around the world. Accordingly, despite the seemingly impossible task they had, and despite the inabilities of their superiors to agree in Committee One, the largely unmolested fishery people in Committee Three sat down and hammered out a straight, sound, business deal which became the "Convention on Fishing and the Conservation of the Living Resources of the High Seas."

Had the entirety of the membership of Committee One at that conference packed their bags, gone home at the Easter Recess, and stayed there, the fish people of Committee Three would have also settled the breadth of the territorial sea and the issue of fishery limits too. They had an agreement worked out behind the scenes among themselves on these points which would have done that. But the Home Governments, having all their experts in Geneva, made inexpert decisions and prevented this agreement from coming to light. Thus the three mile limit has seemed to disappear from the scene and nothing has replaced it.

So we came to the Second Conference on the Law of the Sea. Here the diplomats, the international lawyers and the military men absolutely dominated. The fish people's advice in all delegations was pretty well ignored and brusquely brushed aside. The upshot was that nothing was agreed upon. None of the remaining problems were solved.

Personally I think this was a good thing. There will be no Third Conference on the Law of the Sea for a long while. The diplomats, the lawyers and the military men have gone back to their lasts and are out of our hair. We fish people have been left the fruits of our labors over these years in the "Convention on Fishing and the Conservation of the Living Resources of the High Seas." This is a sound document under which we can govern ourselves if the others will let us alone to do so. In these short eight months several steps in this direction have already been successfully initiated.

Thus the center of the diplomatic-military storm seems to have passed us by at last, the waves are already subsiding in height and violence, and we fish people can get down to the job of getting food out of the sea with which to feed the hungry world, which was what we hired out to do in the first place.

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Fractionation And Purification Of Triglycerides, Fatty Acids And Methyl Esters From Fish Oils

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INTRODUCTION

THE PRODUCTION OF NEW INDUSTRIAL PRODUCTS from fish oils may very well require the use of purified fractions of fish-oil triglycerides or fatty acids.

Similarly, in order that researchers may follow the various pathways of chemical reactions during the syntheses of fish-oil derivatives, it is quite desirable that the starting materials in the reactions be as pure as possible. Fractionation of fish-oil fatty acids or their monoesters provides a means for purification, at the same time enabling reproducible chemical and physical characteristics of the products. The latter feature overcomes an objection to fish oils; i.e., composition is known to vary with season and geographical location of catch, as well as sex and maturity of the fish.

The following are a few of the problems associated with impure raw materials, to show the importance of purification of fish oils and their derivatives. Chemical reactivities may be impaired owing to the inhibiting effects caused by the presence of impurities. The color of a product may be commercially undesirable because of the presence of needless color impurities in the raw materials of manufacturing. For example, certain chemical products destined for the treatment of textiles may be colorless and should not impart color during aging. The physical properties of both the raw materials and the resulting products may be changed owing to the presence of undesirable impurities. These impurities may be either trace amounts of materials of different chemical classifications, or fairly large amounts of some unwanted material in the same chemical class, such as saturated fatty acids in the presence of unsaturated homologs.

METHODS

The most common methods for the fractionation and purification of fish oils and their derivatives include (1) liquid-liquid extraction, (2) fractional crystallization at reduced temperatures, (3) fractionation of urea-inclusion compounds, and (4) fractional or multistage molecular distillations. These methods may be considered as being the most practical for commercial operations. Space does not permit the discussion of other separation techniques that have use in various laboratory operations.

Liquid-Liquid Extraction

In the liquid-liquid extraction method, it is necessary to find a solvent system in which the mixture of fish-oil triglycerides or fatty acids, etc., is partially miscible and in which one component or chemical class of the mixture is more soluble than the others (Pratt, 1953). One such choice of solvent system suitable for fatty acids is isooctane, a relatively non-polar hydrocarbon, and furfural, an active polar solvent immiscible in the hydrocarbon (Freeman, 1942). In this case, an all-liquid system is established, whereby the fatty acids are partitioned between the two phases of the solvent.

Separations of fatty acids, as well as natural triglycerides, involving selective action of solvents give rather poor separation efficiency owing to mutual solubility characteristics. In spite of this poor efficiency, industrial designs of liquid-liquid extraction equipment have improved in recent years to produce very effective separations of fatty acid mixtures (Treybal, 1958). One such design includes a centrifugal contactor in conjunction with a countercurrent flow of the two solvents. Data from this latter process applied to fish oils was not found in the scientific literature.

Fractional Crystallization at Reduced Temperatures

The fractional crystallization method, in which one component of a mixture

to be separated is crystallized, overcomes to a large extent the mutual solubility effects mentioned above. Saturated fatty acids or methyl esters may be separated by virtue of differences in carbon chain length, or those of the same chain length may be separated by differences in degree of unsaturation (Kistler, *et al.* 1946; Muckerheide, 1954).

Table 1 illustrates the effectiveness of fractionating tuna-oil methyl esters by low temperature crystallization from a methanolic solution. The original mixture of methyl esters dissolved in methanol was cooled stepwise from room temperature to -60°C. The result was a concentration of the more highly unsaturated fatty acids, as reflected by the changing iodine values, as lower temperatures were used (Kolb and Brown, 1955).

TABLE 1

TUNA-OIL METHYL ESTERS FRACTIONATED BY LOW TEMPERATURE CRYSTALLIZATION FROM METHANOL

Crystallization fraction	Yield	Iodine value, Hanus[1]
	Wt. —%	
Original	100	168.0
Precipitate, —5°C.	22.0	40.1
Precipitate, —25°C.	14.9	123.9
Precipitate, —60°C.	44.1	199.2
Filtrate, —60°C.	19.0	278.4

[1] Analysis made on the fatty acids.

This method of fractionation removes a large part of the color impurities by concentrating them in the final filtrate fraction. Also, the saturated carbon chain acids are generally separated in the initial fraction, producing a nearly pure unsaturated product after one crystallization. A disadvantage of this method is the lack of separation of color bodies and polymeric material from the polyunsaturated fraction. The latter fraction is the most valuable asset to the development of new products from fish oils. In regard to the fish-oil triglycerides, this method would have only a slight effect in the separation based on unsaturation by assuming a more or less random-type distribution of fatty acids on the glyceride molecules.

Fractionation of Urea-Inclusion Compounds

The use of urea-inclusion compounds for the fractionation and purification of fatty acids and their monoesters has become part of a widely accepted laboratory method. Triglycerides, by the nature of their structure, have very little utility in this area of purification. Virtually all natural occurring fatty acids will form inclusion compounds or adducts with urea (Schlenk, 1954). Extractive crystallization with urea provides a simple and efficient means for the separation of fatty acids on the basis of their degree of unsaturation. The method may be adapted to commercial scale operation (Rosenstein and Gorin, 1957); however, it has the usual disadvantages of most crystallization processes.

Work at the Seattle Technological Laboratory has shown the effectiveness of urea-inclusion compound fractionation applied to fatty acids from menhaden oil (Domart, Miyauchi and Sumerwell, 1953). Table 2 shows resultant data

TABLE 2

MENHADEN-OIL FATTY ACIDS FRACTIONATED BY UREA CRYSTALLIZATION AT DIFFERENT TEMPERATURES[1]

Fatty acid fraction	Yield	Iodine value, Hanus
	Wt. —%	
Total	100	160
25°C. Complexes	27.8	19.4
1°C. Complexes	17.4	46.0
—18°C. Complexes	6.0	82.7
—30°C. Complexes	0.2	—
—30°C. Filtrate (non-complexed)	48.4	255

[1]Starting mixture contained 9.1:1 mole ratio of urea to fatty acids at 25°C. in methanol.

for urea crystallization of fatty acids at various reduced temperatures. The molar ratio of urea to fatty acids was 9.1 to 1.0, respectively, at the start of the process. As the temperature was lowered, successive fractions of urea adducts or complexes formed according to the degree of unsaturation of the fatty acids. The iodine value data reflect this change in unsaturation.

In Table 3, data are shown for the effect on fractionation by changing molar ratios of urea to fatty acids, while at the same time maintaining a constant temperature of crystallization. As higher ratios of urea to fatty acids are used, the yield of urea adducts increases. This has the effect of increasing the degree of unsaturation in the non-adduct forming fraction. Therefore, one has flexibility in the technique that is used, depending on the extent to which one wishes to fractionate by this method. An interesting innovation of urea-inclusion compound fractionation is to combine the process with a countercurrent liquid extraction system (Sumerwell, 1957).

Here, as in the case of the previously described methods, color bodies are concentrated in the final filtrate fraction, i.e., the fraction containing the valuable polyenoic acids. When compared to the solvent crystallization method (cf., Table 1), urea complexing produces higher yields of the most unsaturated fraction of fish-oil acids. In the laboratory, this method is most helpful in obtaining concentrates of eicosapentaenoic and docosahexaenoic acids (Abu Nasr, Potts and Holman, 1954), from which the acids may be obtained in purest form by distillation combined with partition chromatography.

Distillation Methods

The ability to separate components of a mixture by distillation methods is limited by the differences in boiling points of the components. Theoretically, it should be possible to completely separate by fractional distillation fish-oil fatty acids that differ in chain length by two carbon atoms (Potts, 1956). It is not possible to separate by distillation the saturated and unsaturated fatty acids of equal carbon chain lengths. Ordinary distillation of fatty acids from fish oil is complicated by the fact that high temperatures are required, and at these high temperatures fatty acids are thermally unstable. In the case of fish-oil triglycerides, ordinary distillation techniques are absolutely impractical.

TABLE 3

THE FRACTIONATION OF MENHADEN OIL FATTY ACIDS[1] WITH DIFFERENT MOLE RATIOS OF UREA IN METHANOL AT 1 °C.[2]

Mole ratio of urea to fatty acids	Yield of fatty acids from complexes	Hanus I. V. of fatty acids from complexes	Yield of fatty acids from filtrate	Hanus I. V. of fatty acids from filtrate	Unrecovered fatty acids
	Wt. —%		Wt. —%		Wt. —%
4.6:1	11.6	12.8	80.8	192.7	7.6
9.1:1	29.8	22.1	61.6	243.4	8.6
13.8:1	49.4	48.1	41.6	308.9	9.0
18.4:1	61.0	54.5	36.4	330.7	2.6
23.0:1	63.0	72.7	34.2	341.6	2.8

[1]The Hanus iodine value for the menhaden oil fatty acids from which these fatty acids were prepared was 159.5.

[2]All values represent averages obtained by treating triplicate 50.0 gram samples of the fatty acids.

The techniques of fractional and molecular distillations at reduced pressures permit lower temperatures to be used to bring about distillation. Fatty acids and methyl esters of carbon chain lengths up to C_{20} can be separated satisfactorily by fractional distillation, between 1 and 50 millimeters mercury pressure, without much thermal deterioration. Above C_{20} chain lengths, the thermal hazard becomes greater. Distillation has the advantage over the other separation methods in that polymeric materials, such as major color bodies, can be separated from fish oils or fish-oil fatty acids.

Triglycerides can be effectively purified by molecular distillation methods. Here, the operating pressures are of the order of 10 microns Hg. Fractionation by molecular distillation methods can be accomplished by the use of multiple stage units, or by some means that permits recycling of undistilled portions through a single distillation unit. Depending on the design of the distillation equipment, it is possible to minimize the thermal hazard by minimizing the contact time of the fish oil product with the heated or distillation surface of the still.

TABLE 4

CRUDE MENHADEN OIL FRACTIONATED BY MULTISTAGE MOLECULAR DISTILLATION

Fraction	Yield	Temp.	Pressure	Iodine value, Hanus	Ethylenic bonds per mole
	Wt. —%	°C.	Micron		
Original[1]	100	—	—	161	1.24
1	4.5	185	17	124	0.85
2	24.5	208	15	122	0.97
3	45.5	200	15	164	1.26
4	22.5	195	15	191	1.44
Residue	3.5	—	—	232	1.66

[1]Crude menhaden oil produced from fish caught in the Gulf of Mexico.

The data in Table 4 are typical of the results obtainable by multistage molecular distillation of crude menhaden oil (triglycerides). In this case, an oil of iodine value 161 can be easily separated into major fractions having an iodine value range of 122 to 191. It is expected that the last major boiling fraction is a concentrate of the highly unsaturated portion of the oil, but that it may very well contain saturated groups. Owing to the structural make up of triglycerides, the data would not be expected to show appreciable separation on the basis of chain length and unsaturation.

Multistage molecular distillation of fish-oil fatty acids will permit fractionation, to a degree, on the basis of chain length. In fish oils, the longer chain fatty acids accompany the higher degrees of unsaturation. Stoffel and Ahrens (1960) report that the C_{20}- and C_{22}- pentaegnoic and C_{22}- hexaenoic acids comprise 23.4 per cent of the total fatty acids derived from menhaden body oil.

The results in Table 5 show the separation of fatty acids into four major fractions, each amounting to from 20 to 30 per cent of the total mixture. Both the iodine values and the calculated average number of ethylenic bonds per acid fraction indicate the success of molecular distillation to purify and fractionate on the basis of unsaturation. As stated earlier, these results are a consequence of the degree of unsaturation that accompanies the higher boiling or longer chain fatty acids.

It may be interpreted from Table 5 that the fourth fraction of distilled fatty acids should contain major amounts of pentaenoic and hexaenoic acids. However, the average of 4.45 ethylenic bonds per fatty acid in this fraction indicates that the fraction probably contains appreciable amounts of dienoic, trienoic, and tetraenoic acids. It can be determined from the data that by combining fractions 3 and 4 it is possible to obtain a fraction of over 50 per cent of the oil that has an iodine value of approximately 270.

TABLE 5

MENHADEN-OIL FATTY ACIDS FRACTIONATED BY MULTISTAGE MOLECULAR DISTILLATION

Fraction	Yield	Iodine value, Hanus	Ethylenic bonds per mole
	Wt.-%		
Original	100	191.0	—
1	24.9	83.2	0.85
2	19.8	127.0	1.35
3	30.1	215.8	2.48
4	21.6	346.6	4.45
Residue	3.6	—	—

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The Multiple-Use Of Shrimp Trawlers

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THE HISTORY OF WORLD FISHING is filled with examples of fisheries which have failed to survive and in most cases the failures have resulted from the inability of the fishermen to make a profit using hand-labor; the Grand Banks baited trawl fishery for cod is an example. How many of the graceful schooners sail each year from U. S. ports?