

STUDIES ON THE PRESERVATION OF FISH BY PICKLING

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INTRODUCTION

PICKLING with salt, vinegar, sugars and spices forms a traditional method of food preservation and is also widely employed for fish curing. A great variety of fishery products prepared with vinegar and spices enjoy wide popularity in Germany and other north European countries. Pickling is also practised in the East in countries like China, Japan and the Philippines (Jarvis, 1950). Although pickled products are of a semiperishable nature since the concentrations of salt and vinegar employed are limited by considerations of palatability, they possess a greater appeal to consumers than salted and dried fish. Moreover these methods are better suited for curing fatty fish which are susceptible to rancidity in other salting methods. Apart from a few spiced and pickled products like PADDA and MOLLEI prepared on a domestic scale from Seer fish, Colombo Cure of the West Coast forms the chief commercial method in India which employs principles of pickling. Mackerels, Seer and non-fatty sardines are treated by this process and Malpe in South Kanara exports considerable quantities of Colombo cured fish to Ceylon (Nicholson, 1930). Malabar tamarind or 'Goruka Puli', the dried fleshy pod of *Garcinia cambogea* is used as an adjunct to salt in order to obtain the desired acidity. Though Goruka Puli is specially brought from Ceylon for this purpose, inferior varieties like 'Koda Puli' are also used on a smaller scale. The objectives of the present investigation were to study the chemical aspects of the pickling methods with a view to improve the existing practices and to explore the possibilities for a wider application of pickling methods to smaller varieties of fish like sardines which are mainly sundried at present. Studies on the preparation of high quality spiced and pickled products on the lines of foreign recipes like 'Marinated Herring' and 'Russian Sardine' were also undertaken in an effort to develop new products for our fishing industry.

PROCEDURES EMPLOYED FOR PICKLING

Sardines (*Sardinella* sp.), Rainbow Sardines (*Dussumieria* sp.) and mackerel (*Rastrelliger canagurta*) caught by shore-seines have been utilized for pickling in the present series of experiments. After transporting in ice to the laboratory, the fish were washed thoroughly in tap water and degutted. In the case of mackerel the fish were also split open leaving the backbone on one of the sides by giving a longitudinal incision on the ventral side. After the removal of the viscera and the gills the fish were subjected to further washing to remove completely all traces of blood. Procedures for pickling by the various methods as described below were worked out on lines similar to those mentioned in the references cited.

1. *Marinated Herring*.—Fish were stacked in 5% vinegar (prepared from pure glacial acetic acid in all the present series of experiments) containing in addition 80 g./litre of salt. After the completion of the first stage of this cure which consisted of pretreatment in the above medium they were washed lightly and stacked in glass bottles along with the following spice mixture. Pretreatment period varied from 48 hours in the method described by Watson and Hess (1936) to 24 hours adopted in the second series of experiments with Rainbow Sardines instead of Sardines. Fish transferred to bottles were then covered completely with a sauce containing salt, sugar and acetic acid.

<i>Spice mixture</i> (per 1 Kgm. of fish)	<i>Composition of sauce</i> (per 1 litre)
Pepper.....20 gm.	Salt50 gm.
Mustard 8 gm.	Sugar35 gm.
Cloves 3 gm.	Acetic Acid30 ml. (Glacial)
Onionsa few slices	

2. *Russian Sardines* (*Jarvis*, loc. cit.).—Sardines (*Sardinella* sp.) prepared for pickling as described above, were left immersed in a bath made of 6% vinegar for 18 hours at room temperature. After this preliminary cure the fish were drained and mixed with a powdered mixture of spices and salt of the following composition. The product was then packed in clean glass bottles. Period allowed for this pretreatment was found to be critical since the texture of the fish is affected by prolonged acid immersion and it was cut down to 6 hours in later experiments with Rainbow Sardines.

Composition of salt-spice mixture

(Per 1 Kgm. of fish)

Salt	180 gm.
Sugar.....	90 gm.
Pepper.....	5 gm.
Cloves	3 gm.
Potassium Nitrate (KNO ₃)	3 gm.

3. *Tamarind-Salt Cure*.—Tamarind (*Tamarindus indica*) was substituted for Goruka Puli (*Garcinia cambogea*) employed in the Colombo Process for mackerel described by Nicholson (*loc. cit.*). Rainbow Sardines and mackerel were pickled according to this cure, salt ratio adopted being 1:3 by weight of fish. After applying salt in the conventional manner, a small piece of tamarind was inserted in the belly cavity of the fish. Fish were then packed in a basin with alternate layers of salt and tamarind. About 50 gm. of tamarind was required for curing 1 Kg. of fish. After leaving aside for 3 days fish were transferred to bottles and covered completely with self brine. In our experiments with Rainbow sardines we have conducted a simultaneous study of pickled product prepared by using salt fortified with Sodium Nitrite to act as a preservative. Amount of Sodium Nitrite incorporated was adjusted to form 0.02% of the weight of fish taken. Mackerel was cured in a similar manner in the next experiment but after the initial salting stage, the fish were transferred to a bottle and covered with fresh saturated brine.

4. *Wet Salting*.—For a comparative study of pickling as a method of preservation in relation to the Wet Salting methods of the West Coast, mackerel was cured simultaneously by both Ratnagiri and Colombo methods. Salt ratio of 1:3 was employed for wet salting but only half of the requisite quantity of salt was applied on the first day. The remainder was again applied on the second and third days in equal amounts. After rubbing with salt the fish were stacked in a basin with alternate layers of salt in such manner that the self brine formed drains out freely into another basin placed below.

RESULTS

Experimental procedures employed at this laboratory for the estimation of Total Volatile Basic Nitrogen, Trimethylamine, Formol Nitrogen by Sorensen technique and other chemical observations reported in this

account have been described elsewhere (Suryanarayana Rao *et al.* 1958) and follow closely standard methods for the same. Samples for analysis were prepared by mixing the muscle portion alone from three fish from each lot in a meat mincer. Taste panel studies were also conducted on the pickled products and observers were asked to record their individual opinion regarding the odour, flavour, texture and salt content. Data obtained was analysed by employing a score system.

Products obtained by the different methods were analysed periodically during storage at room temperature to follow the changes for establishing keeping quality chemically in addition to organoleptic judgment. Results obtained during these investigations have been described under the following sections.

(a) *Spiced and Pickled Products.*—It was observed during the preparation of the spiced products according to foreign recipes that prolonged acetic acid treatment is injurious to the texture of the fish and chemical changes occurring during this operation were therefore followed in order to ascertain the period of pretreatment suitable for tropical conditions. Fig. 1 represents graphically the nature of proteolytic changes and salt penetration in this step. The data have also been recorded in Table I. The brine liquors were also analysed after this preliminary cure and appreciable amounts of Volatile Basic and Formol Titratable Nitrogen were detected as shown below.

Composition of the media after pretreatment

	Russian Sardine	Marinated Herring
pH	4.5	4.5
Acidity % (gm. Acetic Acid)	3.21	2.91
T.V.B. Nitrogen per 100 ml.	11.20	17.64
Formol Nitrogen per 100 ml.	83.34	99.45

It may be observed that Volatile Basic Nitrogen (T.V.B.) registers an increase in 4 hours and diminishes thereafter, probably as a result of diffusion into the surrounding medium. Autolytic changes in the fish muscle are revealed by a steady rise in Formol Nitrogen. Maximum penetration of salt takes place within 8 hours in the marinated product and though Formol

Nitrogen continues to show an upward trend up to 24 hours it appears desirable to limit the pretreatment period to 8 hours to preserve the physical condition of the fish. Russian Sardine preparation also shows similar proteolytic changes but autolysis proceeds much quicker and though Formol Nitrogen reaches its maximum after 8 hours, pretreatment period of about six hours appears to be suitable for this cure.

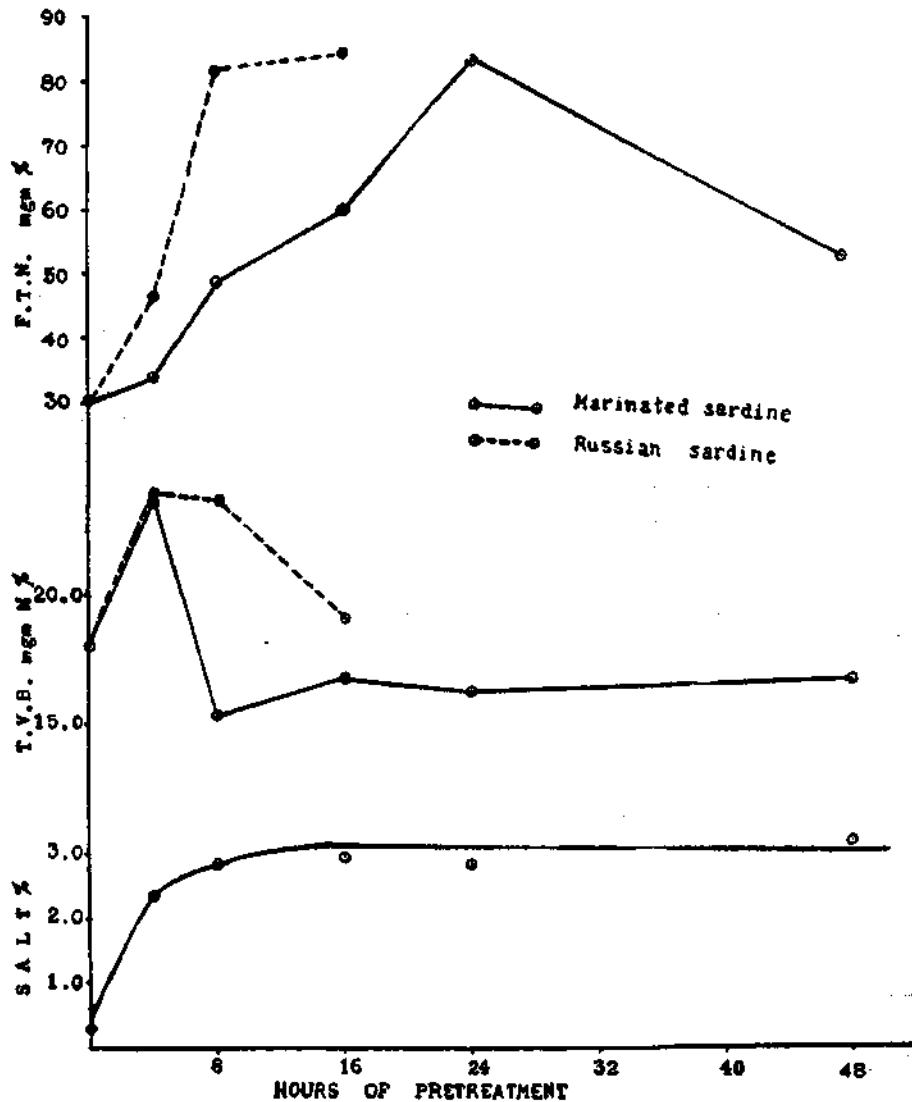


FIG. 1. Chemical changes during pretreatment with vinegar in spiced and pickled sardines.

TABLE I
Changes during curing and storage of spiced and pickled sardines
 (Results expressed on original moisture basis)

Period	Russian Sardine				Marinated Herring			
	Moisture %	Salt %	T.V.B. mgm. N %	F.T.N. mgm. %	Moisture %	Salt %	T.V.B. mgm. N %	F.T.N. mgm. %
0 hrs.	73·60	0·27	18·16	30·19	73·60	0·27	18·16	30·19
4 hrs.	75·63	..	24·01	46·42	68·18	2·39	23·92	34·12
8 hrs.	76·79	..	23·71	81·44	69·97	2·83	15·32	48·77
16 hrs.	76·79	..	19·14	84·39	71·11	2·93	16·68	59·97
24 hrs.	70·87	2·85	16·15	84·10
48 hrs.	71·87	3·20	16·56	56·93
7 days	59·29	10·71	24·17	171·32	71·37	3·16	20·70	158·06
15 days	57·33	..	27·37	169·23	72·36	..	21·62	254·59
9 weeks	59·37	..	23·10	304·90	69·02	..	22·31	343·30
14 weeks	57·86	..	37·74	291·80	73·81	..	45·72	383·70

Keeping quality of the spiced products has been ascertained from the changes observed over a period of 14 weeks (see Fig. 2). Values obtained are also recorded in Table I. T.V.B. Nitrogen remains practically at the same level till 9 weeks and increases rapidly thereafter, more so in the case

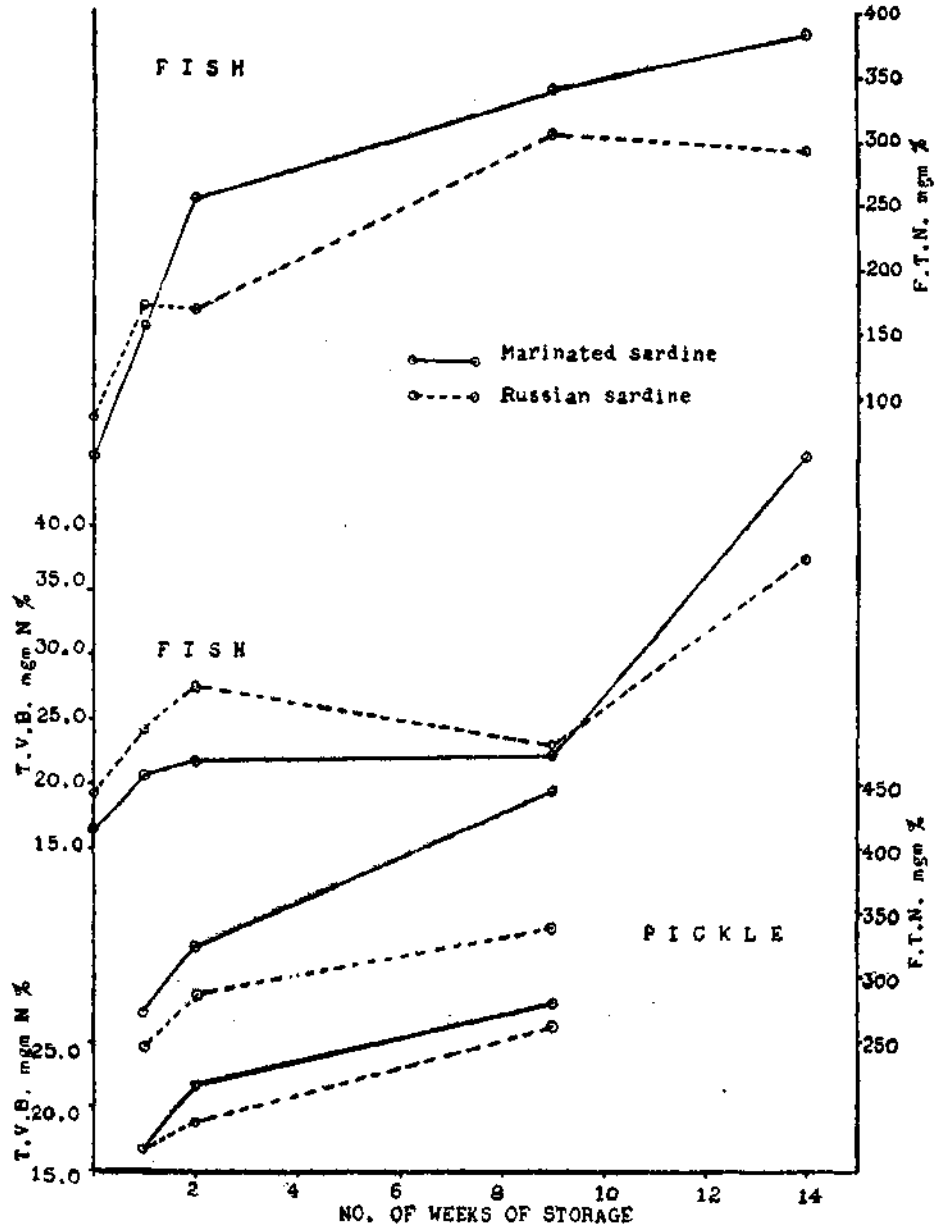


FIG. 2. Chemical changes during storage in spiced and pickled sardines.

of Marinated Herring. Brine analysis reveals a slow increase in T.V.B. even while the fish do not record any changes. Formol Nitrogen increases steadily up to 9 weeks but Russian Sardine shows some reduction in later stages.

Spiced and pickled products were also prepared from Rainbow Sardines instead of sardines in a similar manner. Marinated Herring method yielded a product which deteriorated rapidly within 4 weeks while Russian sardine prepared from the same material could be preserved in good condition up to 12 weeks. Another series was also studied with Rainbow sardines as raw material to find out whether the keeping quality could be improved by cutting down the pretreatment period as indicated previously. However no appreciable differences could be detected.

Bacteriological examination of the fish muscle from Marinated Herring from Sardines 15 days after the cure revealed a few micrococci and bacilli (8.54×10^7 per gm. of muscle). In the case of Russian Sardine the muscle itself could not be sampled since the fish had disintegrated to a considerable extent and the product as a whole was plated. All the plates were heavily crowded.

Taste panel studies indicated a favourable opinion regarding these spiced products. Marinated Herring was preferred to Russian Sardine.

(b) *Tamarind Cured Products.*—It was observed that the use of tamarind in addition to salt, lowered the pH of the self brine to 4.8 comparable to vinegar treatment in Russian Sardine method. Results of the chemical examination at intervals up to 125 days in the case of pickled Rainbow Sardines have been tabulated in Table II and the trends of variation of some of the constituents have been also represented by graphic illustration (see Fig. 3). Taste panel opinion regarding these pickled products was satisfactory though in comparison with the spiced products from the same series, observers commented upon the toughness and fibrous nature of tamarind pickled products.

After even 4 months of storage Total Volatile Basic Nitrogen recorded low levels amounting to only 119.1 mgm. % on dry weight basis. However a slow increase is perceptible throughout this period. Brine analysis indicated that some of the Volatile Basic and Amino Acid Nitrogen diffuses into the brine from the pickle which may account for the low T.V.B. values.

It may be readily observed that the addition of sodium nitrite results in a definite improvement in the keeping quality of pickled Rainbow Sardines and retards the development of Volatile Bases. Formol Nitrogen rises

TABLE II
Chemical observations on the keeping quality of pickled Rainbow Sardines by tamarind-salt process
 (Values expressed on dry weight basis)

Observation	Sample	Fresh fish	Period after cure (in days)						
			15	35	55	70	85	105	125
Moisture %	Control	78.38	51.07	53.48	53.14	52.83	53.70	53.02	54.80
	Nitrite treated	do.	52.31	50.47	50.69	50.03	52.26	50.23	52.44
Salt %	Control	0.37	32.42	..	32.62	29.05	29.39	28.97	31.96
	Nitrite treated	do.	31.73	..	30.96	26.56	30.07	28.85	30.95
T.V.B. mgm. N %	Control	103.6	63.0	62.6	89.6	92.0	93.7	119.2	119.1
	Nitrite treated	do.	54.0	47.5	68.1	70.0	73.3	76.0	76.9
Trimethyl- amine mgm. N %	Control	19.4	20.0	24.1	17.9	23.8	21.2	23.8	26.8
	Nitrite treated	do.	14.7	14.1	14.2	16.8	17.6	19.7	23.6
Formol titra- table N mgm. %	Control	169.7	194.2	246.0	326.1	289.5	336.2
	Nitrite treated	78.7	133.9	112.0	142.4	108.5	105.2

rapidly during storage especially in the initial stages and serves as a guide to the proteolytic changes. Sodium nitrite addition brings about a marked lowering in these changes as well. Trimethylamine levels show wide fluctuation during storage though a tendency towards increase is apparent in the final stage. Nitrite treated group differs in this respect by registering a more uniform and gradual increase on storage.

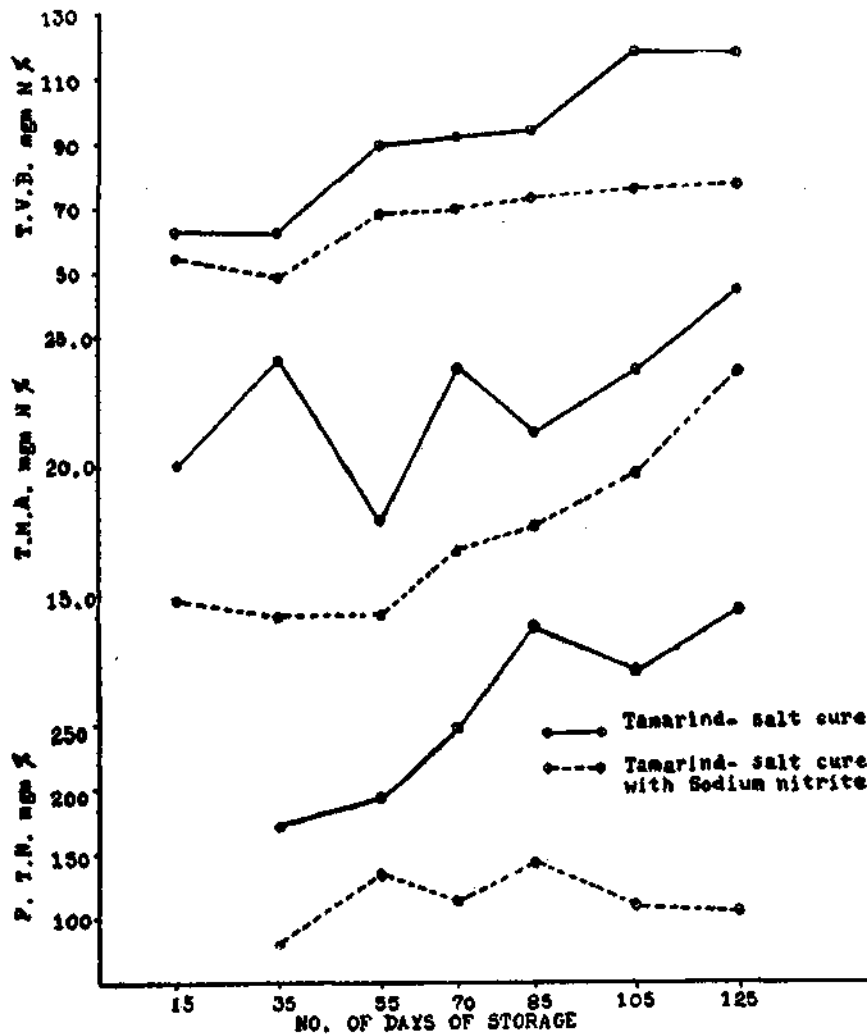


FIG. 3. Chemical changes during storage in Rainbow Sardine pickled with salt and tamarind.

The type of spoilage noticed visually in these tamarind pickled products was mainly mould growth appearing within a month. Fermented odour

was also discernible a little later. Addition of sodium nitrite delayed these changes by about a fortnight.

Results of the comparative study of pickling with tamarind and salt and the Ratnagiri methods are recorded in Table III. When the fish were covered fully with fresh saturated brine and stoppered tightly avoiding contact with air mould growth did not appear even after 6 months and the product remained in a satisfactory condition up to 8 months. Chemical analysis of the products also indicated that proteolytic changes were not pronounced as compared to the Wet Salted products.

TABLE III
Chemical analysis of mackerel cured by Ratnagiri Wet Salting method and pickling
(Results expressed on original moisture basis)

Observation	Sample	Initial	Weeks			
			2	4½	9½	22½
Moisture %	Wet cure	76.32	55.38	54.30	52.67	..
	Pickling method	do.	55.00	57.58	56.35	60.83
Salt %	Wet cure	0.25	19.07
	Pickling method	do.	17.09
T.V.B. mgm. N%	Wet cure	34.71	112.3	137.8	209.7	..
	Pickling method	do.	55.82	63.13	61.12	67.83
Truttwin index ml./N/100 Iodine solution per gm.	Wet cure	5.25	13.17	12.12	27.49	..
	Pickling method	do.	..	8.60	21.33	9.88

DISCUSSION

Apart from brief descriptive accounts of the existing methods of the Colombo Cure (Nicholson, *loc. cit.*; Govindan, 1916) studies on the chemical aspects of the process and the quality of the cured products have been lack-

ing. Venkataraman and Srinivasan (1957) have recently reported a few observations dealing mainly with the bacterial flora of Colombo cured mackerel. Gas forming anaerobes were noted in the pickle and fish, which did not however digest the meat or produce foul odours. They have observed a fruity odour apparently due to the favourable fermentative activity of the anaerobes. Although the replacement of *Garcinia cambogea* employed in the original method by ordinary tamarind (*T. indica*) resulted in lowering the pH to 4.8 as against 5.4 observed by these workers, data from the chemical observations obtained in the present investigation is in general agreement with their findings. Formol Nitrogen and T.V.B. values are fairly low for these tamarind salt pickled products even after prolonged storage and the development of fermented odours formed the main type of spoilage. It may be readily observed that pickling preserves mackerel for much longer periods than Wet Salting as was observed from the present study and observations collected during our previous studies on the curing of mackerel (Suryanarayana Rao *et al.*, *loc. cit.*). There is therefore need for comprehensive studies on the curing of mackerel by pickling which appears to possess greater advantages.

Improvement in biological stability cannot be entirely ascribed to the influence of lowered pH, as factors other than pH like the preservative action of organic acids may be involved. Hess and Gibbons (1942) observed that tartaric, citric and lactic acids were more effective than acetic acid based on concentration by weight in inhibiting the growth of red halophiles in 22.5% skim-milk agar. As Nunheimer and Fabian (1940) observed, organic acids exert a germicidal and antiseptic effect disproportionate to the hydrogen ion concentration produced.

Estimation of the Total Volatile Basic Nitrogen is observed to serve a useful purpose for the assessment of the proteolytic changes accompanying fish spoilage though both the magnitude and the extent of increase is much lower in relation to the other fish curing methods. Analysis of the brines has also been found to be useful as in the case of the spiced products from Sardines. Since the total increase in T.V.B. amounted to only a range of 55.82 to 67.90 mgm. N % in pickled mackerel during storage for a period of five months, limits for T.V.B. may have to be determined by further investigations while 200 mgm. N% has been suggested for other types of cured fish (Velanker, 1952). Changes in Trimethylamine content which were followed in Rainbow Sardines pickled with tamarind and salt rule out the possibility of its use as an index of spoilage to a certain extent. With regard to the observations relating to Formol Titratable Nitrogen it may be mentioned

that in general this index is a fair guide to the autolytic changes induced by enzymes in the fish flesh as opposed to bacterial spoilage which is characterized by a sharp rise in Volatile Basic Nitrogen due to a more rapid disintegration of the proteins (Boury, 1938). Since pickled products owe their characteristic flavour to the curing action of cellular enzymes upon the proteins and fats, F.T.N. estimations may be useful for assessing the completion of the cure in products like Russian Sardine and Marinated Herring as also the extent of proteolytic changes during storage.

Bacteriological examination has revealed that the fish muscle itself contained a few micrococci though the pickle as a whole from Russian Sardines gave high counts. It is possible that the condition of the muscle itself may be similar since the salt content of Russian Sardines is actually much higher (10.71% on wet weight basis). Tendency towards mould growth observed in tamarind pickled products could be considerably controlled as in the case of mackerel by careful packing, avoiding access to air, and covering completely with fresh brine which can also be replaced periodically.

Results of the present investigation show that there is room for improvement of the indigenous methods of curing by the incorporation of harmless preservative chemicals like sodium nitrite. Fortification of the salt employed for curing with a minute amount of nitrite has been observed to improve the keeping quality of pickled Rainbow Sardines as revealed by the results of chemical analysis for T.V.B. and Formol Nitrogen. Tarr and Sunderland (1940) have noticed a significant beneficial effect on the keeping quality of salmon fillets dipped in 15% brine containing 0.1% sodium nitrite and stored at 1.5° C. Nitrite concentration of the self brine formed in our experiments lies between 0.04 to 0.05%. Since only a negligible amount of sodium nitrite could be detected in the fish one month after the cure (108 µg. per 100 gm. of muscle) addition of sodium nitrite may not prove to be objectionable from the food regulations' point of view.

Possibilities of adopting foreign recipes like Russian Sardine and Marinated Herring for preparing high quality spiced and pickled products are cognizable from the results of these preliminary trials though the methods of preparation may have to be modified on the lines indicated so as to suit local conditions. Since the products are highly perishable, deteriorating within a few months, it would be profitable to investigate the possibility of storing them at lower temperatures. Abundant quantities of smaller varieties of fish similar to herring are caught in our waters annually and as vinegar of the best quality can be made available in India from alcohol,

molasses, cereals and toddy, pickling of fish with vinegar and spices locally available, offers many advantages among the methods employed for curing and preservation.

SUMMARY

Since pickling with salt and malabar tamarind (*Garcinia cambogea*) known as Colombo Curing forms an important method for preserving mackerel in India, chemical investigations on the pickling of fish were initiated with a view to improve the existing practices as also to explore the suitability of foreign recipes like Russian Sardine and Marinated Herring for preparing delicious spiced products with vinegar and salt. Sardines (*Sardinella* sp.), Rainbow Sardines (*Dussumieria* sp.) and mackerel (*Rastrelliger canagurta*) were employed for these experiments and ordinary tamarind (*Tamarindus indica*) was substituted for the malabar tamarind.

It was observed that pickled mackerel could be preserved up to 8 months in good condition as compared to wet salted products which deteriorated within 2 months. Smaller varieties of fish like Sardines and Rainbow Sardines which are ordinarily sundried, were observed to yield pickled products of longer biological stability and greater consumer appeal. Incorporation of sodium nitrite as a preservative chemical was found to bring about further improvement in the keeping quality. Large-scale preparation of high quality pickled and spiced products with vinegar and salt appears to be a feasible proposition if the methods are modified slightly to suit tropical conditions on the lines suggested in the present account.

Data from chemical observations collected during storage has confirmed the usefulness of Total Volatile Bases estimation as an index of spoilage in pickled products as well, though the limits for the same may differ from other types of cured products.

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