off, and the residue rather finely ground in a large mortar. After a final extraction of 5 - 10 hours more, most of the ether was driven from the fat and the mixture

filtered through paper. The remaining ether was removed under reduced pressure while heating on the steam bath, the fat again filtered and dried in the same manner as the external fat.

Methods Used - The methods used in the analysis of the fat were those approved by the Association of Official Agricultural Chemists. Specific gravities were taken at the temperature of boiling water in a pycnometer of about 7 c.c. capacity. Refractive indices were determined in a Zeiss butyro-refractometer at 40° C. The Hanus method was used for the iodine number determinations.

Results of Analysis of the Fat - The results obtained from the analysis of nineteen samples of fat from full-fed hams and eighteen samples from slow-fed hams are given in Table IV. The titer test was abandoned because the results seemed to show that the information gained was not commensurate with the time and material required for the determination.

Discussion of Results

Free Fatty Acids - The most marked change observed in the fat as the hams aged is the rapid increase in the free fatty acid content. In the several series there is considerable variation in the extent of hydrolysis during the same

TABLE IV.

Analysis of Meat Fat and External Fat

From Hams of Full-Fed Hogs

MEAT FAT								EXTERNAL					
No. Ham	Age in Months	Spec. Grav.	Refrac. Index	Sapon. No.	Iodine No.	Free Fatty Acids	Titer Test	Spec. Grav.	Refrac. Index	Sapon. No.	Iodine No.	Free Fatty Acids	Titer Test
9944	1.25	--	--	--	67.2	3.28	35.8	--	--	--	68.3	1.55	--
9940	4.25	8946	1.4589	198.2	63.4	8.40	36.7	8952	1.4588	196.8	68.9	7.70	36.5
9951	9	8939	1.4591	197.5	66.1	12.60	35.5	8953	1.4589	195.7	70.4	9.50	35.8
9948	13	8937	1.4584	194.8	66.6	17.20	35.6	8932	1.4584	196.7	66.0	13.70	36.6
9942	20	8928	1.4584	198.4	67.4	24.30	36.6	8928	1.4585	193.1	65.8	16.40	37.7
9946	24.5	8918	1.4587	193.6	68.9	21.40	35.8	8940	1.4589	195.4	69.7	15.04	36.2
2622	0.75	8973	1.4596	193.1	63.9	6.27	37.2	8940	1.4587	193.0	63.1	6.50	37.5
2618	7.5	8935	1.4587	194.1	62.2	10.32	37.6	8939	1.4585	195.6	64.3	11.90	37.2
2604	14.75	8892	1.4572	198.5	67.2	28.59	--	8918	1.4586	195.6	67.7	16.16	--
3208	1	8946	1.4592	196.6	61.8	5.94		8949	1.4594	197.7	65.3	3.54	
3202	4.25	8935	1.4590	197.6	64.6	9.95		8939	1.4592	195.0	65.5	5.92	
3203	8.75	8924	1.4585	199.0	64.6	13.91		8928	1.4585	195.8	63.6	12.07	
3205	12	8914	1.4581	196.3	65.0	18.79		8933	1.4587	195.3	67.3	14.81	
3237	1	8941	1.4594	194.7	64.7	7.62		8936	1.4590	196.2	62.4	4.20	
3229	4	8914	1.4586	194.1	65.3	14.52		8941	1.4591	196.3	67.3	10.17	
3148	0.5	8955	1.4596	194.9	65.1	4.28		8951	1.4591	196.8	65.6	3.46	
3151	8	8906	1.4578	198.1	64.4	23.48		8909	1.4578	199.4	61.4	16.52	
3153	12	8933	1.4585	198.3	65.0	23.38		8921	1.4584	195.3	67.2	17.70	
3157	24	8909	1.4583	192.7	72.3	27.51		8936	1.4587	195.6	71.2	18.54	
Average				195.81	65.56		36.35			195.57	66.34		36.79

TABLE IV. (Cont'd).

Analysis of Meat Fat and External Fat From Hams
Of Slow-Fed Hogs

MEAT FAT								EXTERNAL						
No. Ham	Age in Months	Spec. Grav.	Refrac. Index	Sapon. No.	Iodine No.	Free Fatty Acids	Titer Test	Spec. Grav.	Refrac. Index	Sapon. No.	Iodine No.	Free Fatty Acids	Titer Test	
2525	1	8958	1.4601	196.0	72.4	7.20	35.0	8946	1.4591	194.5	71.8	8.30	35.1	
2528	5.5	8952	1.4576	196.2	67.9	17.30	35.7	8939	1.4588	195.4	71.8	14.10	35.8	
2518	10	8963	1.4592	199.0	68.4	15.60	36.3	8938	1.4590	194.2	68.1	12.10	35.8	
2520	13	8941	1.4585	196.2	71.1	24.49	36.0	8942	1.4586	196.0	68.8	15.90	35.4	
2524	18.75	8918	1.4587	195.5	73.9	29.08	35.9	8928	1.4586	196.3	68.2	19.78	37.0	
2522	24	8942	1.4592	197.9	71.7	24.30	35.9	8939	1.4590	194.1	69.4	17.45	36.3	
2589	0.25	8975	1.4599	196.6	66.1	2.24	35.9	8938	1.4588	193.5	66.3	1.70	36.0	
2593	4.75	8946	1.4589	198.7	68.0	15.9	36.1	8935	1.4585	194.2	63.1	10.70	37.8	
2595	8	8941	1.4590	192.7	67.3	14.6	35.9	8922	1.4581	195.5	67.4	15.77	36.8	
3167	.25	8983	1.4600	194.8	70.5	4.9		8949	1.4598	196.5	70.5	1.70		
3169	5.75	8930	1.4590	196.1	70.5	17.52		8924	1.4588	196.5	69.3	13.77		
3161	8	8926	1.4592	197.5	72.3	22.37		8934	1.4590	197.5	70.4	14.07		
3168	12	8951	1.4598	193.9	70.8	14.92		8942	1.4592	196.4	70.0	10.65		
3170	18	8934	1.4591	196.7	71.2	25.24		8931	1.4589	194.6	71.3	16.64		
3212	.25	8958	1.4600	197.3	65.7	4.91		8932	1.4592	194.9	64.2	4.51		
3220	4.0	8944	1.4600	192.7	70.8	12.57		8939	1.4592	196.8	69.6	10.36		
3213	8.75	8923	1.4589	193.5	70.2	17.14		8937	1.4589	196.7	68.3	12.96		
3217	12		1.4590		70.6	16.46			1.4590		70.1	12.89		
Average				195.95	69.96		35.85					195.5	68.81	36.22

period of aging, but very definite relations appear when averages are struck from values for hams of comparable ages. In Table V, the average free fatty acid contents of the different fats are given, and in Figure III, these are plotted against the average time of aging.

TABLE V.

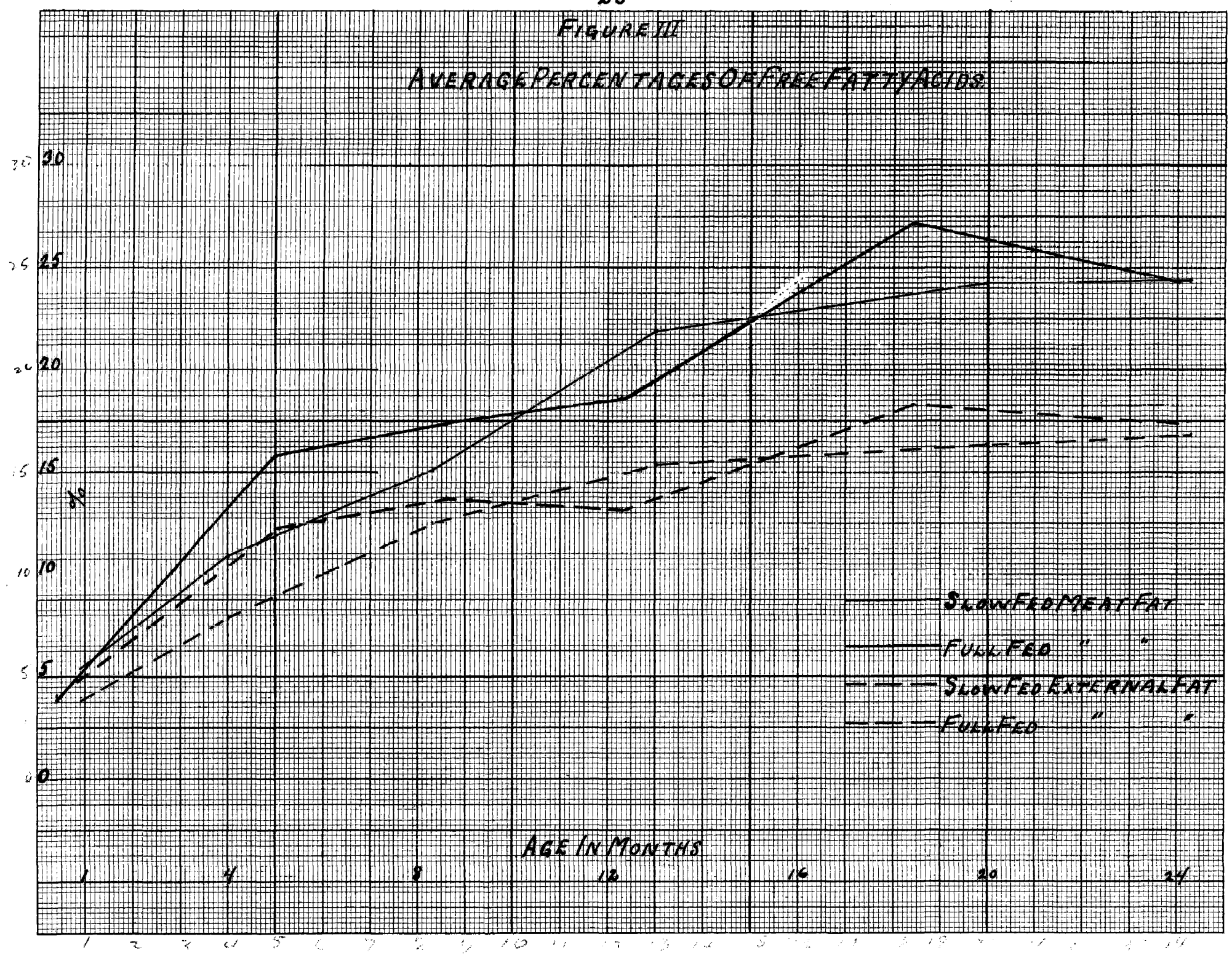
Average Free Fatty Acid Content After
Different Periods of Aging

SLOW-FED				FULL-FED			
No. of Samples	Age in Months	% Free Acids		No. of Samples	Age in Months	% Free Acids	
		Meat Fat	External Fat			Meat Fat	External Fat
4	0.4	3.85	4.05	5	0.9	5.48	3.85
4	5.0	15.82	12.23	3	4.0	10.96	7.93
4	8.6	17.43	13.73	4	8.3	15.08	12.50
3	12.3	18.62	13.15	4	13.0	21.99	15.49
2	18.4	27.16	18.26	1	20.0	24.30	16.40
1	24.0	24.30	17.45	2	24.3	24.45	16.78

The most important point brought out by the above data is the difference in the extent of hydrolysis in the meat-fat and external fat. It can plainly be seen that after

FIGURE III

AVERAGE PERCENTAGES OF FREE FATTY ACIDS



the first few months of aging, hydrolysis in the external layer shows up quite rapidly, while the effect is much less noticeable in the external fat.

It is impossible to definitely account for this difference, although there is one consideration which may furnish a partial explanation. There can be little doubt that hydrolysis in these hams is due to enzyme action. In the hydrolysis of fats by enzymes, the proportion of water to fat has been shown to have a great effect on the extent and rate of the reaction; the greater being the amount of water, the more rapid and complete the hydrolysis.⁽¹⁾ It has already been shown that the moisture content of the external fat layers decreases about 50 percent, (from 8% to 4%), in the first eight months of aging. Analysis of the lean meat, however, showed the moisture content to drop only about 10 percent, (from 55% to 45%), in the same time. Hence, relative loss of moisture in the two groups may account for some of the difference noted in the rates of hydrolysis in the two types of tissue.

In an effort to determine whether there was a selective hydrolysis of any particular fatty acids in preference to others, some very interesting data were obtained.

Three samples of meat-fat, having free fatty acid contents of 4.5 percent, 16.0 percent, and 27.5 percent,

together with a sample of meat-fat from a ham in which hydrolysis had been accelerated considerably by the injection of a lipase solution and having a free acid content of 23.0 percent, were separated into free acids and neutral fat by the following method.

A suitable sample of fat was dissolved in 75 c.c. of petroleum ether, and 50 c.c. of 95 percent alcohol added. The free fatty acids were then neutralized with alcoholic KOH, and sufficient water added to make the alcohol concentration 50 percent. The two layers thus obtained were separated in a funnel. The petroleum ether fraction was washed with 50 percent alcohol, and the alcohol fraction washed with petroleum ether. The neutral fat is contained in the ether layer, and the potassium salts of the free fatty acids in the alcohol layer. Both fractions were evaporated on the steam bath and saponified completely with alcoholic KOH, and the acids freed from the soaps, dried and filtered.

Portions of acids of each fraction were used to determine the neutralization values, (c.c. N/10 NaOH to neutralize 1 gram of acids), and iodine numbers. The results are given in Table VI.

TABLE VI.

Iodine Numbers and Neutralization Values
Of the Free and Combined Acids of Fats Having Undergone
Different Degrees of Hydrolysis

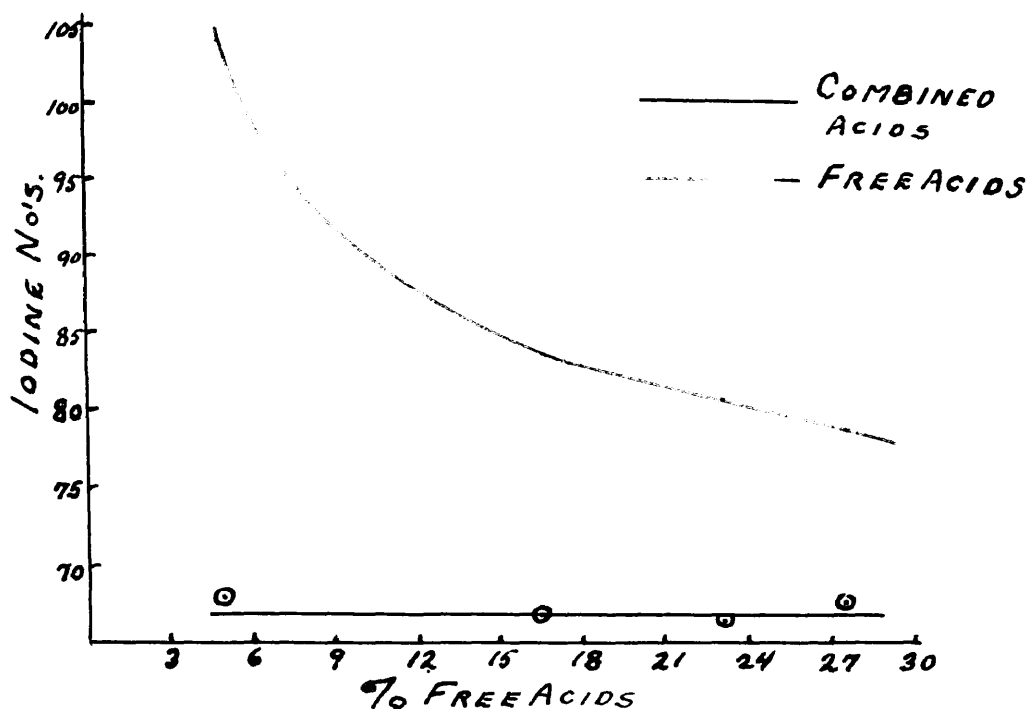
SAMPLE NO.	I		II		III		IV	
	Free Acids	Com- bined Acids	Free Acids	Com- bined Acids	Free Acids	Com- bined Acids	Free Acids	Com- bined Acids
Free Acids (%)	4.9		16.5		23.0		27.5	
Iodine No's	104.0	68.2	83.9	66.9	80.7	66.8	78.8	68.2
Neutraliza- tion Values	33.5	35.7	33.7	35.1	33.9	35.5	33.8	35.5

Ellis and Isbell⁽³⁾ found the iodine numbers of the unsaturated acids in the fat of hogs fed a similar ration to that used in this work to vary from 102 to 111, according to the iodine numbers of the fats from which they were separated. Thus, it is evident that the free fatty acids in Sample I, having an iodine number of 104.0, must have been practically pure unsaturated acids. The lower neutralization values show, also, that these acids are of slightly higher average molecular weight than those making up the neutral fat. As hydrolysis proceeds

the proportion of saturated acids of higher molecular weight split off increases very rapidly, thus causing a decrease in the iodine numbers of the free acids. This is more clearly brought out by Figure IV.

FIGURE IV.

Variation in the Iodine Numbers of the Free Acids as Hydrolysis Proceeds



In view of the rather conflicting data obtained in investigations relating to the ease of hydrolysis of various fatty acids, the results given here seem particularly interesting. Thum,⁽⁴⁾ as a result of a study of the

action of KOH on a mixture of oleic and stearic acids came to the conclusion that both were affected to the same extent by this reagent. He also separated the free acids from the neutral fat of samples of olive oil and palm oil, which had been partially hydrolysed, presumably as a result of enzyme action. The iodine numbers of the free acids and neutral fat acids in both types of oils were practically the same. Thum concluded that oleic, palmitic and stearic acids are liberated in the same proportion to that in which they exist in the original fats, when the latter become rancid. The samples studied had undergone rather extensive hydrolysis, the olive oil having a free fatty acid content of 46.75 percent and the palm oil 47.0 percent.

Taylor,⁽⁵⁾ states that there is evidence that in the fermentation of a mixed fat, the tristearin is first and most easily hydrolysed.

There can be no doubt that under the conditions existing here unsaturated acids are at first more readily freed from the esters, but that as hydrolysis proceeds, the proportion of unsaturated to saturated acids split off decreases rapidly. It remains to be proved, however, whether the effect noticed is due to the ease of hydrolysis

of the acids themselves or to selective action of the hydrolytic agent.

Iodine Numbers - The results of this determination seem to have some significance with regard to the general problem of fat metabolism as related to the type of feeding employed. It can be seen from the averages of the iodine numbers (see Table IV.), that the fat from the slow-fed hogs is distinctly more unsaturated than that of the animals which were full-fed.

Ellis and Hankins,⁽⁶⁾ have shown clearly that as pigs become fatter and better finished, more of the body fat is derived from the carbohydrate and protein of the ration through synthesis, and proportionately less from the feed fat; thus bringing about a lowering of the iodine numbers of the body fat because of the more saturated nature of synthesized fat.

The relationship pointed out in the data presented here seems to be another point in confirmation of their results.

It has been shown,⁽²⁾ that there is but little difference in the gain in weight per pound of feed concentrate on full-feeding and slow-feeding. Full-fed pigs lay down considerably more fat, however, and hence more fat per pound of feed than slow-fed animals. It follows then

that a greater proportion of their fat must be synthesized, and as a consequence the iodine numbers are lower.

Saponification Numbers - The saponification values seem to have no significance, the average values being entirely comparable for the several types of fat.

Titer Test - The titer test figures bear out the results on the iodine numbers, the acids from the more saturated full-fed fat solidifying at a slightly higher temperature than that from the slow-fed.

Specific Gravity and Refractive Index - There seems to be a good deal of contention among analysts as to the effect of the free acid content of oils and fats on specific gravity.

Allen ⁽⁷⁾ states that in the case of olive oil, each 5 percent free fatty acids diminishes the specific gravity about 0.0007. Thomson and Ballantyne, ⁽⁸⁾ in disparagement of Allen's contention, show cases where free acids seem to have raised the specific gravity and hold it to be futile to try to compare one specimen of fat with another in this respect. On the other hand, Ransome ⁽⁹⁾ gives the results of experiments which he contends to be in support of Allen's views. He freed several samples of olive oil from free fatty acids and in all cases got an increase in the specific gravity

of the neutral oil over the acid oil. Finally, Lewkowitsch⁽¹⁰⁾ states that a definite relation does not exist between the acid content and the specific gravity, and cites analyses on olive oils of different free acid contents in which highly acid oils often were shown to have higher specific gravities than samples with a low percentage of free acids.

In view of the conflicting views and data obtained, it seems that the results obtained in this work may have some value with respect to this question. Casual observation of any of the series of results will show that there is a marked tendency for the specific gravities to fall as the free fatty acids increase, and also that the refractive indices follow the specific gravities. (See Table IV.) Certain samples of rather high acidity gave high specific gravities, and vice versa, but the general trend is unmistakable. This trend is brought out more clearly below, where the samples have been grouped on the basis of the percentage of free fatty acids. The samples were divided into three groups - those having less than 10 percent free fatty acids, those having between 10 percent and 20 percent, and those having more than 20 percent. The average specific gravities and refractive indices are shown in Table VII to drop progressively as the percentage of free fatty acids increase.

TABLE VII.

Variation of Specific Gravity and
Refractive Index With Free Fatty Acid Content

No. of Samples	Average Acidity	Specific Gravity	Refractive Index
21	5.65%	.8950	1.4593
38	14.66%	.8934	1.4588
11	24.92%	.8923	1.4585

In view of the slight solubility of glycerol in ether and its insolubility in fats and oils, it is possible that the progressive drop noted here is due to very small losses of this product of hydrolysis when the fats were extracted.

Regardless of the cause of the variation, it is evident that in examining fats in which there is the possibility of any very extensive hydrolysis having occurred, the free acid content must be taken into consideration.

Comparison of the average values for the samples of full-fed fat with less than 10 percent free fatty acids, (average 6.41%) with those of the slow-fed fat, (average free fatty acids 4.43%), shows the latter to have the higher

refractive index and specific gravity, a relationship that should be expected in view of the higher iodine numbers, these three constants generally varying in the same sense in all types of fat. (See Table VIII.)

TABLE VIII.

Comparison of Refractive Index, Specific Gravity
And Iodine Numbers of Full and Slow-Fed Hams of Low
Free Fatty Acid Content

	No. of Samples	Average Acidity	Specific Gravity	Refractive Index	Iodine Number
Full-Fed	13	6.41%	.8947	1.4591	65.95
Slow-Fed	8	4.43%	.8955	1.4596	69.39

Results of Tests for Oxidation
In the Fat.

A change in the fat which would have considerable significance from the standpoint of palatability is that of oxidation, resulting, as it does, in the condition known as "rancidity" when occurring to any very considerable extent. Because of the relative ease with which fats undergo oxidation when not properly handled, and

the importance of guarding against this change because of its general deteriorating effect, a great amount of work has been done in efforts to determine the exact reactions which take place, the factors accelerating and inhibiting these changes, and accurate means of detecting the extent to which it has occurred or the susceptibility of a fat to it. None of these efforts seems to have been entirely successful. There is no doubt, however, that oxidation occurs at the double bond of unsaturated acids regardless of the exact reactions which occur. The recent work of Holm and Greenbank⁽¹¹⁾ seems to point strongly to the oxidation of oleic acid as being mainly responsible for true rancid odor. Among other things, aging and the presence of free fatty acids seem to have an accelerating effect, while moisture seems to inhibit the development of rancid odors if not oxidation.⁽¹²⁾

The most reliable test for the quality of a fat, as regards palatability, is that based on the senses of taste and smell. A test which has been proved of value in conjunction with the odor in the assaying of oils, however, is that known as the Kreis test. It is carried out as follows: 10 c.c. of oil are shaken vigorously in a test tube for 30 seconds with 10 c.c. of concentrated hydrochloric acid. Ten c.c. of a 0.5 percent solution of phloroglucinol in ether

is added and the mixture again shaken. If, on standing, a pink or red coloration appears in the acid layer which separates, the test is positive and indicates that oxidation has occurred. Kerr and Sorber,⁽¹³⁾ after extensive use of this test, state that all rancid fats react, but that it is too delicate to be used alone as a criterion for rancidity, giving positive tests in some cases with sweet oils as measured by odor. Other investigators⁽¹⁴⁾ have also found it to give positive reactions with fats which have been exposed to the action of oxygen but which are still "sweet", indicating that oxidation products other than those which are responsible for the rancid odor give the test, or that a condition of rancidity in its very early stages is detectable.

In view of these considerations this test was applied to the fats from a number of hams of different ages; while the odor of all the hams was noted at the time of dissection.

Of the thirty-seven hams taken for analysis, in only five cases was an odor described as rancid, although change in the aroma of the hams was the general rule, as aging progressed.

The results of the Kreis test on the purified fat from thirteen hams of varying ages, given in Table IX below,

seem to indicate that, as the hams age, the substances giving the test occur more and more frequently, and that the external fat, in the few cases tested, seems to be affected somewhat more regularly than the meat-fat, through oxidation.

TABLE IX.

Summary of Kreis Test for
Oxidation of Fat.

Age of Fat in Months	1	4	8	12	18	24
Meat Fat	1 \pm , 1-	1+, 2 \pm , 1-	4+, 1-	2-	1+	1 \pm
External Fat			1+	1+, 1-	1+	1+

(2+ indicates that 2 samples reacted positively,
± represents a doubtful reaction.)

In view of these results it would seem that the development of the odor and flavor of the fat of these hams may be due in part to oxidative changes, but that these changes are rarely of sufficient extent to give rise to a typical condition of rancidity.

Effect of Free Fatty Acids on Flavor

Lewkowitsch⁽¹⁵⁾ and others have pointed out that free fatty acids have the tendency to impart slight not unpleasant odors and sharp acidic tastes to odorless and more or less tasteless, or insipid, pure neutral fats. This fact then seems to point to a possible source of some of the changes in flavor and aroma notes as hams age.

There is another consideration which may be well worth mentioning in connection with the free fatty acid content. On eating a quantity of cooked aged ham, a peculiar film is noted to be left coating the mouth and tongue. This quality has been frequently referred to as a "cheesyness" and is very characteristic of aging. It does not seem unreasonable to suggest a connection between this characteristic and the presence of the large amount of free fatty acids in the meat. These acids may, during mastication, interfere with the usual "wetting" of the meat by the saliva, hence making possible the formation of an adhesive film which clings in the mouth and throat. The flavor associated with this film is of such a quality as to suggest a possible formation of minute quantities of soap, either in cooking or in the mouth, by the interaction of the salt which is present in large amounts and the free fatty acids.

ANALYSIS OF THE LEAN MEAT

Several of the chemical relationships which would seem to be most significant with regard to the changes taking place in the lean tissue during aging have been studied. The results obtained and the methods used may be best presented under separate headings.

Determination of Moisture, Fat, Total Soluble Nitrogen and Soluble Amino Nitrogen.

Eight samples of the lean tissue of hams from two slow-fed series and nine samples from two full-fed series were extracted in the following manner.

The sample of lean tissue was washed from the storage flask into an evaporating dish with warm 95 percent alcohol. The alcohol-water mixture was driven off very slowly on a steam bath and the material covered again with 95 percent alcohol and evaporated to dryness. This was repeated four to five times to remove all the water from the tissue. After the final evaporation the meat was transferred with ether to a dry, weighed, extraction thimble, the thimble placed in a Soxhlet apparatus and extracted with ether for 8 - 10 hours. The thimble was then removed from the apparatus and the traces of ether driven from the material being extracted.

This material was transferred to a mortar and ground. The material was replaced in the thimble and re-extracted 10 hours with ether. The thimble was then removed, the traces of ether driven off, and the material dried in a vacuum desiccator over sulfuric acid to constant weight.

Most of the ether was driven off the ether-extract and the residue transferred to a small beaker and brought to constant weight in an electric oven kept at 100-105°. The ether extract was calculated as fat and the insoluble material as solids-not-fat. The sum of the fat and solids-not-fat was subtracted from the wet weight to get the moisture content.

The thimble containing the solids-not-fat was replaced in the Soxhlet apparatus and extracted for eight hours with 95 percent alcohol. The material was then removed from the thimble to a beaker, 50 c.c. of water added, and the mixture heated on a steam bath with stirring for 15 minutes, at a temperature less than 75° C. The beaker was removed and the supernatant liquid poured through the extraction thimble. This operation was repeated nine times and the alcohol and water extractions combined and made to a liter, a few drops of chloroform being added as a preservative.

Aliquots of this soluble material were analyzed for

total soluble nitrogen, amino nitrogen and salt. Total soluble nitrogen was determined by the Kjeldahl method. Amino nitrogen was determined by the Van Slyke method. For the salt determinations aliquots were made alkaline with sodium carbonate and evaporated to dryness; the residues were ignited at a dull red heat and extracted with dilute nitric acid. The chlorides were then precipitated and weighed as silver chloride.

Discussion of Results

The results of these determinations are given in Table X. Moisture is calculated as percentage of the wet tissue. Because of the loss in moisture and the great variation in the fat content, the fat, nitrogen, and salt are reported as percentages of the fat-and-moisture-free material. Strictly speaking, the fat is not a part of the solids-not-fat, but as the latter gives the most invariant basis for comparison, the fat is here presented as percentage of this material.

Moisture. It is evident that all the hams undergo a great loss in moisture during aging. Results on individual hams vary a great deal but it is evident, despite this, that the loss is considerably more rapid the first year than the

TABLE X.

Analysis of Lean Meat of Hams After Various
Periods of Aging.*

Full-Fed Series No. I.

Ham No.	Age in Months	Water	Fat	Total Soluble Nitrogen	Soluble Amino Nitrogen	Salt
9944	1	55.00	60.14	2.206	0.534	-
9940	4	48.42	42.90	2.676	0.936	22.12
9948	13	46.17	34.09	3.934	1.755	16.18
9942	18	37.00	36.08	3.680	1.789	17.84
9946	24	41.46	27.11	3.454	1.804	17.65

Full-Fed Series No. II.

3148	$\frac{1}{2}$	58.47	31.87	2.388	0.744	16.03
3151	8	46.44	32.79	2.815	1.470	16.57
3153	11	45.72	31.57	3.437	1.536	16.75
3157	24	39.64	26.53	4.021	2.290	15.26

Slow-Fed Series No. III.

2525	1	56.92	29.73	2.435	0.866	15.67
2528	$5\frac{1}{2}$	50.53	26.02	3.313	1.628	16.10
2520	13	43.81	33.39	3.323	1.693	17.97
2524	19	42.12	20.65	3.332	1.586	19.21
2522	24	36.60	21.50	3.122	1.393	15.03

Slow-Fed Series No. IV.

3167	$\frac{1}{2}$	61.23	20.01	2.131	0.575	20.73
3161	8	51.23	16.50	2.656	0.798	21.88
3170	18	41.53	18.83	2.984	1.136	20.86

* Water as percentage of the wet tissue.

Fat, nitrogen and salt as percentage of the fat-and-moisture-free material.

second. Also, it seems that the loss in the slow-fed groups is the more extensive, though the number of hams analyzed is not sufficiently great to establish this point definitely.

This loss of moisture is evidently responsible for the greater portion of the shrinkage which is found to occur in these hams. In view of the fact that the typical high flavor and aroma of country cured hams occur no sooner than the eighth month of aging, it seems very possible that loss of water may be one of the most important features of the aging process.

There is another aspect of moisture loss which seems worthy of mention. Desiccation of tissues has long been used as a means of preservation of meats; the activity of microorganisms in general being reduced by a dry environment. Hence, it seems quite logical to suppose that as these hams age their general susceptibility to bacterial growth is lowered.

Fat. The data obtained on the determination of the fat content of the lean tissue seem to show entirely too

much variation between different hams to give a basis for any very definite conclusions. Hams 9944 and 9940 were the first two which were dissected in this work, and it is possible that the high fat content shown was due to a less clean separation of the intermuscular fat than was carried out in later work. The general trend of the results in all the series analyzed, however, in view of the drippage of fat noticed during storage, indicates strongly that there was an actual and not inconsiderable loss of fat from the lean of these hams as they aged.

Unfortunately, the number of samples which have been analyzed is too small to furnish any more than an indication of the changes in this constituent.

Salt. The data on the salt content show that there is no noticeable change in the percentage on the moisture-and-fat-free basis. As would be expected, the penetration of salt in individual hams varies to some extent, but not enough to have any significance. Calculated on the wet weight, the salt content as seen in Table XI, below, rises gradually as the hams lose water.

As the preservative action of salt is a function of the concentration,⁽¹⁶⁾ this increase which occurs as

aging progresses may be of considerable significance from the standpoint of the relative susceptibility of hams of different ages to spoilage.

TABLE XI.

Percent Salt on Wet Basis

Full-Fed

Ham No.	Age	% Salt		Ham No.	Age	% Salt
9944	1	--		3148	0.5	5.05
9940	4	7.98		3151	8	6.68
9948	13	6.59		3153	11	6.90
9942	18	8.26		3157	24	7.28
9946	24	8.13				

Slow-Fed

Ham No.	Age	% Salt		Ham No.	Age	% Salt
2525	1	5.22		3167	0.25	6.70
2528	5.5	6.32		3161	8	9.16
2520	13	7.57		3170	18	10.27
2524	19	9.24				
2522	24	7.84				

Total Soluble Nitrogen and Soluble Amino

Nitrogen: The data obtained in these determinations show that there is a change both in the amount and character of the nitrogen bearing material as the hams age. All four of the groups studied show a distinct increase in the total soluble nitrogen as well as free amino groups, the relationship between the two percentages changing in a rather significant manner. The ratio of soluble amino nitrogen to total soluble nitrogen is given in Table XII on the next page. It can be seen that in general a low ratio is characteristic of the hams which have not been aged. The decrease in this ratio indicates that there is a hydrolysis of complex protein material into smaller fragments and amino acids with the freeing of amino groups.

In Figure VI, the results of the two determinations for each group are plotted against the time of aging. The manner in which the two determinations parallel in different hams is very evident and indicates strongly that the two increases have a distinct relation to one another. Bradley⁽¹⁷⁾ points out the presence of two tissue enzymes which cause autolysis in tissues. One acts on acid native proteins and converts them by primary cleavage into less complex bodies. The other acts on the primary cleavage products, converting them finally into amino acids. It is possible then that the

TABLE XII.

Ratio of Soluble Amino Nitrogen to
Total Soluble Nitrogen in Hams of Different Ages

Full-Fed Group I.

Ham No.	9944	9940	9948	9942	9946
Age (Months)	1	4	13	18	24
% Total Soluble N.	2.206	2.676	3.934	3.680	3.454
$\frac{\text{Soluble Amino N}}{\text{Total Soluble N}}$.24	.35	.44	.49	.53

Full-Fed Group II.

Ham No.	3148	3151	3153	3157
Age	0.5	8	11	24
% Total Soluble N.	2.388	2.815	3.437	4.021
$\frac{\text{S.A.N.}}{\text{T.S.N.}}$.31	.52	.44	.57

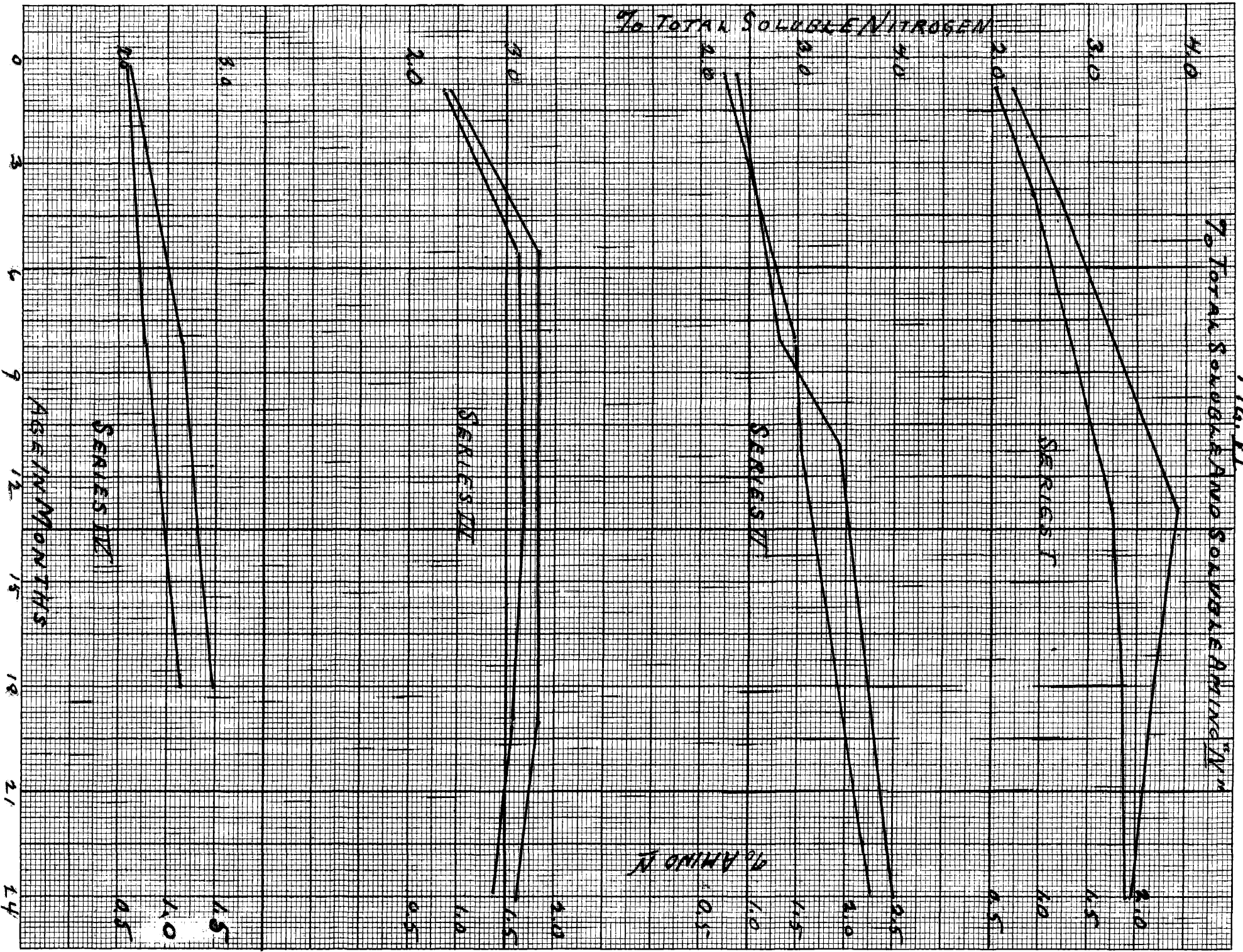
Slow-Fed Group III.

Ham No.	2525	2528	2520	2524	2522
Age	1	5.5	13	19	24
% Total Soluble N.	2.435	3.313	3.323	3.332	3.122
$\frac{\text{S.A.N.}}{\text{T.S.N.}}$.36	.43	.51	.48	.45

Slow-Fed Group IV.

Ham No.	3167	3161	3170
Age	0.25	8	18
% Total Soluble N.	2.131	2.656	2.984
$\frac{\text{S.A.N.}}{\text{T.S.N.}}$.27	.30	.38

FIG. VI



two increases noted are due to the slow action of these enzymes; the first being responsible for the increase in total soluble nitrogen, and the second for most of the increase in the free amino nitrogen groups. In addition to this there is the possibility of the increases being contributed to by enzymes of bacterial origin, many micro-organisms producing ferments which have an effect on tissue proteins similar to that occurring in autolysis.

Regardless of the primary cause, the significant points brought out are that an increase occurs in both the soluble amino and total soluble nitrogen, and that increase of the ratio of these two is a characteristic of aging.

In the introduction to this paper it was mentioned that white "flecks" are often noticed in the tissue of older country-cured hams. Several hams investigated in this work showed white semi-crystalline masses, which on purification, were shown to be almost pure tyrosine. Tyrosine is one of the most insoluble and also one of the first amino acids split off during protein hydrolysis.⁽¹⁸⁾ These two characteristics combined with the loss in water from the lean tissue are doubtless responsible for the appearance of these bodies.

So far as the writer knows there is no data available which would suggest a relationship between this freeing

of amino acids and flavor of the meat. Further investigation of this freeing of amino acids, in view of the chemical nature of these substances, would seem worthwhile.

Determination of Sugar in Hams of Different Ages

The sugar content was determined in samples of the lean tissue by the tentative method of the Association of Official Agricultural Chemists.⁽¹⁹⁾ The results obtained are given as percentages of invert sugar in Table XIII. The results of this determination show that there is a disappearance of sugar, though the extent of the decrease during the same period of aging is quite variable in different hams.

This decrease must be attributed to the fermentative action of microorganisms, numerous types of which decompose sugar with the production of various alcohols, acids and aldehydes, as well as carbon dioxide and water. The importance of this disappearance of sugar from the standpoint of flavor and aroma would seem to be considerable. The lower fatty acids such as propionic, butyric and acetic, as well as the alcohols, all have odors and flavors which even in minute quantities may contribute in no small measure to the changes noted in the aroma and

flavor of these hams.

TABLE XIII.

Sugar Content in Hams of Different Ages

Slow-Fed

Ham No.	Age	% Wet Weight	% Moisture-and fat-free	Ham No.	Age	% Wet Weight	% Moisture-and fat-free
2525	1	0.706	2.123	3167	0.25	0.634	1.891
2528	5.5	0.295	0.753	3161	8	0.107	0.298
2520	13	0.348	0.872	3170	18	0.000	0.000
2522	24	0.585	1.121				

Full-Fed

Ham No.	Age	% Wet Weight	% Moisture-and fat-free
3148	0.50	0.676	2.146
3151	8	0.975	2.418
3153	11	0.234	0.568
3157	24	0.356	0.746

Determination of Titrable Acidity

Titration of the filtered, boiling water extracts of samples of the lean tissue of hams of different ages showed a very marked increase in the total titrable acidity. The results are given in Table XIV, as c.c. of N/10 NaOH required to neutralize the extract from 1 gram of meat.

TABLE XIV.

Titrable Acidity of Lean Meat of Hams
of Different Ages

Age	1	4	9	12	18	24
Slow-Fed	0.64	0.80	1.12	1.11	1.85	1.95
Full-Fed	0.63	0.98	1.03	1.24	--	2.14

c.c. of N/10 NaOH per gram of lean tissue

It is not possible to definitely account for this acidity. A small portion is doubtless derived from the emulsification of free fatty acids arising from hydrolysis of the fat. Another possible source is the formation of small quantities of lactic acid from the normal tissue sugar, an

autolytic change which is usually held responsible in part for post-mortem acidity.⁽²⁰⁾ Many types of microorganisms produce short chain fatty acids during sugar dissimilation, and it is possibly to this source that some of the acidity is due, as it has been shown previously that there is a disappearance of sugar with age.

The above mentioned factors would all be more significant the first year than the second, whereas, the increase in total titrable acidity is seen to be somewhat greater during the second year of aging than the first. This seems to indicate that all the way through the aging process there is some effect which is more important than any of these noted above, or even their combined effect in determining the increase in titrable acidity.

It should be pointed out that this increase in acidity, except for moisture loss, is the most consistent change noted during aging. The values given above were obtained from individual hams of various ages from several different series, and are not averages except in one case - the value for one year's aging in the slow-fed groups. This suggests that if there was a need for a simple test for aging progress, the titrable acidity seems to furnish the greater possibilities. It would be a relatively easy matter

to sample a ham by merely removing a small cube of the lean meat, leaving the rest of the ham intact. This regularity of acidity increase is brought out in Figure VII.

Comparison of the Chemical Characteristics
of Two Types of Hams Produced
by Meat Packers.

In the course of the investigation of the quality of Maryland hams, two types of products with widely different characteristics, produced on a commercial basis by meat packers, were used at various times for the purpose of comparison. One of these is a brine-cured product which may for convenience be spoken of as the "packers ham". The aroma and flavor of this product, both raw and when cooked, are typically those of the quality characterizing freshly cured meat. The other type goes under the general name of "Virginia hams", and has the pungent, cheesy aroma and high flavor typical of aged Maryland hams. It seemed to be of interest to see if the chemical differences existing between freshly cured and aged Maryland hams also existed between these two types of commercial products.

c.c. N/10 NaOH

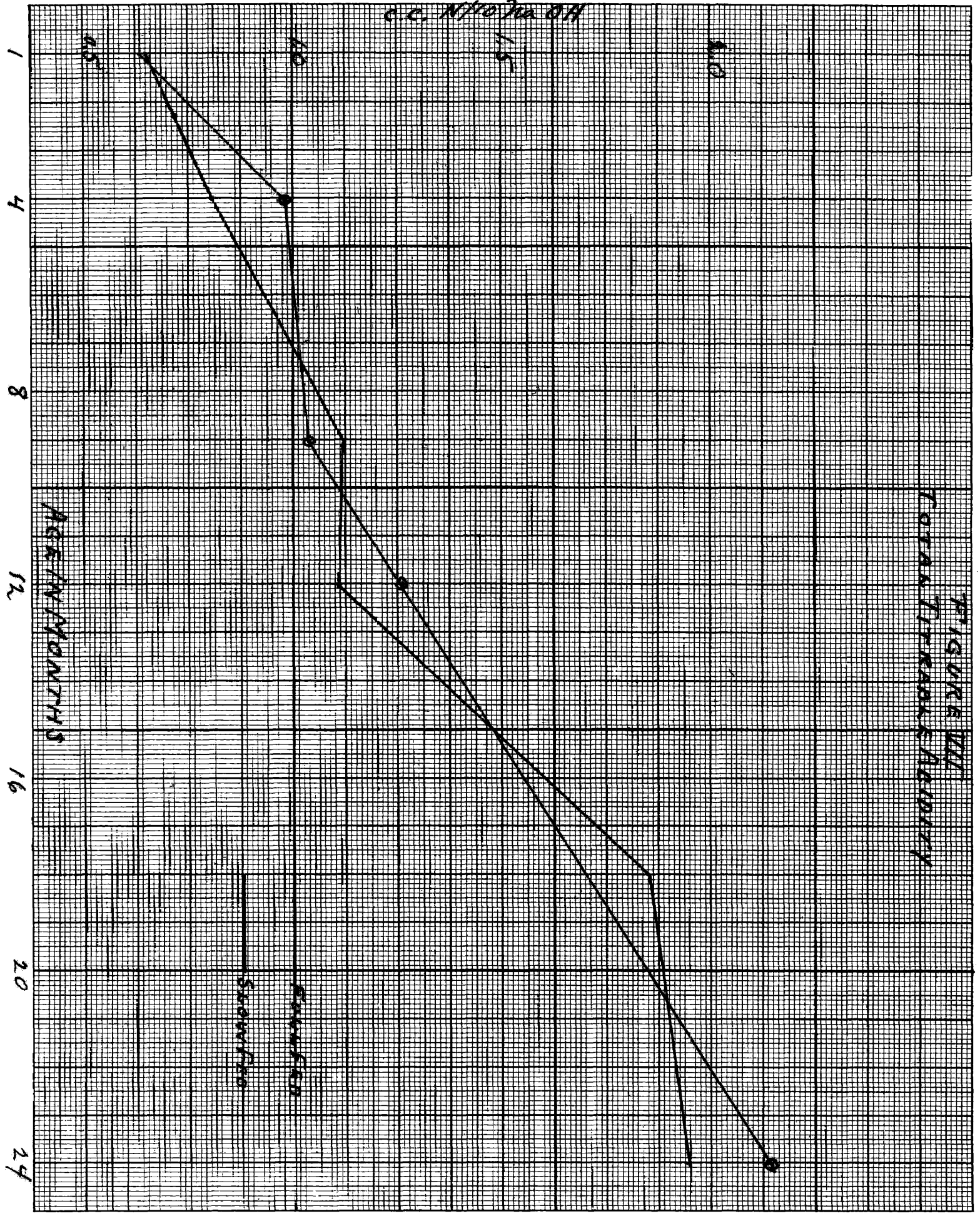


FIGURE III
TOTAL TITRABLE ACIDITY

AGE IN MONTHS

Summer

Winter

1
4
8
12
16
20
24

95

100

150

150

An analysis was made of the lean meat of these two hams, and the free fatty acid content was determined in the meat fat and external fat. The results are given below in Table XV. The analyses of two Maryland hams, which had been aged one month and one year respectively, are given for the sake of comparison.

TABLE XV.

Comparison of the Analysis of "Packers"
Hams and "Virginia" Hams *

	Total Soluble Nitrogen	Soluble Amino Nitrogen	Sugar	Acidity	Free Fatty Acids	
					Meat Fat	External Fat
"Packers"	1.855	0.470	1.500	0.53	6.02	1.57
"Virginia"	3.075	1.590	0.000	1.33	20.0	9.88
Maryland 1 month	2.388	0.744	1.629	0.64	4.28	3.46
Maryland 11 months	3.437	1.536	0.432	1.15	23.38	17.70

* Nitrogen on the basis of the moisture-and-fat-free material.

Discussion of Results

It has been pointed out in the preceding discussion that the soluble nitrogen content of aged Maryland hams is considerably higher than that of freshly cured hams, and also that another very significant indication of aging is a high ratio of soluble amino nitrogen to total soluble nitrogen. The nitrogen percentage of the "Packers" ham is seen in Table XV to be lower even than that of the freshly cured Maryland ham, while the Virginia ham, on the other hand, compares very favorably with the year old Maryland ham in this respect.

The differences in the soluble nitrogen is even more clearly shown below where the total soluble nitrogen to soluble amino nitrogen ratios are given.

Type of Ham	Packers	Maryland 1 month	Virginia	Maryland 11 months
<u>Amino Nitrogen</u> Total Nitrogen	0.25	0.31	0.52	0.45

It can be clearly seen that there is little evidence of freeing of amino groups by hydrolyses of the protein in

the "Packers" ham, while the Virginia ham ratio indicates that considerable hydrolysis has occurred.

This analogy between the "Packers" ham and the fresh Maryland ham on the one hand, and the Virginia ham and the aged Maryland ham on the other, is borne out in the other determinations which have been seen to measure aging; the sugar content is high in the "Packers" ham, while the titrable acid is low; the Virginia ham showed no sugar and high acidity. The figures on the free fatty acid content shows relatively little hydrolysis of fat in the "Packers" ham, and an extensive hydrolysis in the Virginia ham.

These results furnish strong evidence that there is an intimate relationship between the aroma and flavor of hams, and the chemical changes occurring subsequent to curing.

General Summary of the Investigations of
The Chemical Changes Occurring During the Aging
Of Country Cured Hams.

1. Analysis of the external fatty tissue has shown that there is an extensive loss of moisture during the first few months of the aging process. The results also seemed to point to a loss of fat from the fatty tissue of the full-fed hams during the second year of aging.

It has been pointed out that the loss in moisture may account for some of the physical changes frequently noticed in the fatty tissue.

2. Analysis of the purified fat has shown that there is a great increase in the free fatty acid content of the meat fat and external fat during the first year of aging. The ^{rate}velocity of hydrolysis slows down considerably during the second year of aging, the decrease being much more noticeable in the external fat than in the meat fat. It has been shown that during the early stages of fat hydrolysis the unsaturated fatty acids are freed in much greater quantities than the saturated, but that as hydrolysis proceeds the proportion of saturated acids split off increases rapidly, resulting in a fall in the iodine numbers of the

free fatty acids.

Also, it has been pointed out that the average refractive indices and specific gravities of the fats decrease as the free fatty acids increase.

The results of the Kreis test indicate that incipient oxidation generally occurs in both the internal and external fat of country cured hams as they age.

The iodine numbers show the fat of the full-fed hams to be slightly "harder" than that of the slow-fed hams.

3. Examination of the lean meat has shown that a great loss of moisture occurs during aging, the loss being somewhat greater the first year than the second. This loss seems to be more extensive in the slow-fed hams than in the full-fed.

The fat content of the lean tissue seems to decrease, the evidences of the decrease being more noticeable in the hams having the higher percentage of meat fat.

The total nitrogen and the nitrogen present as free amino groups both have been shown to increase, indicating a hydrolysis of the protein into more soluble fragments and amino acids.

The salt content has been shown to increase sufficiently, due to the loss in water, to have a possible

significance with regard to the relative resistance of hams of different age to the action of microorganisms.

The titrable acidity of the boiling water extracts increases in a very regular manner throughout the aging period. Decrease in the sugar, added in the curing mixture, has been shown to occur, and the possible effect on the flavor and aroma pointed out.

4. Analysis of two commercial products which resemble respectively, freshly cured Maryland hams and aged Maryland hams, has furnished evidence that there is a relationship between aroma and flavor, and the chemical characteristics as measured in this work.

Changes Produced in Hams by Injected Enzymes

It seems appropriate to mention some experimental work which has been carried out with the object of hastening the hydrolysis of the fat and protein of hams.

A method of injecting solutions into the main artery which leads into the ham has been devised by Mr. Hunt, of the University Department of Animal Husbandry. By this means several hams which had been cured but not smoked were injected with proteolytic and lipolytic anzyme suspensions. The hams were then smoked and stored in the usual manner. After two months aging, two of these hams were examined with the following results.

1. Ham injected with a suspension containing sufficient quantities of steapsin and trypsin to give a concentration of 0.1 gram of enzyme per pound of meat.

The lean of this ham was found to have undergone a great amount of hydrolysis, particularly along the path of the artery into which the suspension was injected. The meat was very soft and a great quantity of white flecking was noticeable.

Examination showed a great amount of hydrolysis to have occurred in the meat fat, while the external fat was

practically unaffected. The free fatty acid content of the meat fat was 24.0 percent and that of the external fat 4.5 percent.

The odor of this ham was very offensive, being identical with that of the enzyme suspension injected.

2. Ham injected with steapsin alone.

Contrary to what would be expected the lean meat of this ham was also very soft, indicating extensive hydrolysis of the protein. This was probably due to the steapsin preparation being contaminated with proteolytic enzyme.

The free fatty acid content of the meat fat was 23.0 percent and that of the external layer 4.0 percent.

The odor of this ham, also, was very offensively suggestive of the enzyme suspension.

3. Several hams were injected before curing with a solution containing curing ingredients and erepsin, trypsin and steapsin. These hams were then coated with dry curing mixture and cured, smoked, and stored in the usual manner.

After seven weeks aging one of these hams was examined and found to have undergone much less lean hydrolysis than the two hams which were injected after curing.

There was only a trace of the enzyme odor. The meat fat had undergone about the same amount of hydrolysis noted above in the hams injected after curing, the free fatty acid content being 23.7 percent. The external fat showed 3.7 percent of free fatty acids.

Discussion of Results Obtained.

The principal thing pointed out in these experiments is that hydrolysis can be hastened tremendously by increasing the enzyme content of the tissues. Before there would be any possibility of the use of enzymes in speeding up aging, however, the effects of various concentrations of the enzymes would have to be studied, and a means of purification of the enzyme solution devised.

Another possibility is suggested, however, on the basis of these results. Enzyme action is a function of the temperature as well as the enzyme concentration. Hence, by raising the temperature at which hams are aged the normal ham enzyme activity would be speeded up with an elimination of the need for adding accelerators. In this manner, the possible fermentation action of microorganisms would also be speeded up and the drying of the tissues facilitated.

CONCLUSION

The results of the work reported in this paper indicate that there are several factors of importance in the development of flavor and aroma in country cured hams. To which the most significance should be attached, it is impossible to say. Loss of water, hydrolysis of both the lean and the fat, and the fermentation of the sugar of the curing mixture each undoubtedly contribute a share.

It seems safe to suggest from the nature of the above changes that experimental work designed to hasten the various reactions occurring during aging would be of great value. The most reasonable starting point would seem to be in raising the temperature at which the aging process is carried out. Hydrolysis, drying, oxidation and fermentation all should be speeded up considerably by incubating cured hams at a temperature ten to fifteen degrees higher than room temperature. The factor of added danger of spoilage would seem to be the only point in such a procedure which would give trouble. By experimental work with varying types of curing mixtures and methods of application of the ingredients, the danger of spoilage could be doubtless controlled.

The shortening of the aging process from twelve or more months now required to produce a real aged ham, to three or four, would furnish grounds for the development of a phase of meat packing which, in this section at least, would find fertile grounds for development.

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