PRESERVATION OF COTTON FISH NET TWINES BY TANNING: I. OPTIMUM CONCENTRATION OF TANNING BATH

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Samples of tannin-containing preservatives used by fishermen in India for treating cotton nets were collected and qualitative and quantitative characterisation of the tannins made. The concentrations of different tannins required to impart optimum periods of preservation to the net were worked out and found to be 2% in 8 out of 10 materials studied.

INTRODUCTION

Tanning is by far the most widely adopted method of preservation for fishing net twines of vegetable origin. Migita (1943) has expressed the view that for economic treatment, a 4% solution of cutch may be used, while maximum effectiveness is afforded by a solution having 6-7% concentration. Takayama and Shimozaki (1957) used 3-4% cutch or tannin extract In fresh or salt water for their experiments. Firth and Carlson (1949) used a 5% treating solution of cutch extract or tan bark of 5.9 kg (13 lbs) in the same weight of water. In the Philippine method, Clague and Datingaling (1950) reported the use of a 6% cutch solution while Sulit and Panganiban (1954) recommended a 5½% solution. Chubb (1954) described the proportion used in some parts of England as 3.2 kg (7 lbs) of cutch per 45.5 l (10 imp gal) of water. The Danish method (Anon, 1956) preserved the net material in 4-5% cutch in water. von Brandt (1955) and Koura (1963) advocated a 2% cutch solution for the primary treatment and doubled the strength for retreatments. Miyamoto and Shariff (1959) used powdered dry shells of myrobolan nuts in water in the ratio of 1:3, crushed *Panachikka (Diospyros embryopteris)* fruit paste in 1:1 and dried bark in 1:5. Kuriyan and Nayar (1961) and Nayar and Naidu (1962) used 5% solution of the extracts of bark containing tannin and Nayar *et al* (1962) indicated the use of 4% solution for the preservation bath. While giving the methods of preservation of cotton net twines Kuriyan and Nayar (1963)

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recommended the use of 4–5% cutch or 15 to 20% bark in water. Although tannin preservation is quite common, the preservation methods so far conducted do not indicate the relative effectiveness of the preservative bath with respect to the tannin content and the type of tannin present in the raw material. This aspect has been given due emphasis in the present study by the authors and the results of the first series of experiments are incorporated in this paper.

Materials and Methods

Tannin yielding materials commonly used by the fishermen along both coasts of India were collected. The materials under tests were boiled with water in the ratio of 1:10 by weight (Kuriyan and Nayar, 1961, *loc cit*) for one hour. The solution was then filtered and the filtrate examined for tannin content by AOAC (1960) method. Tannin content was determined on dry weight basis in all cases except *Panachikka* where green fruit was used for extraction. The functional groups of tannin in the different extracts were assessed by qualitative tests characteristic of pyrogallol and catechol tannins (Nierstein, 1934; Thorpe, 1954). The outlines of the tests are presented in Table I. Table II presents the particulars of tanning material under study along with the tannin content and type of tannin analysed in the laboratory.

Preservation and method of test

Solutions of varying concentrations of tannin ranging from 1–5% were prepared. Cotton twines of specification 20s/ 4/3 which were previously soaked in water for 24 hours and dried were treated in the respective solution keeping the material to bath ratio as 1:10 (Kuriyan and Nayar 1963 *loc cit.*) The dyeing bath was boiled for half an hour

Table I Qualitative tests for identification of the functional group of tannin

Reactions	Catechol	Pyrogallol
Ferric chloride	A deep green colouration turning red on adding sodium carbonate and violet on adding sod. acetate.	Deep blue colouration.
2. Bromine water	A precipitate formed.	No precipitate.
3. Iron alum	Greenish black precipitate	Blue black precipitate
4. 5 ml tannin mixed with 10 ml acetic acid (10%) and 5 ml lead acetate (10%)	No precipitate	Precipitate of lead tannate, filtered, and the filtrate with a few drops of ferric alum (1%) gave bluish violet colour.
5. 50 ml of tannin solution boiled for a few minutes with 10 ml of 40% formaldehyde and 10 ml of HCl (1:1) and then cooled and filtered.	Tannins completely precipitated. Filtrate with 1 or 2 drops of gelatin and salt solution and 1 ml of ferric alum (1%) with the addition of 5 g of sod. actate gave no precipitate or colour.	Filtrate with 1 or 2 drops of gelatin and salt solution and 1 ml of ferric alum (1%) with the addition of 5 g of sod. acetate gave blue or violet layer at the junction of the ferric salt.
6. Ammonium molybdate.	Red colouration, yellow in dilute solution and destroyed on adding oxalic acid.	

Table II Particulars of tanning materials studied.

Material	Area where used	Local Name	Source of tannin	Type of tannin	Details of the solution used by fishermen		Tannin content of raw material %	Tannin content in the solution used by fishermen %
					Ratio of material to water	Method of preparation		
1	2	3	4	5	6	7	8	9
Terminalia chebula	Kerala	*Kadukka*	Dried fleshy part of fruit.	Pyrogallol	114 g powdered dry shells /300 ml water	Boiled for 15 mts, & filtered.	41.54	—
Odina wodier	Kerala W. Bengal	*Kalasam* *Harithaki*	Bark	Catechol	454-681 g bark / 4.5 l water.	Dried bark chopped and boiled with water.	10.2	1.26
Albizzia lebbek	Madras	*Kattuvaka pattai*	-do-	-do-	10 g bark /100 ml water.	Boiled with water for about 2 hours.	6.1	0.61
Morinda tinctoria	Andhra	*Thogaru chettu*	-do-	-do-	10 g bark/300 ml water.	Boiled with water for sufficiently long time till a brown liquor is got.	20.2	0.67
Meucas sp.	Andhra	*Thumma-chekka*	-do-	-do-	5 g bark /100 ml water	-do-	15.8	0.79
Terminelia crenulata	Goa	—	-do-	-do-	1:10 to 1:15	Dried and crushed bark boiled for 2-3 hours.	16.3	1.28
Terminalia	Bombay	*Sajad*	-do-	-do-	12.5 g of bark / 100 ml water.	Soaking the bark in water and kept exposed in earthern pots, in sun for 3 to 4 days. For urgent use, the bath is boiled in G. I. barrels.	7.2	0.90
Careya arborea	Bengal Madras Kerala Andhra	*Kumbi* *Ayma* *Pelu or Alam* *Araya*	-do-	-do-	1:10 to 1:15	Dried and crushed bark boiled for 2 to 3 hrs.	15.3	1.22

(Contd..... ...)

1	3	4	5	6	6	7	8	9
Avicennia sp.	Gujarat	*Kharod*	-do-	-do-	—	—	27.0	—
-do-	Orissa	*Khayis*	-do-	-do-	12 g bark /100 ml water	Crushed bark mixed with water and kept for 2 days	8.0	0.96
Diospyros embryo-pteris	Kerala Bengal	*Panachikka Gab.*	Fruit	Mixed: catechol and Pyro-gallol	2 parts of water for one part of paste of fruit.	Crushed well to a paste and kept for 2 to 3 days	10.2	5.6
Tamarindus indica	Kerala Madras	*Pulinkuru Puliankottai*	Seed coat	-do-	10 g powder /100 ml water.	Powdered seed coat boiled with water and hot bath used.	15.6	—
-do-	Andhra	*Gedari chekka*	Bark	-do-	10 g bark /270 ml water	Heated for sufficiently long time till dark colour.	18.2	0.66
Acacia arabica	Bombay Bengal Madras	*Babul Babla Karivelum pattai*	-do-	-do-	10 g bark /100 ml water	-do-	11.7	1.17

Table III Hydrographic details of the test site during the test period

Material and period of immersion				Month of observation	Water surface temperature °C			Salinity ‰		
					Average	Maxi-mum	Mini-mum	Average	Maxi-mum	Mini-mum
Kadukka	12-12-1967	to	29-12-1967	December, 1967	29.1	30.0	28.5	31.9	34.0	28.2
Kalasam	12-12-1967	to	5-1-1968							
Kattuvaka pattai	12-12-1967	to	23-1-1968	January, 1968	28.5	29.5	27.0	32.5	35.0	28.2
Thumma chekka	12-12-1967	to	8-1-1968	,,						
Terminalia crenulata	12-12-1967	to	23-1-1968	February, 1968	29.2	30.5	28.5	32.7	34,7	28.2
Kumbi	29-3-1968	to	16-4-1968	,,						
Khayis	29-3-1968	to	16-4-1968	March, 1968	30.4	31.0	29.5	28.6	29.3	27.8
Panachikka	8-2-1968	to	7-3-1968	,,						
Pulinkuru	8-2-1968	to	7-3-1968	April. 1968	31.0	32.0	29.5	28.3	32.6	26.2
Gedari chekka	12-12-1967	to	23-1-1968	,,						

and the treated material allowed to remain in the cooling solution overnight. The next day the material was taken out, dried at room temperature to uniform moisture level and kept in desicator for 3 hours. The impregnation of the preservative was assessed on the basis of the weight of material before and after treatments.

The treated twines along with the control were subjected to continuous immersion test in Cochin back-waters. Table III shows the exposure time, water temperature and salinity observed during the test period.

The strength of twines was tested at periodic intervals.

Results

Fig 1 shows the course of rotting of twines treated in 1–5% tannin concentrations of different tanning materials belonging to the three groups of tannin.

The data on the percentage impregnation of the preservative in 1–5% tannin concentrations are presented in Table IV.

Discussion

It is evident from the impregnation data that with increase in concentration of tannin bath the treated materials show increase in the values of impregnation. It is to be mentioned that among the tanning materials studied, the impregnation values are comparatively low in the case of *'Panachikka'* and *'Pulinkuru'*. The effective days at 50% strength level was determined from Figs 1 to 10 for the various treatments and the effectiveness was calculated by the method suggested by Nayar *et al* (1962 *loc cit*) Fig. 11 depicts the relation between the effectiveness and concentration of bath of the various samples studied. It is evident from this graph that the increase in effectiveness with respect to concentration of dye bath is not linear, there is an optimum level to get the maximum effectiveness and thereafter the effect of the different preservatives seems to be more or less in the same level as that of optimum concentration. Out of the samples studied, pyrogallol tannin was inferior to catechol and mixed tannins in the unfixed state.

The data were statistically analysed to obtain the optimum concentration of the different tanning materials. The average breaking strength ($\overline{X}$), variance (S^2) and the co-efficient of variation (C.V.) at different levels of concentrations of

Table IV Percentage impregnation of cotton twines treated in 1–5% tannin concentrations

Material	% impregnation of treated material in concentration of tannin : 1%	2%	3%	4%	5%
Kadukka	5.39	5.09	7.44	10.20	12.99
Kalasam	3.50	3.72	4.64	6.76	6.78
Terminalia crenulate	4.37	5.58	9.81	9.76	12.22
Kattuvaka pattai	2.07	3.66	6 43	12 94	13.45
Khayis	3.41	5.71	6.74	12.58	13.52
Kumbi	2.97	4.38	5.58	8.55	9.82
Thumma chekka	5.29	9.68	7.99	6.20	9.38
Panachikka	0.49	1.17	2.23	4.43	6.54
Pulinkuru	0.79	0.96	2.37	3.64	5.66
Gedari chekka	4.45	4.95	8.19	9.71	13.32

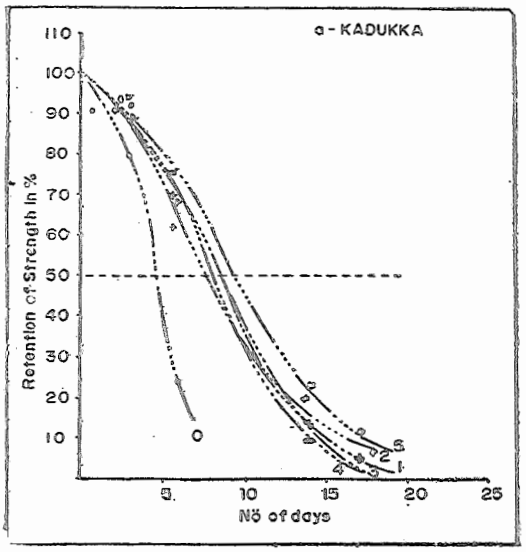

Fig 1. Course of rotting of twines treated in *Kadukka.*

0: Untreated.
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

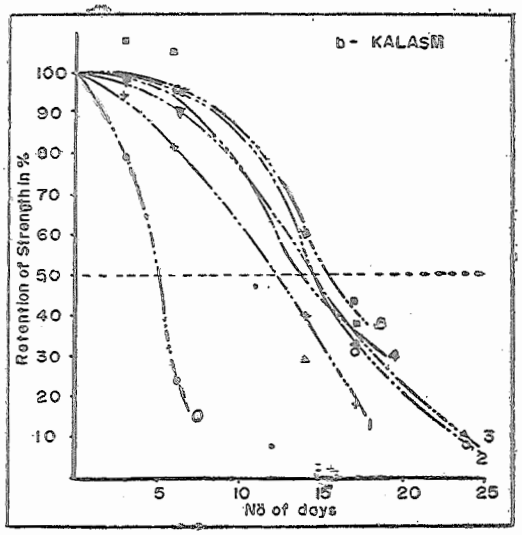

Fig 2. *Kalasam*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

pyrogallol, catechol and mixed tannins were calculated for the preservative effect and the same is presented in Table V.

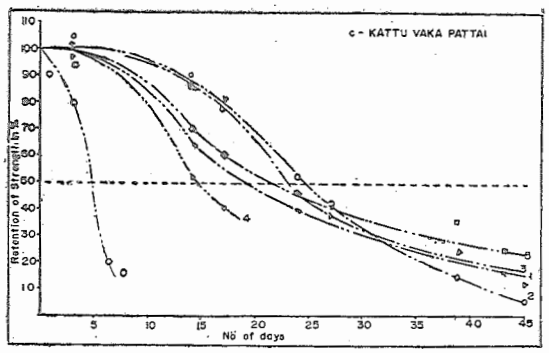

Fig 3. *Kattu vaka pattai*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

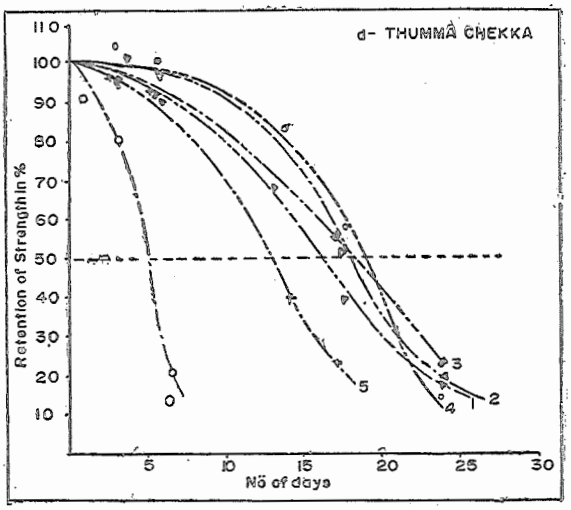

Fig 4. *Thumma chekka*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

The average breaking strength was taken as a measure of effectiveness and the co-efficient of variation as a measure of consistency.

It is evident from the table that in case of *'Kadukka'*, the optimum concentration is 1%, while all the catechol tannins studied and two of the mixed tannins come under 2% concentration level. The optimum concentration of *'Pulinkuru'* is

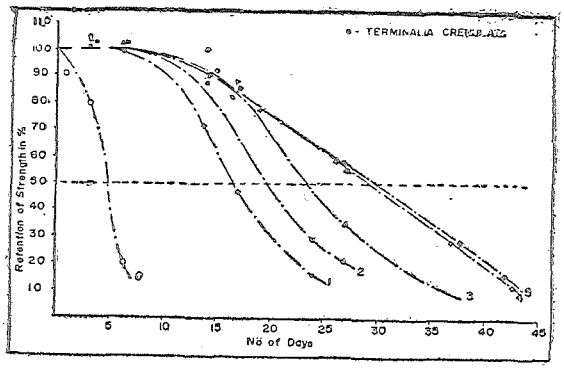

Fig 5: *Terminalia crenulata*

0: Untreated.
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

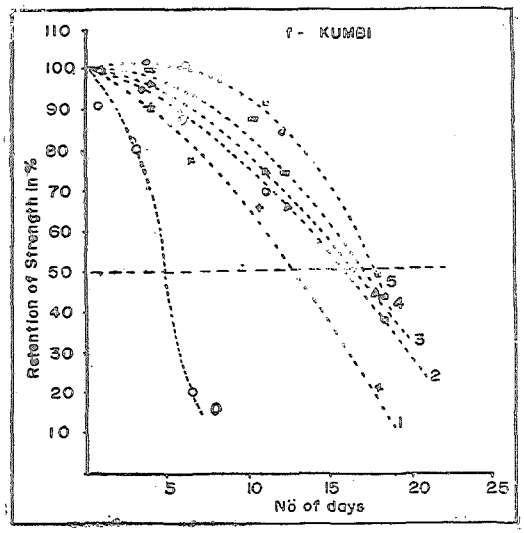

Fig 6. *Kumbi*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

3%. It is also seen that the efficiency of preservation is more in catechol and mixed tannins compared to pyrogallol type. It is to be mentioned that *'Kadukka'* in higher concentration did not show any enhanced effectiveness. This may perhaps be due to the higher solubility of pyrogallol type of tannin over the other two groups. However, the behaviour of the three groups of tannin by fixation will be dealt

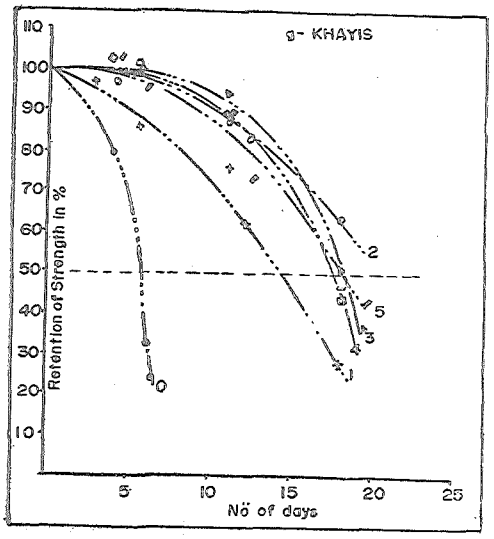

Fig 7. *Khayis*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

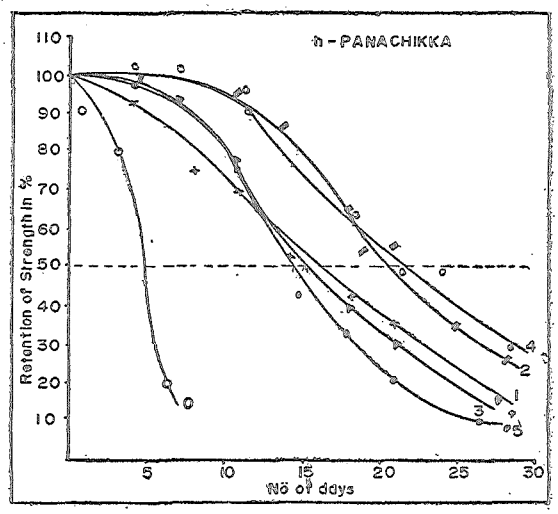

Fig 8. *Panachikka*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

in detail in the next series. The proportion of tanning material to water to get the optimum concentration was worked out and presented in Table VI.

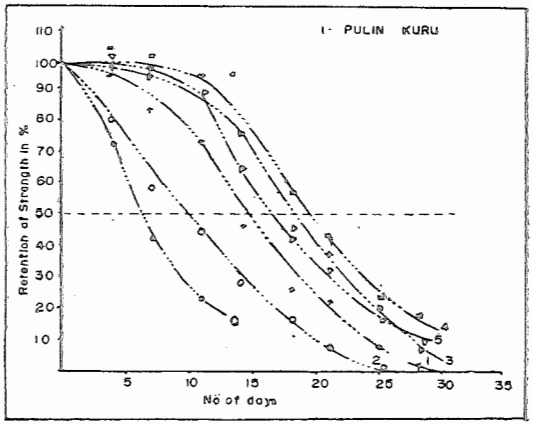

Fig 9. *Pulinkuru*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

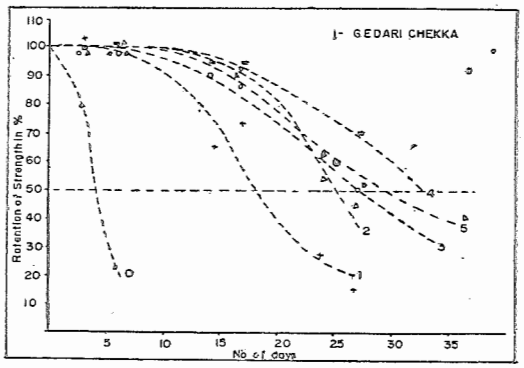

Fig 10. *Gedari chekka*

0: Untreated
1: Treated in 1% tannin
2: ,, 2% ,,
3: ,, 3% ,,
4: ,, 4% ,,
5: ,, 5% ,,

The optimum concentration to produce the maximum effectiveness when compared with the actual concentration used by fishermen (Table 1) shows that the concentration of tannin used by fishermen is far below the optimum in many cases. Among local fishermen as well as fishing industrialists, the popular method of preservation is still tanning without fixation. In such cases, if the optimum concentrated dye bath is used for preserving nets, it will not only

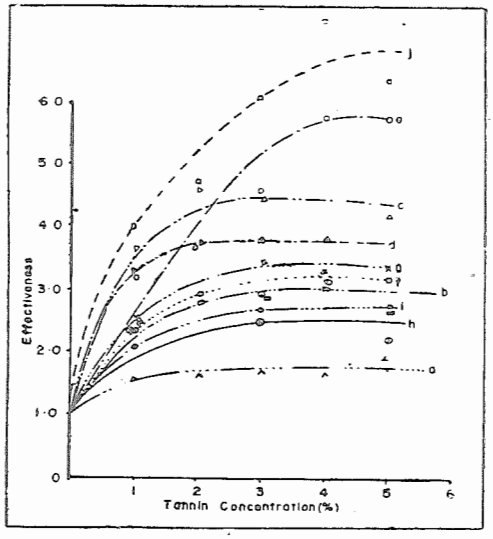

Fig 11. Relation between tannin concentration and effectiveness.

Kadnkka, a.
Kalasam, b.
Kattuvaka pattdi, c.
Thumma chekka, d.
Terminalia crenulate, e.
Kumbi, f.
Khayis, g.
Panachikka, h.
Pulinkuru, i.
Gedari chekka, j.

effect the full utilisation of the preservative more economically, but also avoid re-treatment frequently. The present studies also bring to light the fact that if the concentration of tannin bath is more than the optimum, it will not bring any added benefits.

SUMMARY

A survey of the methods of preservation of cotton nets used by the fishermen in India was conducted and information regarding the type of material, preparation of dyeing bath etc collected. Samples of preservatives were procured and extraction, estimation and analysis of the functional groups of tannin were carried out. The optimum concentration of tannin to get the maximum effectiveness was assessed and it was found that the majority of the material comes under 2%

Table V Statistical analysis on the concentration of tannin and the effectiveness of the treatments

A. Pyrogallol:

Group and source of tannin	Level of concentration %	n	Average ($\bar{X}$)	Variance (S^2)	Co-efficient of variation (C.V.) %
(1)	(2)	(3)	(4)	(5)	(6)
A. Pyrogallol					
1. *Kadukka*	0	5	40.64	2142.15	113.90
	1	,,	55.10	1582.57	72.19
	2	,,	54.10	1718.37	76.61
	3	,,	55.36	1921.24	79.16
	4	,,	57.36	2263.84	82.94
	5	,,	59.24	1624.88	68.05
B. Catechol:					
1. *Kalasam*	0	,,	40.64	2142.15	113.90
	1	,,	67.06	1270.24	53.14
	2	,,	77.60	956.18	39.85
	3	,,	70.24	1291.86	51.19
	4	,,	80.80	723.20	33.29
	5	,,	74.86	912.05	40.33
2. *Kattuvaka pattai*	0	,,	40.64	2142.15	113.90
	1	,,	83.80	564.07	28.34
	2	,,	94.40	49.92	7.49
	3	,,	96.20	27.57	5.46
	4	,,	95.20	43.20	6.91
	5	,,	97.30	109.80	10.77
3. *Thummachekka*	0	,,	40.64	1713.72	101.90
	1	,,	80.74	608.69	30.56
	2	,,	88.50	443.00	23.79
	3	,,	82.80	330.45	21.96
	4	,,	87.40	363.43	21.81
	5	,,	71.00	1265.08	50.09
4. *Terminalia crenulata*	0	,,	40.64	2142.15	113.90
	1	,,	83.80	564.07	28.34
	2	,,	94.40	49.92	7.48
	3	,,	96.20	27.57	5.46
	4	,,	95.20	43.20	6.91
	5	,,	97.30	109.80	10.77
5. *Kumbi*	0	6	35.40	1976.74	125.60
	1	,,	68.30	786.74	41.07
	2	,,	77.73	542.93	29.97
	3	,,	77.60	423.39	26.52
	4	,,	84.62	409.76	26.68
	5	,,	87.92	371.49	21.93

(Contd.....)

(1)	(2)	(3)	(4)	(5)	(6)
6. *Khayis*	0	,,	35.40	1760.26	118.50
	1	,,	74.70	713 53	35.76
	2	,,	88.15	188.13	15.56
	3	,,	88.72	542.53	26.25
	4	,,	85.55	520.43	26.67
	5	,,	86.10	366.69	22.24
C. Mixed:					
1. *Panachikka*	0	,,	41.62	1535.79	92.02
	1	,,	71.50	601.89	34.32
	2	,,	88.25	345.78	21.07
	3	,,	76.63	604.88	32.09
	4	,,	81.60	433.49	25.52
	5	,,	73.73	869.43	39.98
2. *Pulinkuru*	0	,,	41.60	1538.45	94.26
	1	,,	55.70	984.73	56.33
	2	,,	72.65	883.60	40.92
	3	,,	82.33	417.15	25.38
	4	,,	87.90	321.82	20.41
	5	,,	82.75	1371.94	44.75
3. *Gedarichekka*	0	5	40.64	2142.15	113.90
	1	,,	87.60	300.80	19.80
	2	,,	97.40	6.30	2.58
	3	,,	90.56	247.07	17.36
	4	,,	97.80	4.83	2.25
	5	,,	93.90	22.80	5.08

Table VI Proportion of tanning material to water to get optimum concentration

Material	Optimum Concentration (%)	Tannin content of raw material (%)	Material required for optimum concentration (g/100 ml)
Kadukka	1	41.5	2.41
Kalasam	2	10.2	19.65
Kattuvaka pattai	,,	6.1	32.80
Thumma chekka	,,	15.8	12.70
Terminalia crenulata	,,	16.3	12.30
Kumbi	,,	15.3	13.10
Khayis	,,	8.0	25.00
Panachikka	,,	10.2	19.60
Pulinkuru	3	15.6	19.25
Gedari chekka	2	18.2	11.00

concentration in the unfixed state. The proportion of tanning material to water to get the optimum concentration of tannin bath was worked out, compared with which the strength of solution used by local fishermen was found to be far low. The use of optimum concentrated tannin bath is suggested to derive the full benefits of preservation.

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