CHEMICAL STUDIES OF LIPOID EXTRACTS FROM MENHADEN FISH MEAL 1/

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ABSTRACT

Deteriorative changes taking place in the fatty protein of menhaden meal during the manufacture and storage, resulted in a decrease in the total fatty acid content, and an increase in the water-soluble and resinous materials. Experimental spoilage of the meal to simulate unfavorable storage produced only relatively minor further changes.

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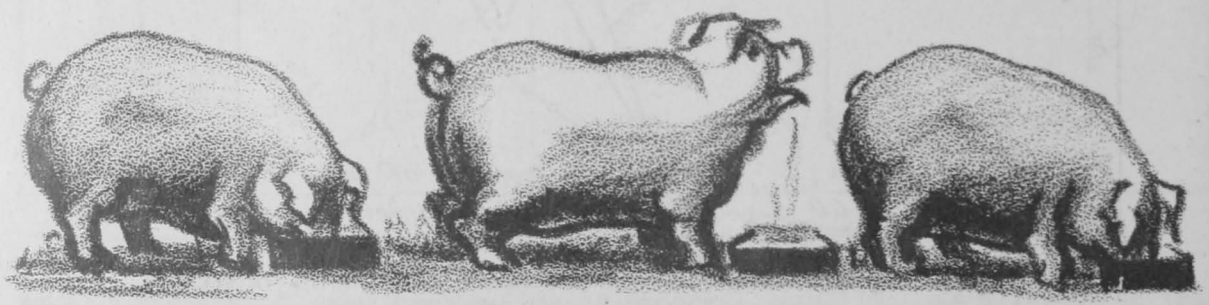
INTRODUCTION

Poultry and swine producers are finding that fish meals are one of the best sources of animal protein for balancing rations. Before the war, fish meals, tankage, meat meals, and dried or semi-solid milk products were used as sources of animal protein; mostly in combinations. The fish meal content of the ration was seldom in excess of five percent. During the wartime shortages of protein concentrates, it was found that a few percent of fish meal alone would balance the cereal proteins to furnish reasonably good growth and production. At the other extreme, Lanham and Nilson (1947) have reported that as much as 30 percent of fish meal in an otherwise properly balanced ration will not cause deleterious results with chicks.

Besides protein, fish meals also contain variable quantities of oil, vitamins, mineral matter, and fibrous material. The oil, vitamins, and mineral matter contribute some nutritive value, but their importance is secondary to that of the protein. Fish meal producers try to remove as much oil as is economically practical, since the oil can be sold at a higher price as a carrier of vitamins A and D, or for industrial purposes, than when left in the meal. Generally, the oil content is less than 15 percent of the meal as marketed. This residual oil usually has undergone certain degradative changes which may produce offensive flavors and



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odors. Some feeders are fearful that poisoning may result if meals containing highly decomposed oils are fed.

It is very difficult to extract all of the lipoid material from fish meal with most fat solvents. This is an important consideration which affects the choice of analytical procedures. The object of the investigation reported herein was to determine some of the chemical characteristics of lipoids which had been extracted from commercial menhaden meal, and from a meal that had been subjected to unfavorable storage so as to produce about the maximum of deleterious changes. Concurrent feeding tests with rats were conducted to determine the possible toxicity of the extracted materials (Kraybill and Nilson, 1946).

There are many articles in the literature which deal with the deterioration of fats and oils, and there is no apparent agreement among investigators as to the relative importance of the different chemical changes which are involved. There is not even general agreement as to the choice of analytical methods, and possibly more important, no agreement as to the significance of the different analytical variables in measuring deterioration of fats and oils. Bailey (1945) and the Office of the Quartermaster General (1945) have issued quite comprehensive reviews on the subject of deterioration of fats and oils, so no attempt will be made here to analyze or summarize the available data. The data obtained in this investigation are presented without attempting to corroborate or disprove any specific hypothesis as to the mechanism involved in deterioration.

EXPERIMENTAL DATA AND INTERPRETATION

Extraction of Lipoids from Meal

Two types of meal were used. One was a commercial menhaden meal such as is regularly sold for animal feeding. This was a sample of recent production which was obtained from the factory shortly before the tests were started. The other was a sample of the same meal which had been subjected to experimental spoilage, a process which was intended to cause a high degree of the same type of deterioration as would occur commercially under unfavorable conditions of heat and moisture. To accomplish this deterioration, the meal was moistened and allowed to remain damp for about three weeks at about 38° C. This treatment resulted in extensive bacterial and mold growth. The meal was dried at a temperature under 50° C. The data in Table 1 show that the composition of the two meals was similar except that about twice as much material was extracted by diethyl ether from the commercial meal as from the spoiled meal.

Table 1 - The Proximate Analysis of Commercial and Experimentally Spoiled Menhaden Meal

Sample	Moisture	Protein (N×6.25)	Diethyl ether extract	Mineral matter
	Percent	Percent	Percent	Percent
Commercial	9.20	59.37	11.42	17.32
	9.80	60.36	11.71	17.30
Experimentally spoiled	7.70	66.02	5.81	20.62
	7.72	64.61	5.39	20.69

This finding indicated that further study was needed to select a solvent which would more efficiently extract the oil from the fish meals. Conditions of extraction which would keep chemical changes to a minimum during the process also had to be determined.

Harrison (1931) and Oshima and Suguwara (1937) had reported a decrease in the ether-extract content of fish meals during storage. The latter authors stated that this decrease was due to the oxidation of fatty acids to ether-insoluble

products because they found a simultaneous decrease in the iodine and bromine values of the oil and a slight increase in the free fatty acid content. These workers found also that this ether-insoluble material was soluble in acetone and the greater part was also soluble in 20 percent aqueous solution of hydrochloric acid when the oil was heated in the acid. Hydrolysis with papain did not give the same results.

In order to minimize the possibility of chemical change during our extractions, either anhydrous sodium sulfate or calcium chloride was mixed with the meal before the various solvents were added and the extractions were carried out at refrigerator temperatures. Forty grams of meal were placed in an Erlenmeyer flask together with 10 grams of anhydrous sodium sulfate or calcium chloride. Two volumes of solvent were added, and the flasks were shaken and then permitted to stand for 24 hours at about 10° C. The solvent was decanted, and the extraction was repeated until the solvent remained colorless. At this stage, the extraction was

Table 2 - Data on the Quantity of Material Extracted from Commercial Menhaden Meal with Various Solvents in the Presence of Sodium Sulfate or Calcium Chloride at about 10° C.

Solvent	Chemical	Material Extracted	Solvent	Chemical	Material Extracted
		Percent			Percent
Acetone	sodium sulfate	8.10	Chloroform	sodium sulfate	10.44
		7.25			10.40
"	calcium chloride	4.33	Ether, diethyl	sodium sulfate	11.61
		4.47			11.43
Alcohol, ethyl	sodium sulfate	10.91	"	calcium chloride	5.56
		10.61			5.60
"	calcium chloride	4.40	Ether, petroleum	sodium sulfate	6.18
		4.86			6.19
Benzol	sodium sulfate	8.01	Solvent mixture 1/	sodium sulfate	12.51
		7.80			12.36
"	calcium chloride	5.68	Trichloroethylene	sodium sulfate	8.84
		5.71			8.66
Carbon disulfide	sodium sulfate	7.49			
		7.33			

1/ Benzol, 50; methanol, 25; and acetone, 25 percent by volume.

considered complete. The yield of extract was determined by drying to constant weight at 20° C. under vacuum. The data in Table 2 show that both the solvent and the added chemical affected the quantity of material extracted.

Table 3 - Data on Extraction at about 10° C. of Commercial and Experimentally Spoiled Menhaden Meal with Diethyl Ether and Solvent Mixture, Using Sodium Sulfate as a Dehydrating Agent

Type of Product	Solvent	Material Extracted
		Percent
Commercial meal	Ether	9.98
	Solvent mixture	16.35
Spoiled meal	Ether	6.21
	Solvent mixture	16.80
Ether extracted spoiled meal	Solvent mixture	11.31
Solvent mixture extract from spoiled meal	Ether	5.99

A solvent mixture consisting of 50 percent by volume of benzol, 25 percent of methanol, and 25 percent of acetone extracted the most material. More extract was obtained with anhydrous sodium sulfate than with calcium chloride under these conditions. Solvent addition compounds were undoubtedly formed with calcium chloride.

The results presented in Table 3 (see p. 10) show that the solvent mixture extracted lipoid material equally well both from the commercial and spoiled meals. Apparently, products are formed during the experimental spoilage of the meal which can be extracted by the solvent mixture but not by diethyl ether.

Effect of Storage Conditions

In order to estimate the degradation that occurs in the constitutive oil in the meal as affected by temperature, 25-pound samples of commercial meal were stored in paraffin-lined cans at temperatures of -23°, 25°, and 37.5° C. These temperatures cover the extreme range of practical storage conditions. Initially, and after storage periods of 3, 8, and 12 months, portions of each sample were extracted with the solvent mixture at 10° C. as described previously. The iodine and saponification numbers were used as the preferable criteria for following the trend of deterioration. The peroxide and aldehyde values seem less reliable indices, but did prove useful for comparative purposes.

Table 4 - Analytical Data on the Oil Extracted by the Solvent Mixture at about 10° C. from Samples of Commercial Menhaden Meal stored in Parrafin-Lined Cans at Various Temperatures

Period of Storage and Temperature in °C.	AVERAGE VALUES			
	Iodine Number	Saponification Number	Peroxide Value	Fat Aldehyde Value
Initial sample:				
-23	128	182	50	10
25	128	181	49	9
37.5	128	182	51	10
After 3 months:				
-23	126	185	71	13
25	126	189	69	12
37.5	122	194	114	11
After 8 months:				
-23	126	190	7	27
25	118	211	8	37
37.5	81	220	8	68
After 12 months:				
-23	116	194	8	7
25	113	218	9	7
37.5	68	228	9	12

Note: The iodine number was determined by the Hanus method (Association Official Agricultural Chemists, 1935). The saponification number was determined according to the method of the Association of Official Agricultural Chemists (1935).

The peroxide value was determined according to a modification of the Wheeler method as follows: 3 to 10 g. of oil are dissolved in 50 ml. of a mixture of glacial acetic acid and chloroform (3 to 2 by volume), and 1 ml. of saturated potassium iodide solution is added. Nitrogen gas is fed into the flask containing the reaction mixture, and the flask is rotated periodically. Better results are obtained if the flask is placed in an ice and salt bath. After 5 or 10 minutes, 50 ml. of water are added, and the titration is carried out immediately with 0.005N thiosulfate, starch being added as an indicator near the end point. The aldehyde value was determined according to the Schibsted (1932) method. This method was satisfactory for light-colored oils, but with dark-colored oils there was a masking effect which required comparing an orange red with a red color.

The data in Table 4 show that degradation proceeds at an accelerated rate in the extract after the first three months of storage. The rate appeared to be influenced by the temperature of storage, but chemical changes occurred even at -23° C. These changes were indicated by a decrease in the iodine number and an increase in the saponification number after three months of storage. There was a rather marked increase in the peroxide value. The extract from the meal stored at the highest temperature showed the greatest change.

After eight months of storage, the changes in the iodine and saponification numbers followed the pattern observed after three months of storage. There was, furthermore, a marked decrease in the peroxide value and a significant increase in the aldehyde value. After 12 months of storage, similar changes were again indicated in the iodine and saponification numbers. Both the peroxide and aldehyde values, however, were small.

The data suggest that there was an initial formation of peroxides, which were later destroyed with the production of aldehydes. These decomposed with the formation of free fatty acids.

A few experiments were carried out at a later date to identify the aldehydes. Qualitative tests with reagents such as fuchsin sulfurous acid and dimethyldihydroresorcinol indicated the presence of the aldehydes but did not identify them except for small amounts of acrolein and valeraldehyde.

Analytical Data for Extracts

Fractionation studies were carried out with the several extracts and also with a sample of commercial, cold-pressed menhaden oil in order to determine what chemical changes took place in the oil during the preparation of the commercial and the experimentally spoiled meals. It must be emphasized, however, that only a single sample of menhaden meal was used. Time did not permit extracting other lots to determine what variability might be expected in the analytical data. The main concern was to determine the general nature of the changes to be expected during the preparation of commercial-grade fish meal and what the nature of further changes are during subsequent experimental spoilage.

FLASKS AND LIEBIG CONDENSER

A continuous extraction apparatus was used for extracting the oil from the fish meals. This consisted of a 12-liter, round-bottom flask supported on a sand bath heated by an electric hot plate. The round-bottom flask retaining the solvent was connected by means of a syphon tube to a Knightware ceramic extractor with a capacity of about 10 liters. A Liebig condenser for condensing the solvent was fitted to the top of the extractor. The solvent mixture was used since it extracted about the same quantity of material from both the commercial and spoiled meal.

With this apparatus, the extraction could be carried out rapidly with the possibility of relatively insignificant chemical changes in the extract; so the slower method of mixing the solvent with the meal and storing the mixture in the cold was not used. Precautions were taken to maintain a rapid rate of extraction under an inert atmosphere. The extracts were kept under an atmosphere of nitrogen in subsequent manipulations at any time that conditions favored degradative changes.

The two extracts and a sample of cold-pressed oil (the only sample of menhaden oil available at the time this study was carried out) were saponified with 2N alcoholic potassium hydroxide in accordance with the method of Mattill (1931) and Olcott (1932). The soaps were dissolved in water after the removal of the ethanol under reduced pressure and in an atmosphere of nitrogen. The unsaponifiable fraction was extracted with diethyl ether.

The soaps were acidified with 20 percent sulfuric acid, and the liberated fatty acids were extracted with diethyl ether. The fatty acids were separated into saturated and unsaturated fractions by the lead salt - alcohol method of Twitchell (1921).

The data in Table 5 show that the extracts from the two types of meal contained about 55 percent of total saturated and unsaturated acids, as compared with 88 percent in the cold-pressed oil. About one-third of the acids in the extracts and about one-fourth in the cold-pressed oil were saturated. The ratio of saturated to unsaturated acids found in the extracts is very similar to that reported by other investigators for menhaden oil when no mention was made of the degree of refinement. The iodine number of the unsaturated acids in the extracts was markedly less than for the unsaturated acids from the cold-pressed oil.

Table 5 - Yields and Iodine Numbers of the Various Fractions of Cold-Pressed Menhaden Oil and Extracts from Commercial and Experimentally Spoiled Menhaden Meal

Source and fraction	Yield		Iodine number	Source and fraction	Yield		Iodine number
	Grams	Percent			Grams	Percent	
Cold-pressed oil:				Commercial-meal extract (Cont.):			
Combined acids:	443.0	88.1	176.6	Water-soluble material	142.2	28.0	
Saturated	112.9	25.5	5.3	Resinous material	75.0	14.8	37.0
Unsaturated	330.0	74.5	237.0	Unsaponifiable matter	15.0	3.0	69.0
Water-soluble material	43.5	9.8		Spoiled-meal extract:			
Resinous material	0.2	0.1		Combined acids:	289.0	55.6	60.0
Unsaponifiable matter	10.4	2.1		Saturated	92.3	31.9	1.2
Commercial-meal extract:				Unsaturated	197.0	68.2	100.0
Combined acids:	273.0	53.7	67.5	Water-soluble material	154.4	29.8	
Saturated	104.0	38.1	13.2	Resinous material	50.0	9.6	
Unsaturated	169.0	61.9	108.3	Unsaponifiable matter	26.0	5.0	

There was almost three times as much water-soluble fraction in the extracts as in the cold-pressed oil. The constituents of this fraction have not been identified, but some of them are undoubtedly such fatty acid degradation products as short-chain fatty acids and aldehydes.

An ether-insoluble fraction was obtained which is identified as resinous material in Table 5. This material was suspended as a tarry mass in the fatty acids after the latter were liberated with 20 percent sulfuric acid from the soaps of the cold-pressed oil and of the extracts from the meals. The resinous material became relatively hard and brittle on exposure to air after having been removed from the fatty acids by filtration. It had an iodine number of 37, indicating the possible presence of a small amount of unsaturated compounds. The resinous materials from the commercial and spoiled meal extracts also contained 1.50 and 2.78 percent nitrogen, respectively. This suggests that the resinous material is a mixed product of unsaturated glycerides and nitrogenous compounds.

The unsaponifiable matter amounted to 2.06 percent in the cold-pressed oil and 2.96 percent in the extract from the commercial meal. It is doubtful that this difference is significant. In the extract from the experimentally spoiled meal, 5.0 percent of this product was found. This difference is undoubtedly significant, and may be the result of a degradation of the resinous material through microbial action during spoilage of the meal.

The component fatty acids of the extracts from the commercial and spoiled menhaden meals were estimated in order to obtain additional information on the degradation of lipoids. This was accomplished by fractionation of the methyl esters derived from the saturated and unsaturated acids.

The methyl esters were prepared in the usual manner with absolute methanol and dry hydrogen chloride gas. The distillation apparatus consisted of a round-bottom distillation flask which was heated by an electric mantle. The flask was

Table 6 - Data on Yields, Mean Molecular Weights, and Iodine Numbers of Fractions Obtained from the Distillation of Methyl Esters of Fatty Acids from Commercial Menhaden Meal

Fraction	Yield	Boiling point (0.5 to 1.0 mm)	Mean molecular weight	Iodine number	Unsaturation value 1/
	Grams	°C			
Saturated fatty acids: 2/					
1	0.4	119 - 125	245.1	0.6	
2	1.0	125 - 135	248.9	0.4	
3	8.5	135 - 140	296.6	0.1	
4	6.8	140 - 144	273.9	0.0	
5	0.9	144 - 150	281.4	2.1	
6	3.1	150 - 165	295.4	2.1	
7	1.5	165 - 174	309.4	3.7	
Residue	4.6		374.4	5.0	
Unsaturated fatty acids: 3/					
1	2.3	129 - 135	238.8	23.5	0.44
2	2.9	135 - 140	252.1	39.1	0.77
3	8.1	140 - 145	264.2	86.4	1.60
4	2.5	145 - 152	271.0	83.6	1.78
5	6.2	152 - 156	276.9	93.9	2.05
6	3.1	156 - 160	283.6	102.2	2.28
7	2.7	160 - 165	286.2	100.5	2.29
8	6.6	165 - 172	294.8	101.2	2.35
9	0.9	172 - 180	324.1	113.1	2.88
Holdup	3.0	180 - 185	391.4	108.6	3.35
Residue	6.8			96.2	

1/ The unsaturation value equals iodine number divided by 100, times the mean molecular weight, divided by the atomic weight of iodine. This represents the mean number of hydrogen atoms required to completely saturate the unsaturated fatty acid molecule.
2/ With saturated fatty acids, 26.8 g. of esters were recovered from a total of 27.5 g.
3/ With unsaturated fatty acids, 45.2 g. of esters were recovered from a total of 47.0 g.

connected directly to a vertical, electrically-heated glass tube about three feet long which was filled with glass helices. A No. 6632 glass distillation head was fitted to the top of the tube. This head was designed for total reflux, and permitted partial take-off. All connections were standard-taper, ground-glass joints. The distillation was carried out under a pressure of 0.10 to 0.50 millimeter of mercury.

The data in Tables 6 and 7 permit an estimation of the component fatty acids from the mean molecular weight of the fractions (Table 8). It is believed that enough fractions of the methyl esters were separated to permit this interpolation from a nomograph calculated on the assumption that no fraction contained more than two fatty acids in a homologous series, and that the percentage distribution of the two acids was proportional to the mixed molecular weight. This method has been found useful in the estimation of approximate values, but cannot be depended upon to indicate actual distribution, especially for the unsaturated acids of higher molecular weights.

The data in Table 8 indicate that the conditions of manufacturing commercial fish meal alter the composition of the oil. There was a considerable increase in the quantity of C_{16} and C_{18} acids, and a decrease in the quantity of the C_{14} saturated acids as compared with the analysis for menhaden oil reported by Stingley (1940). There was also an increase in the quantity of C_{14} and C_{16} acids, and a decrease in the quantity of C_{18}, C_{20}, and C_{22} unsaturated acids. It is not possible

to determine exactly what happened to the different fatty acids during the production of the meal, but apparently the unsaturated acids having C_{18} or more carbon atoms were decomposed to unsaturated acids of shorter molecular weight and to

Table 7 - Data on Yields, Mean Molecular Weights and Iodine Number of Fractions Obtained from the Distillation of Methyl Esters of Fatty Acids from Spoiled Menhaden Meal

Fraction	Yield	Boiling point (0.5 to 1.0 mm)	Mean molecular weight	Iodine number	Unsaturation value[1]
	Grams	°C			
Saturated fatty acids:[2]					
1	3.2	119 - 124	250.9	1.5	
2	3.2	124 - 134	265.8	1.8	
3	5.9	134 - 139	271.2	0.0	
4	7.4	139 - 140	266.6	3.6	
5	3.7	140 - 142	275.1	2.5	
6	4.9	142 - 165	275.7	0.9	
7	3.0	165 - 174	289.9	0.9	
Residue	3.5		329.7	5.1	
Unsaturated fatty acids:[3]					
1	0.5	118 - 125	213.2	33.7	0.56
2	1.9	125 - 130	231.2	35.6	0.65
3	1.2	130 - 135	250.5	36.3	0.72
4	2.8	135 - 140	255.8	37.2	1.15
5	4.1	140 - 145	262.0	76.8	1.59
6	3.8	145 - 150	280.8	77.2	1.71
7	5.3	150 - 159	299.5	96.0	2.27
8	4.0	159 - 165	322.8	109.6	2.78
9	3.2	165 - 170	360.1	124.7	3.54
10	0.8	170 - 175	424.4	113.6	3.80
Holdup	2.6				
Residue	2.5				

1/ The unsaturation value equals iodine number divided by 100, times the mean molecular weight, divided by the atomic weight of iodine. This represents the mean number of hydrogen atoms required to completely saturate the unsaturated fatty acid molecule.
2/ With saturated fatty acids, 35.8 g. of esters were recovered from a total of 36.4 g.
3/ With unsaturated fatty acids, 32.7 g. of esters were recovered from a total of 36.5 g.

saturated acids. Undoubtedly, some of the so-called saturated acids are oxidized acids which do not absorb iodine and are, therefore, not true saturated fatty acids. Part of the unsaturated acids may also have been decomposed to form the

Table 8 - Data on the Component Fatty Acids in the Total Acids Extracted from Commercial and Experimentally Spoiled Menhaden Meal, as Calculated from the Mixed Molecular Weights of the Methyl Esters

Source of total acids	Acids, percent by weight						
	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
Saturated:							
Commercial meal	0.0	1.9	21.5	5.8	0.8	1.8	4.6
Spoiled meal	0.0	3.2	20.6	3.4	2.7	0.4	0.0
Menhaden oil[1]	-	7.0	16.0	1.0	-	-	-
Unsaturated:							
Commercial meal	0.4	8.5	28.7	20.0	1.5	0.0	0.0
Spoiled meal	4.0	9.4	17.1	15.5	11.0	5.3	2.6
Menhaden oil[1]	-	trace	17.0	27.0	20.0	12.0	-

1/ Data reported by Stingley (1940).

water-soluble material reported in Table 5. Under these circumstances, it is not possible to determine what changes are due to hydrolysis, hydrogenation, or oxidation.

The experimental spoilage of the commercial meal by means simulating unfavorable storage produced relatively minor further changes in the fatty acid components of the oil. There was a six percent decrease in the quantity of saturated acids as compared with the extract from commercial meal, with an approximately equal increase in the quantity of the unsaturated acids. There was a decrease in the content of the C_{24} saturated acids and the C_{16} and C_{18} unsaturated acids. There was an increase in the quantity of the C_{12}, C_{20}, C_{22}, and C_{24} unsaturated acids. It is rather difficult to explain the increase of C_{20} to C_{24} unsaturated acids except that they were synthesized from shorter-chain acids by bacteria and molds. It is interesting to note that 0.02 percent of C_{10} (not reported in Table 8), and 4.0 percent of C_{12} unsaturated acids were found in the spoiled-meal extract. Unsaturated acids of this length have been seldom reported as being present in foods.

A quantitative determination of total lipoid material by the method of Bloor (1926) was also carried out. The data in Table 9 show that the commercial-meal

Table 9 - Data on the Yield, Color, and Iodine Numbers of Lipoid Fractions Obtained from a 100-gram Sample of Commercial Menhaden Meal

Fraction	Yield	Calculated on Basis: Dry meal	Calculated on Basis: Total extract	Color	Iodine number
	Grams	Percent	Percent		
Alcohol-ether extract	12.76	14.14	-	Dark brown	105
Combined phospholipides	1.90	2.10	14.85	-	-
Lecithin	1.79	1.98	14.02	Light brown	120
Cephalin	0.11	0.12	0.83	Yellow white	195
Acetone extract	7.83	8.68	61.38	Brown red	-
Fatty acids	7.51	8.33	58.90	Yellow	93
Unsaponifiable matter	0.34	0.38	2.69	Brown	-
Ether-insoluble matter	1.53	1.69	12.00	Light brown	138

extract contained about 12 percent ether-insoluble material. This was found to be a resinous material quite similar in quantity and appearance to that reported in Table 5. The iodine numbers for the lecithin and cephalin fractions were rather high, indicating that the fatty acid fragments in the compounds must be highly unsaturated.

DISCUSSION

The data on iodine values in Table 5 indicate that considerable degradation of oils takes place during the manufacture of the meal. This conclusion is confirmed by the data in Table 8 on the estimated component fatty acid content of the extract. There was a less significant change as a result of experimental spoilage to simulate the effects of unfavorable storage. Aside from a change in the fatty acid composition, degradation of oil definitely promotes the combination of some of the constituents of the oil with protein break-down products to form resinous material. This material amounts to about 15 percent of the extract from commercial meal. There is also a fragmentation of the fatty acids to increase greatly the content of water-soluble material. The latter two components have not been identified. It is suggested that considerable new information on the mechanism of the degradation of oils could be obtained if these identification studies were completed.

It is recognized, of course, that simultaneous chemical changes occurred in the protein of the meal. These changes were probably not very extensive during the manufacture of the commercial meal, but most certainly considerable degradation took place during the experimental spoilage. The spoiled meal had a very foul odor and also smelled strongly of ammonia.

In general, it may be surmised that the chemical changes which took place in the lipoids of the commercial meal were a result of reactions begun during the initial steam-cooking process, and were likely due to the later drying of the pressed fish scrap to produce the dry, commercial meal. Degradation reactions initiated in these manufacturing steps, however, continued during storage under conditions which did not promote marked decomposition of protein, the rate being influenced by the temperature of storage and undoubtedly by other environmental factors (Table 4). The differential changes which were found to have taken place in the lipoids of the experimentally spoiled meal were more probably due to the hydrolytic and synthetic actions of bacteria and molds.

SUMMARY

1. A solvent mixture consisting of 50 percent by volume of benzol, 25 percent methanol, and 25 percent acetone produced the highest yield of extract from fish meals, regardless of the degree of deterioration of the oil.

2. Deteriorative changes taking place during the manufacture and normal storage of the meal resulted in a decrease in the total fatty acid content, and an increase in the water-soluble and resinous materials.

3. Experimental spoilage of the meal to simulate unfavorable storage produced relatively minor changes in the fatty acid composition. There was a decrease in the quantity of the saturated acids with a corresponding increase in the unsaturated acids. There was also an increase in the unsaponifiable matter and a decrease in resinous material, as compared with the extract from the commercial meal.

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BALLOON TRAWL CONSTRUCTION

(LONG ISLAND TYPE)

Several kinds of balloon trawls are used successfully along the Atlantic Coast for catching butterfish, porgy, weakfish, etc. These trawls are constructed much the same as the so-called "flat" net which is used in trawling for flounder and fluke, except that in the balloon trawl enough fullness is built into the wedge or gore to allow the net a higher opening at the mouth. As a result of the higher opening, the balloon trawl will take fish which are at times off the bottom a sufficient distance to allow them to escape a "flat" trawl.

Like any other fishing gear, balloon trawls vary considerably in accordance with the individual operator's ideas of the best design and construction to fit his particular circumstances. The trawl described in this leaflet is one of the types used in Long Island waters by small dragger vessels usually about 35 to 45 feet in length. Larger vessels with greater propulsion power use larger balloon trawls, but the trawl specified herein is well fitted for use with the smaller type of vessel.

--Fishery Leaflet 245