STUDIES ON MANGROVE BARK TANNINS

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ABSTRACT

Of the 10 M m^2 of raw hides produced annually in Bangladesh only a fifth is tanned by 175 odd tanneries, using imported tanning materials. Vegetable tannins can be extracted from roughly 10,000 tons of mangrove barks available annually at the felling coupes in the Sundarbans. Amelioration of the properties of these tannins is, however, a precondition to their use as tanning materials.

Tannins were extracted by various methods from goran (*Ceriops decandra*), kankra (*Brugiera gymnorrhiza*) and passur (*Xylocarpus molluccensis*) barks collected from the Sundarbans. The percentages of tannins obtained were 24, 21 and 17 respectively. A method was developed for overall purification and improvement of colour and quality of tannin. Chemical analysis indicates that the tannin is of catechol group and quantitative analysis of the extractives shows that the production of mangrove tannins would be an economically viable proposition. Tanning experiments with goat skin show that light coloured and fine-grained uppers and soles can be made with the purified tannins.

সারসংক্ষেপ

বাংলাদেশে কমবেশী পৌনে দু'শ ট্যানারী আমদানিকৃত রাসায়নিক দ্রব্য দিয়ে প্রতিবছর স্থানীয়ভাবে উৎপাদিত ১ কোটি বর্গমিটার কাঁচা চামড়ার মাত্র এক পঞ্চমাংশ পাকা করে থাকে। প্রতি বছর সুন্দরবন থেকে প্রাপ্ত প্রায় ১০ হাজার টন ম্যানগ্রোভ গাছের বাকল থেকে ভেষজ ট্যানিন আহরণ করা যেতে পারে। তবে চামড়া পাকা করার ক্ষেত্রে এই ভেষজ ট্যানিন ব্যবহারের পূর্বে এর গুণগত মানোন্নয়ন করা অপরিহার্য।

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সুন্দরবন থেকে সংগৃহীত গরান, কাঁকড়া এবং পশুর গাছের বাকল থেকে বিভিন্ন পদ্ধতিতে ট্যানিন নিষ্কাশন করা হয়। এগুলো থেকে যথাক্রমে শতকরা ২৪, ২১ এবং ১৭ ভাগ ট্যানিন পাওয়া গিয়েছে। ট্যানিনের সার্বিক বিশুদ্ধিকরণ এবং এর রঙের গুণগত মান উন্নয়নের একটি বিশেষ পদ্ধতি নির্ণয় করা হয়েছে। ট্যানিনের রাসায়নিক বিশ্লেষণে প্রতীয়মান হয় যে এই ট্যানিন ক্যাটিকল গোত্রভুক্ত।

উৎপাদন পরিমাণ থেকে অনুমিত হয় যে ম্যানগ্রোভ প্রজাতির গাছের বাকল থেকে ট্যানিন তৈরী আর্থিকভাবে লাভজনক হবে। এই শোধিত ট্যানিন প্রয়োগে ছাগলের চামড়া দিয়ে হাল্কা রঙের উন্নতমানের জুতো তৈরীর চামড়া প্রস্তুত করা যায়।

INTRODUCTION

There are more than 175 tanneries in Bangladesh. Some of them are medium sized but the majority are of small and cottage industry scale. These tanneries are mostly located in Dhaka and Chittagong zones, the lions share going to the former. All these tanneries use imported tanning materials for tanning their hides.

Leather is the third highest foreign exchange earner in the country. Over 10 M m^2 of raw hides are produced annually in the country. Of these about 1.5 M m^2 of hides are needed for domestic consumption, and the rest is exported. During 1982–83, 1983–84 and 1984–85, 19,919, 20,710 and 17,365 metric tons of leather were exported, earning Tk 1,581, Tk 2,198 and Tk 1,921 million respectively (Rabbani 1985).

Bark in many countries is considered to be a waste material or sometimes a nuisance to the wood using industries. Now-a-days bark is used for extraction of acetic acid, methanol, tannin, polyphenols and other chemicals in the developed countries. Mangrove bark is known to be rich in tannin, which is endowed with the property of converting hide into leather. Bangladesh has a large mangrove forest area in the coastal belt of the Sundarbans. Of the various mangrove species gewa (*Excoecaria agallocha*) is used for newsprint; sundri (*Heritiera fomes*) for hardboard and transmission poles; keora (*Sonneratia apetala*), goran (*Ceriops decandra*), passur (*Xylocarpus molluccensis*) etc. are used as fire wood or construction material.

It is estimated that about 3,500 tons of bark of each of the major industrial species can be collected from the Sundarbans for utilization on perpetual basis (Latif 1964). They are potential source of extractable tannin. The felled boles are generally brought to the mill site by rafting, causing loss of tannin by leaching during transportation. It has been seen that the bark collected from wood transported to the mill site by rafting process loses half the tannin content during the process (Latif and Wallin 1964). Collection and transportation of bark from the felling coupes in the forests, and keeping it clean and uncontaminated for extraction

of tannin are problems of high magnitude. Any project-plan in this regard must take into consideration the economic feasibility of the project at the very outset.

Bangladesh Forest Industries Development Corporation established a tannin extraction plant at Khulna with mangrove bark as the vegetable raw material. Tannin produced by the plant could not be marketed due to extremely low quality of the product. Chemical analysis done at the Bangladesh Forest Research Institute showed the product to contain less than 10% tannin. Amelioration of the properties of the tannin produced from mangrove species is, thus, of paramount importance.

MATERIALS AND METHODS

Several mangrove species in the Sundarbans yield tannin from their barks. Gewa is known to have 11.5% tannin (Latif and Wallin 1964). Goran, kankra and passur barks have high percentages of tannins. Many other species have varying percentages of tannins. Not all the species are harvested in large quantities. It would be impracticable to collect barks from standing trees. A large quantity of sundri is exploited from the Sundarbans every year, but the bark is not well-endowed with tannin. For experimentation on the amelioration of the properties of tannin, goran, kanra and passur barks were collected from the Sundarbans. All these large tree species grow gregariously in extensive stands in the Sundarbans. Barks constitute about 10% of the bole by weight.

Barks collected from the forest were cut approximately to 3 x 1 cm size and air dried. Large extraneous matters were separated by handpicking. The chips were quickly washed to remove adhering dust with clear water, taking care not to allow any leaching of tannin. The chips were then again air dried.

The bark was then hand cut to approximately 4 mm square size for extraction of tannin. Some of the barks were ground in a small laboratory Wiley mill. Fine dust and dirt were removed by screening in a 20 mesh sieve. Tannin was extracted from the processed bark either soaking in cold water for 24 hr or for 1/2, 1 or 2 hr in hot water. Water at 80–95°C was used in various experiments. The bark/water ratio varied from 1 : 4 to 1 : 8. In cases of hand-cut chips a second extraction was effected with equal or reduced time. Extracted tannin was analysed according to the methods of American Leather Chemists' Association.

Filtration preceded by activated charcoal treatment was used in one experiment for improving the colour of the tannin. Some bleaching experiments were also conducted for this purpose.

Tanning experiments were conducted separately with goran, kankra and passur barks. Most of the tanning experiments were done following the process recommended by U. S. Department of Agriculture (Frey *et al* 1954). Some variations were followed in some cases (Hobson 1981). These tanning experiments were conducted with small goat skins following the usual processes of stretching, scraping, salting, storing, soaking and fleshing the hides. Dehairing by liming and subsequent deliming preceded the tanning experiments. Minor

changes in rinsing, drying, softening and finishing processes were effected to suit local conditions. Various equipment needed were in most cases improvised. Neat's foot oil recommended for softening and finishing of leather (Hobson 1981) was replaced by locally available oils and fats.

The tanning solution was prepared by pouring boiling water on finely ground bark. The mixture was kept in a plastic jar. The infusion was stirred occasionally and kept covered. The bark was then strained off through a coarse sack. Vinegar was added and stirred. The sides, from the deliming, were placed hanging on horizontal sticks. Care was taken to allow as few folds and wrinkles as possible. The sides were moved from time to time to get an even colour. A quarter of the soaking solution was changed with fresh infusion every five days. After 20 days a generous portion of ground bark was added to the tanning jar and the hide was practically buried in them. After a week of soaking, tests showed that the tannin has pervaded throughout the hide.

Vegetable tannin is not recommended for tanning fur. It spoils the fur and gives it a leathery brown colour (Hobson 1981). For tanning fur, a combination tannage may be followed. After following the usual steps of stretching, cleaning, salting and fleshing, the furskin was stretched out flesh side up. A thick coating of powdered goran bark in a paste form with water was sprayed over the hide and kept for a week. Examinations were conducted by slitting a small end portion of the hide for tannage (Anon 1946). The process was repeated thrice with fresh bark paste. At the end of three weeks the fur was properly tanned.

RESULTS AND DISCUSSION

Several modifications of two different methods were employed for extraction of tannin from barks. Attempts were made to extract tannins by soaking the finely chipped barks in cold water for 24 hr. The yield of tannin in cold soaking process was not as good as in the hot percolation process. A double extraction yielded somewhat better results (Table 1), albeit with increased nontannins. A double percolation for two hours each at 95°C yielded the best result. Two hours hot percolation and one hour double percolation gave similar results. Half an hour's hot percolation of ground bark gave comparable results with those of two hour percolation of chipped bark. Goran, in almost all cases, gave higher yield. All the three species under investigation gave better yield than gewa (20.2%) and chhota bhanda (*Loranthus globosus*) (21.6%) (Latif 1964; Hoque 1979).

The highest percentages of extractives obtained by double percolation for 2 hr each contain higher percentages of nontannins. The same phenomenon occurs with ground bark. In both the cases filtration becomes difficult, time consuming and expensive. These practices, therefore, are not recommended. Results obtained by the next best treatment have, thus, been mentioned as the total extractives.

Two hours percolation in hot water yielded somewhat better result than one hour treatment. A double extraction again

Table 1. Tannin content of mangrove barks

Process of extraction	Treating conditions	Species	Total extractives %
1. Cold soaking	24 hr at room temperature	Goran	10.45
		Kankra	9.97
		Passur	9.02
2. Hot percolation	1-hr at 95°C	Goran	19.42
		Kankra	16.22
		Passur	13.11
3. Double percolation	(1+1) hr at 95°C	Goran	29.18
		Kankra	21.52
		Passur	18.11
4. Hot percolation	2-hr at 95°C	Goran	23.98
		Kankra	21.03
		Passur	16.73
5. Double percolation	(2+2) hr at 95°C	Goran	27.22
		Kankra	28.95
		Passur	27.45
6. Hot percolation (Ground bark)	30 minutes at 95°C	Goran	23.19
		Kankra	21.26
		Passur	20.56

Table 2. Chemical analysis of mangrove bark tannins

Species	Total solids %	Solubles %	Insolubles %	Tannins %	Non tannins %	Ratio of tannins to Non-tannins
Goran	23.98	19.68	4.30	16.66	3.02	5.51
Kankra	21.08	20.07	0.96	7.83	12.24	0.63
Passur	16.73	16.25	0.48	9.16	7.09	1.29

yielded better result than a single extraction. Double extraction (2 + 2 hours) as mentioned earlier, gave the highest extractive (Table 1). A larger portion of other soluble substances also result (White 1958). Percentages of tannin obtained from mangrove species compared favourably with those of many Philippine species, the latter varying between 11 and 17% (Mitchell 1923).

Tannins, which are in effect tannic acid, are extracted from the barks of various wood species such as mimosa, sumac, wattle and mangrove. Vegetable tannins protect the molecular form of the collagen fibre by packing the amorphous regions of fibrillar structure. The crystalline parts of leather are ptotected by orderly arrangement of the molecular chain in these regions and as such do not require tanning against penetration of water and attack by bacteria (Haslam 1966). Initially the hydroxyl groups present in the vegetable tannins combine with active sites in the exposed amorphous regions of the collagen structure.

Tannin is divided into hydrolyzable and condensed tannin classes. The hydrolyzable tannins are readily hydrolyzed by acids and enzymes, and are subdivided into gallotannins and elagitannins. The condensed tannins, in contrast, do not readily break down on acid or enzymic hydrolysis; instead they polymerize to phlobatannins (Haslam 1966; White 1958). Depending on the action of heat, the tannins are roughly classified as catechol and pyrogallol tannins. Natural tannins when heated to 200°C yield one or the other or both. Three different tests indicated the absence of pyrogallol. On heating, catechol was obtained from the tannin. The mangrove bark tannins, thus seem to belong to the catechol group.

Goran was found to yield high tannin/non-tannin ratio, followed by passur. Kankra was poor in this respect. The result of Chemical analysis of the mangrove bark is given in Table 2.

Tannins extracted from the mangrove barks by the defunct Mangrove Tannin Plant at Khulna yielded only about 9% soluble matter, the bulk of the insoluble matter being mud and other extraneous matter. These presumably originated either from the contaminated raw materials or from the untreated river water used while extracting tannin. It has been found during the experiment that precautionary measures to avoid mud, dirt and other extraneous matter were helpful. Similarly, clear solution was obtained by using pure water during extraction. A rapid wash in cold water of the bark materials before extraction removed most of the mud and dirt. These measures gave clear tannins from mangrove barks. Experiments conducted to clarify the tannin solution by using activated charcoal before filtration improved the colour. Caustic-hypochlorite bleaching experiments also gave light coloured tannins. However, filtration with activated charcoal and bleaching operations are expensive and redundant for normal tanning of hides. Soaking of the sides in tannin extracts is time consuming but gives the best result. The colour obtained was bright and the touch was plump, full, soft and leathery. The leather was pliable. The moisture content was found to be 18.22% indicating that tannage was of good quality. Particular precautions

were taken during tanning and drying to keep the sides and leather fold-and wrinkle free. For softening the leather, staking was resorted to. The hide was worked back and forth over the edge of a hard, smooth surface until it was supple and soft. Unstaked leather was always found to be stiff and brittle. Staking must be done while the leather is still damp. If the hide dries, it should be dampened before staking. Cod liver oil used for softening and preserving the leather gave an undesirable dark colour to the leather. Castor oil may be used for cod liver oil to minimise cost.

A coating of warm dubbin was used on the hair side for finishing the tanned leather. The dubbin was prepared by mixing equal proportions of mutton tallow and castor oil. After cooling, the dubbin was applied with a paint brush. The process was repeated after the leather dried. Best result was obtained when the leather was rubbed on both sides with a zero-zero sand paper and coated for a third time with the dubbin and wiped with a piece of soft cloth. For water proofing of the leather, an even coat of wax was given. The wax was made by melting together equal parts of bees wax and mutton tallow. The cold and hardened wax was converted to a paste with castor oil and applied.

CONCLUSIONS

1. Commercially utilizable quantities of tannin can be extracted from the barks of the three species investigated, i. e., goran, kankra and passur. Goran gives the highest yield. Economic viability of any project to exrtact tannin from mangrove barks must be studied in depth.
2. Bark raw materials collected must be clean, and water used in the processing must be purified before use.
3. Excellent grades of leather are produced from the mangrove bark tannins, goran bark yielding the best colour and texture. The tanning process is, however, longer than the process involved in chrome tanning.

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