Permeability of Acetostearin Products to Carbon Dioxide, Oxygen, and Nitrogen

N. V. LOVEGREN and R. O. FEUGE
Southern Regional Research Laboratory, New Orleans, La.

The acetostearins are modified fats capable of being formed into waxlike films, potentially useful as protective coatings. Permeability to carbon dioxide was measured by modification of the standard cup method, using Ascarite as the absorbent. An apparatus was developed which could measure in about 8 hours the passage of a few hundredths of 1 ml. of gas through a film of acetostearin, $2^3/_8$ inches in diameter, into a sweep gas which was analyzed. Permeability of the acetostearins to carbon dioxide was less than that reported by other investigators for ethylcellulose and approximately the same as for polystyrene and polyethylene. Nylon and regenerated cellulose have lower permeabilities. Polystyrene and ethylcellulose are more permeable to oxygen and nitrogen than acetostearin; polyethylene has approximately the same permeability. Cellulose acetate, regenerated cellulose, and nylon are less permeable.

ACETOSTEARIN PRODUCTS, consisting to a large extent of di- and triglycerides containing one and two acetyl groups, respectively, are unique, in that they ordinarily solidify to solids which are simultaneously nongreasy and waxlike (*4*). This peculiar physical property has been shown to be associated with the alpha and subalpha polymorphic modifications of the individual acetoglycerides (*6, 11*). Although the products are thermodynamically unstable in the waxy state, they are stable for all practical purposes. Only when the individual acetoglycerides are isolated and purified do they readily revert to the thermodynamically stable, nonwaxy form. The acetostearin products studied are technical grade mixtures containing not only acetoglycerides of palmitic and stearic acids but also monoglycerides and in some instances di- and triglycerides of these fat-forming acids.

Because the acetostearin products are waxlike, they are potentially useful as protective coating materials. Thin, almost invisible films might be applied to processed meats, cheese, baked goods, vegetables, and other foods. The only obstacle to commercial use appears to be a lack of sufficient proof of edibility, and this has been investigated by several groups. Preliminary results indicate that these compounds are utilized in the same way as ordinary triglycerides containing the same long-chain fatty acids (*1, 5, 8, 9*).

As an aid in the commercial utilization of acetostearin products, a knowledge of their permeability to water vapor and the common atmospheric gases, oxygen, nitrogen, and carbon dioxide, is important. Permeability to water vapor has been described (*7*). In the present article the permeability of several acetostearin products to carbon dioxide, oxygen, and nitrogen is compared with that for several types of polymeric materials.

Materials and Methods

Materials Two series of acetostearin products were used in the experimental work. Series A was prepared from technical grade monoglycerides derived from highly hydrogenated cottonseed oil and containing about 60% of monoglycerides, 35% of diglycerides, 5% of triglycerides, and no free glycerol.

Series B was prepared from a commercial, molecularly distilled monoglyceride (Myverol 18:05), which contained 91.5% of monoglycerides and approximately 1% of free glycerol. The product had been derived from triple-pressed stearic acid having an average molecular weight of 270.9.

The monoglycerides were acetylated by mixing and heating with acetic anhydride for 1 hour at 110° C. The reaction was stopped by adding water, and the reaction product was washed with water to remove acetic acid. Bleaching with neutral activated clay and mild deodorization by the conventional technique completed the purification of the products.

The melting range, monoglycerides content, and hydroxyl value of the purified acetostearins are listed in Table I.

Cup Method The well known cup method, modified slightly (*7*), was used to obtain most of the data on permeability to carbon dioxide. A sodium hydrate–asbestos mixture

Table I. Products Used in Permeability Determinations

Product[a]	*Hydroxyl Value*	*Monoglyceride Content, %*	*Acetyl Content, %*	*Melting Range, ° C.*	*$(CH_3CO)_2O$ per OH*[b]
A–1	107.3	10.5	7.3	44.5–46.8	0.5
A–2	49.4	2.5	11.3	30.0–39.8	1.0
A–3	27.7	0.2	13.0	32.4–35.6	2.0
B–1	136.1	14.2	10.3	35.0–41.0	0.5
B–2	95.5	5.0	12.8	32.8–37.2	0.75

[a] Series A was prepared from technical monostearin (approximately 60% monoglycerides) made from hydrogenated cottonseed oil (iodine value, approximately 1). Series B was prepared from Myverol 18:05.

[b] Ratios are moles of acetic anhydride per hydroxyl equivalent used in preparation of acetostearins.

(Ascarite) was used as the absorbent for carbon dioxide and was placed inside the glass cups used in the measurements. The product whose permeability was to be measured was cast into a film by allowing the molten product to solidify on a mercury surface as the mercury cooled to below the melting point of the product. A circular section of the cast film was sealed over the cup with the aid of a hot wire.

When the assembled cup was stored in a desiccator under carbon dioxide, commercial cylinder quality, the film of acetostearin product was permeated at a rate that eventually reached a constant value as determined by successive weighings. From the rate of gain in weight and the dimensions of the film a permeability constant for the particular product under test was determined.

Sweep Method

Permeability to oxygen and nitrogen could not be determined by the cup method, because there is no convenient absorbent for these gases. An extensive modification of the Davis apparatus and procedure (*3*) was used, which essentially involved placing the gas whose permeability was to be measured on one side of a film of acetostearin product. As the gas passed through the film it was swept away by a second gas, carbon dioxide, into a 50% solution of potassium hydroxide, which reacted with the carbon dioxide and left the test gas unchanged.

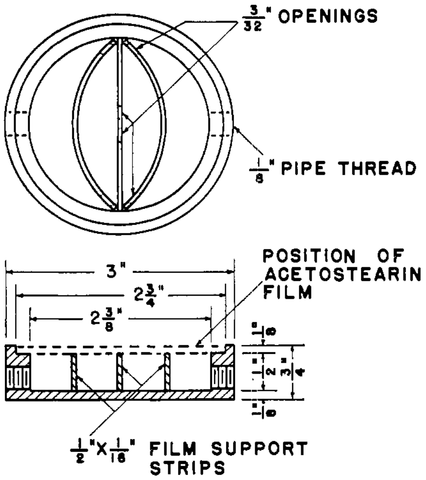

Figure 1. Aluminum film holder

The holder for the film of acetostearin product under test consisted of an aluminum cup machined as shown in Figure 1. Three aluminum strips were used to give support to the film and to distribute the sweep gas to all parts of the film. Good distribution was assured by perforating the middle section of the straight inner strip and the end sections of the curved outer strips. The film, formed as described previously, was sealed to the holder by melting the edge of the film with the aid of an electrically heated wire, and allowing it to resolidify while in contact with the metal. Additional product was used where necessary to make a good seal.

The entire sweep apparatus for measuring the permeability to oxygen and nitrogen was assembled as shown in Figure 2. The film holder, *H*, was sealed in a chamber consisting of a short section of large-diameter glass tubing capped at the ends with rubber stoppers. Inlet and outlet tubes of borosilicate glass were provided as shown in Figure 2. This unit was mounted in the constant-temperature bath, *I*.

Prior to making a permeability determination for oxygen or nitrogen the apparatus and film of product to be tested were equilibrated as follows: The sweep gas, carbon dioxide, was introduced at the inlet, *A*, and passed through the drying tube, *C*, containing specially prepared anhydrous calcium sulfate (Drierite), then through the film holder, *H*, and finally through the left unit of the pressure regulators, *J*. The oxygen or nitrogen was introduced at the inlet, *M*, passed through the drying tube, *L*, containing anhydrous calcium sulfate, then introduced into the film holder, *H*, and finally discharged through the right unit of the pressure regulators, *J*. By means of the pressure regulators, *J*, which contained mineral oil, the pressures of both the test and sweep gases were adjusted to slightly above atmospheric, 2 to 5 mm. of butyl phthalate, as indicated by the three-way manometer, *G*. The sweep gas was maintained at a pressure slightly greater than that of the test gas. The rate at which the test and sweep gases were introduced into the assembly was controlled to produce 10 to 20 bubbles per minute in each of the pressure regulators, *J*. These rates were maintained until the film of acetostearin product became adjusted to the change in humidity and the rate of transfer of the test gas through the film became constant. Usually 1 to 4 days were required, depending upon the thickness and composition of the acetostearin product.

To make an actual measurement of permeability to oxygen or nitrogen, the following procedure was used: Some of the sweep gas was passed into the nitrometer, *K*, to flush out the connecting tubes. A small amount of oxygen or nitrogen was put into the nitrometer to bring the meniscus down to the first graduation marks. Then the flow of sweep gas to the film holder was stopped by turning the stopcock nearest the film holder, and the stopcock in the line to the pressure regulator was closed. The 100-ml. gas buret, *F*, was filled with sweep gas, which was passed through the apparatus into the nitrometer over a 15-minute period by raising at a uniform rate the mercury reservior attached to the bottom of the 100-ml. sweep gas buret, using an electric motor and gear arrangement, *D* and *E*. During the operation the pressure was adjusted by means of the nitrometer reservoir. The volume of residual gas collected in the nitrometer was termed the sweep gas blank.

Figure 2. Sweep method apparatus used in determination of oxygen and nitrogen permeability

B. Sweep gas overflow
D. Gear reducer
E. Electric motor
K. 1.5-ml. Pregl semimicronitrometer
M. Oxygen or nitrogen inlet

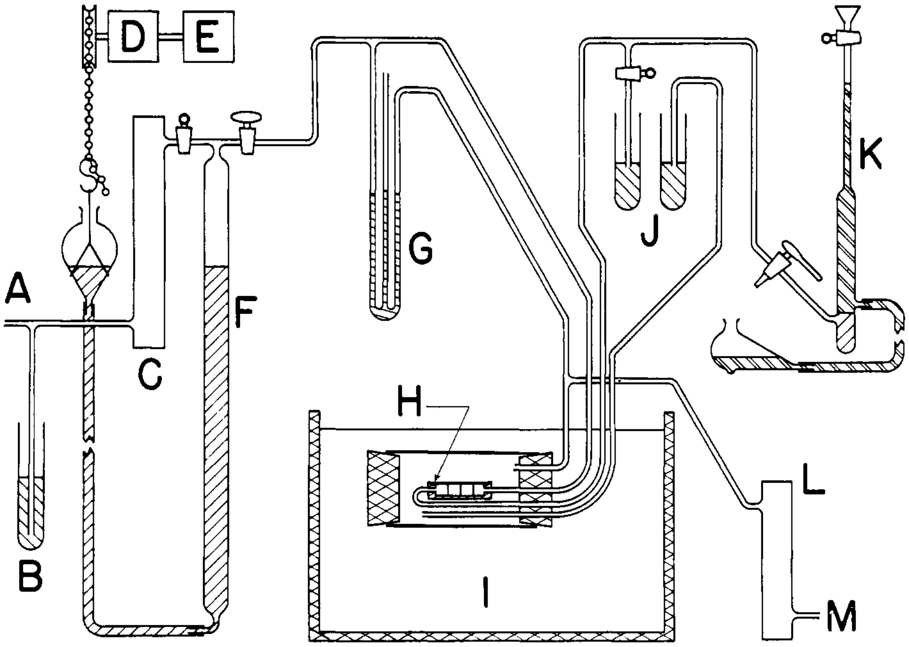

Table II. Permeability of Acetostearin Films to Carbon Dioxide Determined at 25° C. by Cup Method

Product	Film Thickness, Mm.	Area of Film, Sq. Cm.	Permeability, Mg./Hr.	Permeability Constant × 10^{12}
A-1	1.24	9.9	0.035	0.16
	1.70	10.4	0.020	0.12
	2.53	9.5	0.012	0.12
A-2	1.69	10.6	0.071	0.41
	1.96	11.0	0.074	0.48
	2.51	11.0	0.052	0.43
	3.03	10.0	0.042	0.46
	4.19	10.8	0.029	0.41
A-3	1.85	8.3	0.074	0.60
B-1	1.87	10.5	0.054	0.35
	2.02	8.6	0.042	0.36
	2.84	6.4	0.025	0.40
	2.85	9.7	0.037	0.40
	3.69	10.6	0.030	0.38
B-2	1.86	4.2	0.034	0.55

An apparatus black was determined from a run of several hours' duration, during which carbon dioxide was used for both sweep and test gases. The size of the blank was proportioned to the duration of each test run and was influenced by the length of the rubber connection, which was kept as short as possible.

After the blank determinations *F* was refilled, and only enough sweep gas was introduced into the apparatus from time to time to maintain a slight pressure. At the conclusion of the test period (3 to 8 hours), the remainder of the 100 ml. of gas was passed through the apparatus into the nitrometer over a 15-minute period. The volume of residual gas collected this time was corrected by subtracting sweep gas and apparatus blanks.

In calculating permeability values, gas volumes were reduced to weights of gas using accepted density values.

Dry ice was used as a source of carbon dioxide because it contained only 0.04 to 0.06% of gas that did not dissolve in a 50% solution of potassium hydroxide under the conditions employed in the sweep method. The residual gas in carbon dioxide from commercial cylinders was about 1%. The oxygen and nitrogen used were of commercial quality.

As a check on the cup method for determining the permeability of films of acetostearin product to carbon dioxide, the permeability to carbon dioxide was also determined by the sweep method. However, for these tests the assembly represented in Figure 2 had to be modified and a different procedure employed. The nitrometer, *K*, was replaced by an absorption train consisting of a U-tube containing Drierite, followed by a U-tube containing Ascarite. The flow of the test gas, carbon dioxide, and the sweep gas, nitrogen, was adjusted to a slow, steady rate which was interrupted only when the U-tube was removed for weighing. A blank run using the sweep gas indicated that a slight positive correction, which was proportional to time, should be applied to the increments in weight of the Ascarite-containing U-tube. This correction, which probably represented a slow drying of the Ascarite, was made.

Table III. Permeability by Sweep Method of Product A-2 to Carbon Dioxide[a]

Temperature, ° C.	Permeability Constant × 10^{12}
22	0.26
26	0.35
30	0.56

[a] Film thickness, 1.735 mm. Two test runs at each temperature.

Permeability Constant

In order to facilitate the comparison of permeability under various conditions, permeability constants were calculated on the basis of Fick's linear diffusion law and Henry's solubility law, assuming that under equilibrium conditions the diffusion constant times the solubility constant equals the permeability constant (*2*). In the present investigation the permeability constant, *P*, is defined by the equation

$$P = \frac{(w)(x)}{(A)(t)(p)}$$

where w is the weight of gas, in grams, diffusing through a film of thickness x, in centimeters, and area, A, in square centimeters, during the time, t, in seconds, when the pressure difference, p, is measured in millimeters of mercury.

Results and Discussion

The permeability constants of the several acetostearin products to carbon dioxide, as determined at 25° C. by the cup method, are shown in Table II. It is apparent that variations in film thickness had no significant effect on the constants, an indication that the mode of transfer followed Fick's law and was uncomplicated by the phenomenon of adsorption. In this respect carbon dioxide differs from water vapor. In earlier work (*7*) it was found that the permeability constant to water vapor increased as the thickness of the film of product increased.

According to the data in Table II, permeability to carbon dioxide varies severalfold as the degree of acetylation of a product is increased. The higher the degree of acetylation, the more permeable the product appears to be. However, it does not necessarily follow that acetoglycerides are less permeable than other solid fats. Product A-3 contains less acetoglycerides than does product B-2, yet their permeability to carbon dioxide is about the same. It is probable that increased acetylation increases permeability because larger proportions of liquid components are formed. The waxy or alpha form of 1,2- diaceto-3-palmitin has a melting point of 22.4° C. (*6*) and hence would be liquid at the test temperature.

Table IV. Permeability by Sweep Method of Acetostearin Films to Oxygen and Nitrogen

Product	Test Gas	Temp., ° C.	Thickness, Mm.	No. of Test Runs	Permeability Constant × 10^{12}
A-2	O_2	22	1.74	4	0.028
		26	1.74	6	0.050
		30	1.74	4	0.081
	N_2	26	1.74	3	0.023
		30	1.74	3	0.033
B-1	O_2	26	1.76	3	0.031
		30	1.76	2	0.056
	N_2	26	1.76	2	0.0095
		30	1.76	2	0.014
B-2	O_2	26	1.70	3	0.033
	N_2	26	1.70	1	0.009

The effect of temperature on the permeability of product A-2 to carbon dioxide is shown in Table III. Over the limited temperature range shown the permeability constants nearly doubled, an indication that this variable has a very significant effect.

A comparison of the cup and sweep methods (Table II and III) shows that similar results are obtained at similar temperatures. By interpolation the sweep method gives a permeability constant of about 0.33 × 10^{-12} for product A-2 to carbon dioxide. By the cup method this value is about 0.44 × 10^{-12}. Because of the different methods of measurement involved, exact agreement between the two methods is unlikely.

The permeability to oxygen and nitrogen by the sweep method of these products at several different temperatures is shown in Table IV. It is evident that at a given temperature the permeability to nitrogen is smaller than it is to oxygen for each product listed. Judging from the permeability constants for products B-1 and B-2, it appears that the degree of acetylation has little effect on the permeability to oxygen and nitrogen. It would seem that permeability to oxygen and nitrogen cannot readily be tailored to meet a specific use.

If the values for product A-2 (Table IV) are compared with the values given for carbon dioxide (Table III), it is also apparent that the permeabilities to oxygen and nitrogen are much smaller than the permeability to carbon dioxide. At 26° C. the relative permeabilities are: nitrogen, 1; oxygen, 2.2; and carbon dioxide, 15.2.

As is true for carbon dioxide, the permeability constant for both oxygen and nitrogen changes significantly over a range of 4° C. These data are insufficient for defining the temperature coefficients. Other investigators (*2*) working with films of polymeric materials have concluded that the change of permeability with temperature is essentially unpredictable. Permeability may increase, remain unchanged, or decrease, though generally a straight line is obtained when the logarithm of the permeability is plotted against the reciprocal of the absolute temperature.

Table V. Effect of Humidity and Gas Composition on Oxygen Permeability of Product B-1[a]

Test Gas	Relative Humidity, %	No. of Test Runs	Permeability Constant ×10^{12}
O_2	75	2	0.034
	0	3	0.030
Air	0	2	0.013+
Air (theory)			0.014−

[a] Thickness of film, 1.72 mm.; temperature, 26° C.

Table VI. Permeability of Polymeric Films to Carbon Dioxide, Oxygen, and Nitrogen

Product	Test Gas	Thickness, Inch	Temp., ° C.	Relative Humidity, %	Permeability Constant[a] × 10^{12}	Reference
Cellulose acetate	CO_2	0.009	21	0	0.116	(*3*)
	O_2	0.009	21	0	0.0113	(*3*)
	N_2	0.009	21	0	0.0018	(*3*)
Ethylcellulose	CO_2	0.0010	21	50	0.903	(*3*)
		0.0035	20	..	0.80	(*2*)
	O_2	0.0010	21	50	0.119	(*3*)
		0.0035	20	..	0.308	(*2*)
		0.0035	40	..	0.486	(*2*)
	N_2	0.0035	20	..	0.083	(*2*)
Regenerated cellulose	CO_2	...	24–25	0	0.000092	(*10*)
	O_2	...	24–25	0	0.003	(*10*)
	N_2	...	24–25	0	0.004	(*10*)
Nylon	CO_2	...	24–25	0	0.00111	(*10*)
	O_2	0.0018	21	50	0.00028	(*3*)
Polyethylene	CO_2	0.0075	20	..	0.24	(*2*)
		0.003	22	0	0.137	(*3*)
		...	24–25	0	0.12	(*10*)
	O_2	0.001	30	..	0.079	(*2*)
	N_2	0.001	30	..	0.022	(*2*)
Polystyrene	CO_2	0.0015	22	0	0.185	(*3*)
		0.001	20	..	0.68	(*2*)
	O_2	0.0015	22	0	0.025	(*3*)
		0.0015	22	75	0.027	(*3*)
		0.001	20	..	0.347	(*2*)
		0.001	30	..	0.343	(*2*)
		0.001	40	..	0.336	(*2*)
	N_2	0.001	30	..	0.098	(*2*)
Ethylene polymer	O_2	..	24–25	0	2.26	(*10*)
	N_2	..	24–25	0	0.63	(*10*)

[a] Converted from permeability data in original articles.

To establish the effect of water vapor on the permeability of an acetostearin product, B-1, to oxygen, the drying tubes (*C* and *L*, Figure 2) were removed from the assembly and both the oxygen and the sweep gas or carbon dioxide were passed through a saturated solution of sodium chloride at 26° C. before being passed over the film. This procedure conditioned the gases to a relative humidity of 75% at the test temperature of 26° C. As is evident from Table V, the presence of water vapor had practically no effect on the permeability constant.

It would be expected that permeabilities determined for oxygen and nitrogen could be used to calculate the permeability for air—that is, at a given temperature the permeability constant for air would be the sum of the constant for oxygen multiplied by 0.21 and the constant for nitrogen multiplied by 0.79. Two experimental runs with air (Table V) confirmed these expectations and provided further proof that the transfer of air through films of acetostearins follows Fick's law.

The sweep method as employed to obtain the results reported here is an extensively modified method. Any inaccuracy of the results caused by minute leaks in the apparatus would probably be very small. The use of the test and sweep gases under a small positive pressure, with the sweep gas being at a slightly greater pressure, prevented outside air from leaking into the apparatus. If a small percentage of the sweep gas had escaped, the resultant loss would have caused an error not greater than the ratio of the amount lost to the total volume of the sweep gas. No detectable leaks were found in the apparatus, as shown by its ability to maintain the test and sweep gases under pressure when all inlets and outlets were closed.

The apparatus correction or blank was found to be proportional to the time and was consistent so long as none of the few short rubber tubing connections in the sweep gas line were changed. It was never more than the equivalent of a permeability constant of 0.03 × 10^{-12}. This correction was reduced considerably in some of the experiments by using standard glass joints in place of the rubber connections wherever possible.

The 100 ml. of carbon dioxide or sweep gas used in the determination of permeability to oxygen and nitrogen was found sufficient to sweep out the apparatus completely. A second 100 ml. of carbon dioxide produced only the regular sweep gas blank in the nitrometer.

The carbon dioxide, oxygen, and

nitrogen used in the experiments had a purity of 99% or better. With these gases it is believed that the permeability constants that were determined were well within 5% of their true values.

Permeability constants reported in the literature for various organic films have been recalculated to the same units used with the acetostearin products and have been recorded in Table VI. It is evident that ethylcellulose, polystyrene, and the ethylene polymer are more permeable to both oxygen and nitrogen than are the films of acetostearin. Polyethylene has approximately the same permeability to these gases, while cellulose acetate, regenerated cellulose, and nylon have a lower permeability.

The permeability of the acetostearins to carbon dioxide was found to be less than that reported by other investigators for ethylcellulose and approximately the same as that of polystyrene and polyethylene. Nylon and regenerated cellulose have lower permeabilities to carbon dioxide.

Literature Cited

(1) Ambrose, A. M., Robbins, D. J., *Federation Proc.* **14,** 314–15 (1955).
(2) Brubaker, D. W., Kammermeyer, K., *Ind. Eng. Chem.* **44,** 1465–74 (1952).
(3) Davis, D. W., *Paper Trade J.* **123,** 97–104 (1946).
(4) Feuge, R. O., Vicknair, E. J., Lovegren, N. V., *J. Am. Oil Chemists' Soc.* **29,** 11–14 (1952).
(5) Hertig, D. C., Ames, S. R., Koukides, M., Harris, P. L., *J. Nutrition* **57,** 369–387 (1955).
(6) Jackson, F. L., Lutton, E. S., *J. Am. Chem. Soc.* **74,** 4827–9 (1952).
(7) Lovegren, N. V., Feuge, R. O., J. AGR. FOOD CHEM. **2,** 558–63 (1954).
(8) Mattson, F. H., Baur, F. J., Beck, L. W., *Federation Proc.* **14,** 443 (1955).
(9) Robbins, D. J., Ambrose, A. M., *Ibid.,* **14,** 382–3 (1955).
(10) Simril, V. L., Hersherber, A., *Modern Plastics* **27,** No. 11, 95, 96, 98, 100, 102 (1950).
(11) Vicknair, E. J., Singleton, W. S., Feuge, R. O., *J. Phys. Chem.* **58,** 64–6 (1954).

Received for review January 22, 1955. Accepted February 27, 1956. Division of Agricultural and Food Chemistry 126th Meeting, ACS, New York, N. Y., September 1954. Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers.

FISH MEAL STABILITY

Changes in Fat Extractability and Protein Digestibility in Fish Meal during Storage

H. J. ALMQUIST[1]
F. E. Booth Co., San Francisco, Calif.

Fish meals prepared by conventional methods from whole California sardines were analyzed periodically up to 331 days' storage for solvent-extractable fat, protein, and pepsin-indigestible proteins. The extractability of the fat progressively decreased, while the pepsin-indigestible protein slowly increased. The latter also increased in samples from which the fat had been extracted initially. Little or no change was observed in sealed-in-glass samples. Oxidation appeared to be responsible for the changes noted. Some arginine was lost during 24 hours' holding of the raw fish.

CHANGES IN EXTRACTABLE FAT of fish meals were studied, because of the report that fish meals several months old might fail to meet the guarantee of fat content. The possibility of alterations in enzyme digestibility of protein was also considered.

Investigation

On the same day as caught, California sardines were processed into press cake and fish meal by conventional equipment, including steam cookers, presses, and a steam tube dryer. No press water was returned to the meals. Some press cake was dried in a laboratory tray-type dehydrator using hot air entering at 160° F. and discharging at not over 140° F. A part of the same catch was held in a large bin for 24 hours until soft, and processed as before. All preparations were made from whole fish.

The commercial meals and laboratory-dried press cakes were passed through a Wiley mill and reduced to the same maximum particle size, not over $^1/_{16}$ inch. Portions of each lot were extracted with ethyl ether in a large Soxhlet-type extractor. All meals were placed in cloth bags and stored at room temperature with free circulation of air around each bag. Each lot was periodically sampled by repeated mixing and quartering. Samples were analyzed for moisture, petroleum and ethyl ether–extractable fat, total protein, and pepsin-indigestible protein. The latter was determined as described by Almquist, Stokstad, and Halbrook (*1*). Fat was determined by continuous extraction for approximately 7 hours and weighing of the dry solvent-free residue. The results were calculated to dry basis and are given in Table I.

Samples of the factory meals were sealed in glass tubes with and without evacuation of air to 10-mm. pressure, and kept for the duration of the study. Results from the sealed samples are given in Table II.

Conclusions

The pepsin-indigestible protein increased slowly with aging. The amount started at a lower value and remained lower throughout in samples that had been extracted with ether. While the presence of fat caused a definite increase in indigestible protein, the majority of the indigestible protein must have arisen from other causes, and the gradual increase of indigestible protein on storage may be attributed to progressive changes in the protein, rather than any increased interference with digestion caused by changes in the fat. This implies that little enhancement in protein value would be caused by removing the normal amount of fat from fish meal.

Progressive alteration of fat was shown by a steady decrease in petroleum ether and ethyl ether–extractable fat.

---

[1] Present address, The Grange Co., Modesto, Calif.