TECHNOLOGICAL STUDIES OF THE STARFISH

PART II-CHEMICAL COMPOSITION

By Charles F. Lee*.

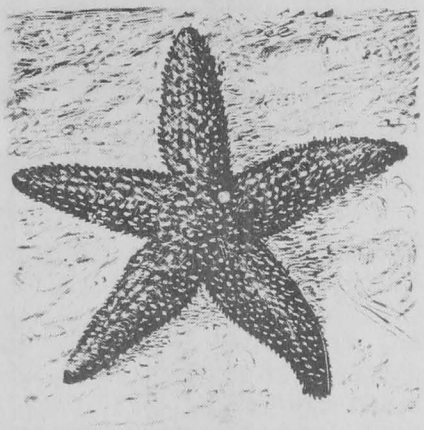
INTRODUCTION

This second section of a series of papers on starfish summarizes all published and available information on the chemical composition of both fresh starfish and starfish meal. The additional information obtained on this subject in the laboratory of the Fish and Wildlife Service is given in detail.

REVIEW OF LITERATURE ON STARFISH COMPOSITION

There are relatively few reports on starfish containing analytical data and those analyses available are, in most cases, not complete. In Table 1, the constituents have been calculated to a uniform basis to facilitate comparison. For example, calcium or calcium oxide are reported as calcium carbonate.

The data are seen to be rather fragmentary, but sufficient to show that starfish are not of constant composition with regard to any single constituent, even when values are calculated on a dry matter basis. Protein, ether extract (fat), and ash with its chief constituent (calcium carbonate), all show a large degree of variation. The data of Hutchinson, et al, (1946) are from an analysis of a small laboratory sample dried at 57° C. (134.6° F.). These values are referred to in several other papers as the composition of the sun-dried meal which was supplied by the Bingham Oceanographic Laboratory group to other laboratories for cooperative studies. That this inference was entirely justifiable is doubtful, as indicated by the check analysis of this same meal reported by Whitson and Titus (1946). Loss of about 10 percent of the protein originally present in the fresh starfish apparently occurred during preparation of the sun-dried meal.



The data of Morse, et al, (1944), also reported in this group of papers, were obtained on a commercially dried experimental batch of four tons of starfish, although the results of their laboratory sample analysis is comparable to data of Hutchinson, et al. A difference equal to 22 percent more protein and 30 percent less ash in the laboratory meal than in the commercial sample is indicated by comparison of these data.

Vachon (1920) emphasizes even more clearly the probable difference between a commercial starfish meal, and a specially prepared sample in the two analyses he reports, one of the material as collected, with seaweed, shells, sand, and other adhering matter as would be used in the practical preparation of large quantities of starfish meal, and the other, the analysis of starfish washed several times and separated from all foreign matter. The value reported for protein in this latter analysis appears to be erroneous.

*Chemical Engineer, Fishery Technological Laboratory, Division of Commercial Fisheries, College Park, Maryland.

NOTE: Part I of this series appeared in the January 1948 issue of Commercial Fisheries Review, pp. 1-6. Also Separate No. 193.

Table 1 - Data in the Literature on the Composition of Starfish and Starfish Meal

Type of Sample and Reference	Dry Matter	Protein (Nx6.25)	Ether Extract	Crude Fiber	Calcium (as $CaCO_3$)	Magnesium (as Mgo)	Phosphorus (as P_2O_5)	Potassium (as K_2O)	Sulfur (as SO_4)	Sand (SiO_2)	Total Ash
Fresh Starfish:	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Wheeler (1913)		11.9			17.2		2.1	0.23			20.3
Galtsoff, et al (1939)	25.12	7.9			10.5	0.57	0.23	0.81			10.9
Hutchinson, et al (1946)		11.3			14.0		0.34		0.87		
Laboratory Dried and Specially Cleaned Meal:											
Kole, C.J. (1919)	87.9	31.6	6.9							3.9	43.9
Vachon, A. (1920)		55.7					1.3	2.42	1.65	0.57	
Hinard & Fillon (1921)		35.62	7.53		47.7						52.95
Morse, et al (1944)	96.89	33.63	7.7	0.4	37.9		1.1				41.7
Hutchinson, et al (1946) 1/		34.0			42.0		1.0		2.61		
Commercial Type Meal:											
Vachon, A. (1920)		11.0			69.8	3.25	0.70		0.73	3.46	
Galtsoff, et al (1939)	89.9	36.3		1.84							
Morse, et al (1944)	47.9	27.54	5.3								60.13
Whitson & Titus (1946)	94.5	30.7	4.5	1.9	44.0		0.80				30.0 2/

1/Also Iron - 0.017%, Manganese - 0.0023%, Fluorine - 0.016%, Boron - 0.0034%, Thiamine - 0.0001%, Riboflavin - 0.00053%, Niacin - 0.0038%, and Pantothenicacid - 0.0012%.

2/Ash was ignited at 900°C. - $CaCO_3$ loses CO_2 at 825°C. so figure for $CaCO_3$ is calculated from value for Ca.

Noddack and Noddack (1939) made an extensive spectrographic study of the various metallic elements in a number of marine animals, including starfish. In general, they found greater concentrations of the heavy metals in the animals than in sea water, but quantities were still on the order of one part per billion, with starfish showing the smallest total concentration. Boron was the only element notable in starfish, with 1 to 10 parts per million.

The purified fat of starfish has been reported by Hinard and Fillon (1921) to have a density of 0.9372, an iodine number of 132.7, a saponification number of 159.1, and unsaponifiable matter content of 38.94 percent.

In general, these data from the literature indicate that composition of commercial meals cannot be predicted from analyses of fresh samples of raw starfish. There is, apparently, a loss of about one-tenth or more of the nitrogen present. This could result from a rapid breakdown to soluble products of a portion of the proteins present and their loss in body fluids. Ash is likely to be considerably higher in commercial meals than in laboratory dried meals. This results, in part, from the inclusion of oyster shell, and many other small shellfish, as well as sand and small rocks that are taken in the dredge along with starfish. This variability in analyses is quite evident in data obtained in the present investigation.

MATERIAL

The lack of drying facilities near the source of the starfish at Milford, Conn., made it necessary to ship the starfish, while fresh and perishable, to the College Park Laboratory, some 300 miles distant. As a result of this, the analyses of the fresh starfish cannot be considered representative of the live starfish immediately after catching. However, the data for the meals are a good approximation of what might be expected of commercial meals receiving ordinary care in transportation and handling.

Starfish were obtained at Milford, Conn., by dredging or were hand-picked from mops through the cooperation of a commercial company and the Fish and Wildlife Service Biological Laboratory at Milford. Lots of 50 to 100 pounds were shipped, either in 5-gallon oyster cans or in small, tight, wooden kegs. Samples in the cans were lightly iced, while cool weather alone limited decomposition of the other lots. On arrival at the laboratory, a considerable volume of free liquor was found to have separated in every case. In some lots, the starfish had undergone some decomposition, though most were in good condition, bright colored, and hard.

PREPARATION OF SAMPLES AND ANALYTICAL PROCEDURES

Portions of the liquor on several of the earlier lots were tested for total solids, salt, ash, and organic material. These data are reported in Table 2. The

Table 2 - Proximate Analysis of Liquor Separating from Starfish

Source	Total Dry Matter	Ash	NaCl 1/	Organic Matter	Source	Total Dry Matter	Ash	NaCl 1/	Organic Matter
	Percent	Percent	Percent	Percent		Percent	Percent	Percent	Percent
Lot 1 A	4.63	2.77	2.11	1.86	Lot 2	2.02	1.26	0.95	0.76
" 1 B	4.67	2.63	1.98	2.04	" 3	3.95	2.88	2.42	1.07

1/ Total chlorine calculated to sodium chloride.

content of total solids was found to be about 4 percent, of which about 60 percent was inorganic (ash). Sodium chloride calculated from chlorine content constituted approximately 75 percent of the ash. Because of the inadequacy of the available

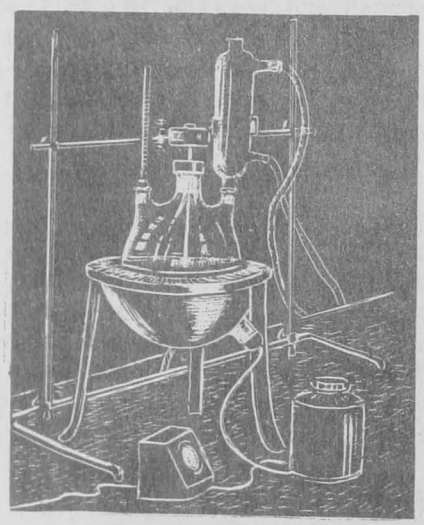
drying equipment and the small amount of organic matter present in this liquor, it was not considered desirable to add it back to the starfish, so the liquor was discarded. The small amount of nitrogen thus lost would not have been retained in usual plant handling practice.

The bulk of the starfish for meal was dried in large galvanized pans in steam heated ovens. The starfish were several inches deep and matted down to a dense layer which retarded drying and the maximum temperature obtained in the oven was 60° C. (140° F.). As a result, complete drying required 5 to 7 days, even when the matted layer was stirred and broken up daily.

In the initial stages of the drying operation, temperatures were sufficiently low to encourage vigorous enzymatic and probably bacterial action. This was desirable since it resulted in a break-down of the exoskeleton of the starfish and greatly facilitated the grinding of the dry meal. It was virtually impossible to grind the tough and hard structure resulting from rapid drying by any means available. Generally, the decomposition was stopped by further drying before it had reached the stage of liberation of ammonia and darkening of the meal, though this did occur in one or two large batches.

METHODS OF ANALYSIS

Dry matter was determined by heating overnight in an air oven, at 105° C. (221° F.). Ash was obtained by ignition of the dry material at 600° C. (1112° F.), until grayish white, and chlorides were determined on the ash by leaching with 1 nitric acid to 3 water and titrating a suitable aliquot by Volhard's method. Total nitrogen (N x 6.25 to give crude protein) was determined by Kjeldahl digestion using copper sulfate as a catalyst. Total organic matter was calculated by difference.



The solvent-soluble portion of the starfish was extractable with ether, but was more readily soluble in acetone. Most of the data on this constituent were obtained from bulk extractions with a Soxhlet type extractor using a mixture of acetone and petroleum ether. The solvent was recovered by distillation and the last portion was removed with aid of a vacuum. Considerable quantities of starfish oil were thus prepared for an investigation of the sterols present in starfish by Dr. Werner Bergmann and coworkers of the chemistry department of Yale University.

In view of the toughness of the starfish "skin," it was thought likely that a chitin-like material might constitute a major portion of the protein present. Chitin was therefore determined on two samples by digestion of the fat-free starfish meal with 20 percent KOH at 60° C. (140° F.) for two weeks. Chitin was determined as the loss on ignition of the dried residue at 550° C. (1022° F.) since the carbonate ash constituted the bulk of the undigested material.

ANALYTICAL RESULTS

The proximate analyses of the meals and some lots of fresh starfish are tabulated in Table 3. Data are not complete on all meals, as several were prepared for special purposes, such as for feeding tests or for the extraction of oil.

All the data for solvent extract except the first value were obtained from bulk extractions, in which the ground meal was placed in canvas bags in the extractor. Caking of the large bulk of meal prevented complete extraction of oil so that these values are perhaps 5 to 10 percent low.

Table 3 - Proximate Analysis of Some Samples of Fresh Starfish and Starfish Meal

Lot	Dry Matter	Protein	Solvent Extract	Total Organic Matter	Chlorides as NaCl	Total Ash
	Percent	Percent	Percent	Percent	Percent	Percent
Fresh Starfish:						
1	35.2		2.7	15.8	2.18	19.4
2	35.0			14.1	1.47	20.9
4	33.6			16.5	1.24	17.1
5	32.6			16.6	1.10	16.0
7	36.0			14.7	1.03	21.3
Starfish Meal:						
1	99.2		7.6	44.4		54.8
2	97.2	27.9	6.9	40.9	2.85	56.3
3	98.7	26.3		39.3	3.81	59.4
4	97.9	29.9	15.1	50.5	3.29	47.4
5	99.1		6.8	42.2	3.73	56.9
6	99.0		8.7	40.1	3.90	58.9
7	99.4		9.3	38.5	3.14	60.8
8	94.9		9.0	36.4		58.5
9	97.2			39.3		57.9
10		28.1				
11		30.6				

Generally, the solvent-soluble material constituted about 7 to 9 percent of the meal. The one high value for Lot 4 of 15.1 percent was obtained with starfish which were full of spawn. As most of the samples were collected in October and November, normally they were spawned out, and this fact may, in part, account for the lower values for protein, as well as oil, and higher ash content than have usually been observed for this species. This particular meal from Lot 4 was the only one to have an ash content under 50 percent. The others ranged from 55 to 61 percent ash, in spite of the fact that an effort was made to pick out most of the shell and foreign matter before drying.

The protein content, as noted before, is lower than some values previously reported, five meals averaging 28.6 percent. Seasonal differences, loss in liquor, and loss during drying may all have contributed to make these low values. The data did not cover a long enough period of time to permit evaluation of all the factors involved in the variable composition of the starfish.

It is evident from the data that the meal dries readily even at the low temperatures used, several meals containing less than one percent water. The starfish before drying contained about 35 percent dry matter, compared to the value of 25 percent reported usually used as a meal factor for freshly caught starfish, indicating a loss of about 10 percent of liquor which separated in transit. Salt content of the meals is well within the permissible limits for fish meals. Chitin content, representing indigestible protein, was found to be low, only 0.55 percent of the dry meal.

The unsaponifiable portion of starfish oil has been examined, particularly in regard to the sterols present, by Bergmann and coworkers. In a preliminary report, Bergmann (1937) had reported that the sterol of starfish, named stellasterol by Kossel and Edlbacher (1915) was a mixture of two or more sterols which were extremely difficult to separate. This sterol mixture, as well as the alcohol, astrol, were present in Asterias forbesi.

This work had been halted by lack of sufficient material until 1942 when the College Park Laboratory supplied Dr. Bergmann with about 12 pounds of oil to permit further investigation.

In 1943, Bergmann and Stansbury reported that the alcohol in starfish oil called astrol by Kossel was identical with batyl alcohol, previously observed in liver oils of sharks and rays. Batyl alcohol is glycerol - 1-octadecyl ether. The structural formula is thus: $CH_3(CH_2)17.O.CH_2.CHOH.CH_2OH$.

In 1944, in a second report on the sterols of starfish, Bergmann and Stansbury had not yet succeeded in complete separation of the sterols. Much had been learned of their molecular structure, however, by selective hydrogenation of the mixture and by other means. The two sterols, tentatively called stellasterol and stellastenol, apparently differed only in the presence of two double bonds in the former, while stellastenol had only a single double bond. Both were slightly dextro-rotatory in contrast with all other animal sterols, therefore, they must lack C 5-6 double bond linkage, having instead a double bond at the Carbon 8. Some of the difficulties in separation and purification of the sterols are thought to be due to a shifting of this double bond from the gamma or delta to the alpha isomer.

These sterols are the first of the principal unsaturated sterols of 28 carbon atoms to be reported in animal tissues. Saturated stellastenol was apparently isomeric with campestanol.

In a more recent publication, Bergmann, et al, (1945) suggest that recent observations support a hypothesis that stellasterol when hydrogenated yields a mixture of campestanol and a 24-carbon atom isomer, and that the starfish sterols are mono- and di-unsaturated derivatives of campestanol, the second double bond being in the C 22-23 position. Some sponge sterols are also related to this compound.

The general study of the sterols of marine invertebrates, contrasting in its complexity with the simple sterol make-up of land animals, is of considerable theoretical interest, especially in connection with theories of the origin of sterols in the body tissues.

NITROGENOUS CONSTITUENTS

The present investigation did not include a study of the amino acids present in starfish proteins. The separation and identification of amino acids was a problem of too great complexity to approach with the personnel and the methods available. In recent years, however, there has been a rising interest in amino acids as special dietary supplements, in medicine, and in nutrition research.

Kossel and Edlbacher (1915) made the only study of amino acids in starfish reported in the literature, and they found taurine in the free state in the sexual organs. Glycine, tyrosine, and glutamic acid were isolated from another fraction of the hydrolysate, while sarcosine, leucine, isoleucine, and proline were also identified. The monoacids, not precipitated as phosphotungstates, accounted for 39 percent of the total nitrogen of the dibasic amino acids. An arginine content of 19.4 percent and lysine content of 11.5 percent were most prominent. Also noted was a small amount of a "histidine fraction." This work was part of an extensive chemical study of starfish, and does not represent any attempt to work out practicable methods of separation. The possibilities for preparation of the various amino acids from starfish, as well as other marine products or byproducts remains virtually unexplored.

It is quite probable that this phase of the utilization of starfish will be emphasized in further investigation of starfish now being considered. The study may be simplified by use of the recently developed microbiological methods for the assay of many of the amino acids, and may result in development of a much more profitable outlet for a product from starfish than the meal and fertilizer preparations hitherto studied.

CONCLUSIONS

The data on the composition of starfish show that the fresh material will yield about one ton of meal per four tons of raw material. The commercial meal contains about one-half as much protein as the common commercial fish meals, but compares favorably in this respect with meals prepared from crab or lobster scrap, shrimp bran, or meals from mussels or other of the less desirable shellfish.

The meal is high in calcium carbonate, while potassium and phosphorus are disproportionately low. Starfish oil contains batyl alcohol, and two newly discovered sterols with 28 carbon atoms related to campesterol. The protein of starfish contains some of the essential amino acids and appears to be a more probable source of a valuable extractive than is the oil fraction.

The use of starfish meal as a protein supplement in rat and chick growth tests and in laying mashes will be reported in a third paper of a series on the utilization of the starfish, Asterias forbesi.

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HOW TO COOK OYSTERS

 

Oysters have a special appeal to the busy homemaker because of the ease with which they are prepared--no waste from trimmings, entirely edible, and easy to serve. They can be served either raw on the half shell, as a cocktail, or cooked in a variety of ways such as stews, chowders, baked, broiled, fried, creamed, scalloped, or in combination with cheese, bacon, celery, spinach, rice, and as a stuffing for poultry. To retain the delicate, distinctive flavor of oysters, never cook them too long, just enough to heat them through and leave them plump and tender.

--Test Kitchen Series No. 3