FREEZE DRYING OF FISHERY PRODUCTS: PART IV* - BIOCHEMICAL CHANGES OCCURRING IN PRAWN MUSCLE DURING FREEZING, FREEZE DRYING AND PROLONGED STORAGE OF THE FREEZE DRIED PRODUCT

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The changes occurring in water and salt extractable protein and non-protein fractions in prawn muscle of different species during freezing, freeze drying and subsequent prolonged storage have been studied. There is no denaturation of water extractable proteins, whereas salt extractable proteins were rendered insoluble to the extent of 21% due to freeze drying. The freeze dried products remained in good edible condition for 32 months of storage up to which storage characteristics were followed.

INTRODUCTION

The earlier communications of this series deal with the freeze drying characteristics of some common Indian food fishes, development and freeze drying of pre-cooked, ready-to-serve fish salads and preparation and freeze drying of instant fish soup mixes and prawn cake. The broad biochemical changes that fresh prawn muscle undergoes during the processes of freezing, freeze drying and further storage form the subject matter of the present study.

MATERIALS AND METHODS

The prawns used in this study belonged to the species *Parapenaeopsis stylifera*, *Metapenaeus dobsoni*, and *Metapenaeus affinis*, procured from the Institute's experimental trawlers, which were landed in the evenings and preserved in crushed ice before using them for the study. In one experiment prawns of the species *Metapenaeus monoceros* caught from the backwaters of the locality and brought to the market for retail sales, many of them still in live condition, were made use of.

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All raw materials were washed clean, peeled and deveined, spread in a single layer on the tray of the freeze dryer and frozen in a plate freezer. Freeze drying and packing of the dried material were conducted as described in the first communication of this series (Govindan *et al.* 1968).

Moisture was estimated by AOAC (1960) method. Water extractable nitrogen (WEN) and non-protein nitrogen (NPN) were estimated by methods employed earlier by the author (Govindan, 1962). Free α-amino nitrogen was estimated by the method of Pope and Stevens as adopted by Velankar and Govindan (Velankar and Govindan, 1959).

Results And Discussion

Values of moisture, WEN, NPN and free α - amino N in the fresh peeled and deveined meat, frozen meat, freeze dried meat and the same after $2\frac{1}{2}$ months of storage in the case of one experiment with *P. stylifera* are presented in Table I. In this case the fresh prawns were held overnight in crushed ice, peeled and deveined next morning and processed immediately. With a view to studying the effect of an initial leaching out of part of the nitrogenous constituents, prawn of the same species were held overnight in crushed ice, peeled and deveined next day and the meat again stored in crushed ice for a further period of two days prior to being processed as before. Results of analyses are presented in Table II. As dilute common salt solution is a more efficient extractant of protein matter than water, in a third experiment prawns of the species *Metapenaeus affinis* were held overnight in crushed ice, peeled and deveined next day, peeled meat again stored in ice overnight and processed as before on the third day. 5% sodium chloride solution containing 0.02M sodium bicarbonate was used to extract protein, non-protein and free α-amino acids according to the method employed by Mannan *et al.* (1961). Results obtained are summarised in Table III. Tables IV, V and VI present results of studies of similar changes during freezing, freeze drying and further prolonged storage of the freeze dried product.

It may be seen from Table I that there is no appreciable decrease in WEN due to the freeze drying process, whereas it is well known that ordinary methods of dehydration are invariably accompanied by de..aturation of the proteins with

Table I

Moisture, WEN, NPN and free α - amino N in fresh and freeze dried prawn meat (*P. stylifera*, raw material held in crushed ice overnight before processing. Each value is the average of three estimations.)

Condition of meat analysed	Moisture%	WEN	NPN	Free α-amino N
		% N on dry weight basis		
Fresh	80.76	5.665	3.170	1.021
Frozen	82.57	5.954	2.157	0.665
Freeze dried*	3.16	5.309	2.933	0.813
Stored $2\frac{1}{2}$ months‡	4.33	5.202	3.108	0.813

*Reconstitution ratio : 95.23 ‡Reconstitution ratio : 89.30

TABLE II

Moisture, WEN, NPN and free α - amino N in fresh, frozen and freeze dried prawn meat (*P. stylifera*, raw material stored overnight in crushed ice, peeled and deveined and the meat stored in ice for further two days. Each value is the average of three estimations.)

Condition of meat analysed	Moisture%	WEN	NPN	Free α-amino N
			%N on dry weight basis	
Fresh	85.78	3.323	0.868	0.141
Frozen	84.63	2.286	0.559	0.127
Freeze dried*	3.01	3.096	0.920	0.127

*ReConstitution ratio : 91.69

TABLE III

Moisture, SEN, NPN and free α - amino N in fresh, frozen and freeze dried prawn meat (*M. affinis*, raw material held overnight in crushed ice, peeled and deveined and the meat again held in ice overnight.

Condition of Meat analysed	Moisture %	SEN	NPN	Free α-amino N
			% N on dry weight basis	
Fresh	84·68	11.14	1.239	0.347
Frozen	83.64	8.83	1.869	0.349
Freeze dried*	3.90	8.72	1.702	0.357

*Reconstitution ratio : 84.2.

consequent reduction in their extractability. This finding is in agreement with that of Takashi *et al.* (1964) who observed that in a few species of fish meat subjected to freeze drying, the extractability of myosin fraction was not so much lowered as in ordinary drying process and in some cases the extractability was even higher than that before drying. Connel also found good evidence to show that sarcoplasmic proteins survived freeze drying virtually intact, the electrophoretic and ultra centrifuge properties of extracts of this group of proteins prepared from freeze dried beef and cod being very similar to those of frozen controls (Connel, 1963). Tamoto (1964) observed that greater part of actomyosin was not rendered insoluble by freeze drying, there being little difference between the contents of actomyosin of fresh and freeze dried muscle.

Table II shows that about 40% of WEN, 74% of NPN and 86% of the free α - amino N had already leached out by the initial storage of the raw material in ice. Such leaching losses have already been observed and reported by the author earlier (*loc.* cit., 1962 and 1969). Levels of these constituents showed a fall on freezing, which may be attributed to drip losses occuring when the frozen material is thawed out for analysis, while in the

TABLE IV

Changes during freezing, freeze drying and storage of the meat of *M. monoceros* (Processed fish)

Condition of meat analysed	Moisture %	Reconstitution ratio	WEN	NPN	Free α-amino N	Organoleptic quality
			% N on dry weight basis			
Fresh	82.90	—	4.668	2.054	0.302	Good
Frozen	82.75	—	3.780	1.669	0.134	,,
Freeze dried	4.91	72.24	4.658	2.201	0.137	Good
Stored 1½ months	3 44	86.32	4.374	2.266	0.264	,,
,, 2½ ,,	4.96	86.30	—	2.153	0.331	,,
,, 3½ ,,	3.30	73.36	4.883	2.002	0.602	Good to fair
,, 5½ ,,	6.59	75.53	4.951	2.113	0.974	,,
,, 7½ ,,	8.34	64.73	4.855	2.473	1.149	,,
,, 9 ,,	3.82	77.69	5.493	2.344	1.040	,,
,, 11 ,,	3.91	77.69	5.145	2.304	0.864	,,
,, 13 ,,	4.39	86.52	3.329	2.102	1.114	,,
,, 15½ ,,	3.56	86.52	—	—	0.850	,,
,, 17½ ,,	4.66	64.74	4.917	2.388	0.972	,,
,, 20 ,,	6.50	64.74	4.420	2.564	1.365	Fair*
,, 24½ ,,	5.38	82 00	5.039	2.527	1.069	,,
,, 27½ ,,	7.36	64.73	3.624	2.118	0.949	,,

* A few pieces blackened on cooking.

TABLE V

Changes during freezing, freeze drying and storage of meat of *M. dobsoni* (Raw material held in crushed ice overnight before processing)

Condition of meat analysed	Moisture %	Reconstitution ratio	WEN	NPN	Free α-amino N	Organoleptic quality
			% N on dry weight basis			
Frozen	80.83	—	3.563	2.052	0.351	Good
Freeze dried	3.17	—	4.299	2.221	0.602	,,
Stored 3½ months	4.80	58.0	5.504	2.454	1.115	,,
,, 6½ ,,	1.75	60.0	5.238	2.794	1.030	,,
,, 9½ ,,	4.50	68.0	5.124	2.350	0,908	,,
,, 12½ ,,	2.54	86.0	5.140	—	0.928	,,
,, 15½ ,,	1.26	68.0	5.032	2.682	1.573	,,
,, 21½ ,,	1.63	72.0	5.036	2.783	0.718	,,

TABLE VI

Changes during freezing, freeze drying and storage of prawn meat (*M. affinis* and *M. dobsoni* mixture). Raw material held overnight in crushed ice before processing.

Condition of meat analysed	Moisture %	Reconstitution ratio	SEN	NPN	Free α-amino N	Organoleptic quality
			%N on dry weight basis			
Fresh	78.43	—	10.34	2.427	0.931	Good
Frozen	81.00	—	9.54	1.760	0.644	,,
Frezee dried	2.03	71.6	7.94	2.841	0.973	,,
Stored 1 month	2.90	67.5	8.05	2.828	0.979	,,
,, 2 ,,	2.95	75.0	9.40	2.941	1.073	,,
,, 5 ,,	1.53	75.0	6.96	—	1.007	,,
,, 7½ ,,	3.07	100.0	7.34	3.254	1.236	,,
,, 11 ,,	2.65	85.0	5.65	3.100	0.930	,,
,, 18 ,,	2.83	87.5	—	2.478	0.802	,,
,, 21 ,,	5.47	80.0	8.132	3.595	1.098	,,
,, 24 ,,	2.53	83.3	8.071	2.914	1.040	,,
,, 32 ,,	4.38	75.0	6.600	3.082	1.510	,,

freeze dried product, their levels were more or less the same as in the unfrozen meat. It may be seen from Table III that dilute salt solution extracts a much higher proportion of proteins than water alone and that 21% of this is rendered insoluble by the freeze drying process. Martein Yanova (1958) also observed a partial denaturation of salt soluble fraction of the proteins during freeze drying.

Table IV shows that WEN and NPN remained more or less constant throughout the period of storage of 30 months, even though some slight fluctuations are observed in some cases. There is considerable increase in the content of free α-amino N from 3½ months of storage onwards. The reason for this is unknown at present and deserves a more detailed investigation. The fact that this is not due to any undesirable deteriorative biochemical changes occurring in the product is amply borne out by its still acceptable organoleptic property. The product remained in highly acceptable condition even after 30 months of storage. Table V shows a slight increase in WEN and NPN during storage of the freeze dried product. A notable increase in free α-amino N contents during storage is observed in this case also. The product remained in good organoleptic quality throughout the 21½ months of storage.

Table VI shows a decrease in SEN due to freeze drying as observed earlier. But the trend during storage was somewhat irregular. The same was the case with NPN also. The observation made earlier about the behavior of free α-amino N content is confirmed in this instance also. The product remained in good acceptable condition throughout the 32 months of observation.

SUMMARY

The results obtained in this study

indicate that practically no denaturation takes place in the muscle of prawns due to freeze drying with respet to water extractable proteins. However, salt extractable proteins are rendered insoluble to the extent of 21% during this process. WEN, SEN and NPN are not affected to any appreciable extent due to prolonged storage of the product, whereas free α-amino N contents exhibit a remarkable increase after 3 to 4 months of storage. The freeze dried products remain in good edible condition even after 32 months of storage up to which observations were made in these studies.

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