STUDIES ON CHIR-PINE (*PINUS ROXBURGHII*) BARK TANNINS AND THEIR LEATHERING QUALITIES

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Summary. *Studies have been undertaken to investigate the suitability of chir-pine* (Pinus roxburghii) *bark tannins as an indigenous material for commercial production of vegetable tanned light and heavy-leather.*

Solids were prepared by extracting chir-pine bark without any treatment as well as with 0.5%, 1.0%, *and* 2.0% *sulphitation and then drying the extract under reduced pressure.*

Pickled and delimed identical pieces of sheep and goat skins were tanned with pine and imported mimosa solids for comparative studies of light leather producing qualities under similar tanning conditions. For production of heavy-leather, depickled buffalo hide pieces were tanned.

Comparative studies of shrinkage temperature, tensile strength and elongation of resultant leather indicate that chir-pine solids produce somewhat better leather as compared to that obtained by tanning with mimosa solids.

It is concluded that chir-pine bark solids can be successfully utilized for commercial production of light as well as heavy leather of desired qualities.

Since supply of vegetable tannins from indigenous source (*Acacia arabica* bark) falls short of meeting daily requirements, mimosa solids are being, by and large, imported by our tanneries (12).

Uptodate survey of indigenous sources of vegetable tannins, conducted in the Chemistry Branch of this Institute, indicates possibility of commercial utilization of chir-pine bark for the purpose.

Although barks of other species of pines are reported to be used for extraction of tannins in different parts of the world (22, 7), chir-pine bark, inspite of having 13.0% tannins (11), has not been exploited on a commercial scale for the purpose. The tannin contents of pine barks reported in literature range from 9 to 16% (5, 21, 22, 23).

Besides fairly high tannin content of chir-pine bark, the other good reason from these investigations was the availability of material in the country. In Pakistan the tree generally

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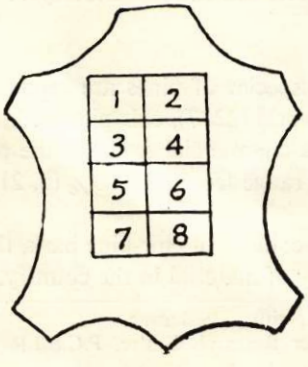
grows between 1,000 and 1,800 m elevation, and is being regularly harvested for timber. The annual yield of chir-pine timber from Hazara, Rawalpindi ,Mirpur and Muzaffarabad Forest Circles is estimated at 43,697 m^3, (3, 4, 6, 9, 10, 13, 14, 17, 20). Generally, the available volume of bark from chir-pine trees having diameter breast height 61 cm,. is about 20% of the total volume (8). Annual supply of chir-pine bark would, therefore, be about 8,000 m^3. The density of chir-pine bark was estimated as 0.40583g/cm^3 by mercury displacement method, using Breuil Apparatus, in Timber Physics Laboratory of Pakistan Forest Institute. Thus, the annual availability of chir-pine bark would be about 3,546 tons.

Material and Method. Bark from approximately 35 years old chir-pine tree was collected from Hazara Forest Circle, dried in shade and then transported to Peshawar in gunny bags. It was powdered in Willey Mill so that about 70% of it passed through 30 mesh sieve.

Preparation of solids. A portion of the powdered chir-pine bark was extracted with water (bark/water ratio 1:5), on water bath (temperature inside extraction beakers 94-96°C). Extraction was also, likewise, made by adding 0.5%, 1.0% and 2.0% of sodium metabisulphite, calculated on bark weight basis, and extraction continued for 30, 60 and 90 minute durations. On completion of extraction, the extract, in each case, was collected by filtration through muslin cloth. Solids were recovered by drying the extracts under reduced pressure (400 mm Hg $\pm$ 10 mm) on water bath.

Estimation of tannin content of solids. Tannin content of solids was determined by dissovling calculated quantities of solids in water ot give 3.75 to 4.25 g tannins per litre. Analysis was made following Official methods (Shake Method) of the Society of Leather Trades' Chemists, described in Chemists' Year Book (1). The method was slightly modified to the extent that instead of using filter candles, solutions were centrifuged at about 1,500 r.p.m. until optically clear. Colour readings were determined by Lovibond Tintometer, using 1 cm cell.

Tanning of pelts. Tanning experiments with solids were performed at the Fuel and Leather Research Centre of P.C.S.I.R., Karachi. For tanning pieces of pickled (pH 3.0) and delimed (pH 8.0) pelts were cut along the back bone as shown:



For the production of light leather (sheep and goat-skins), solids were given in such a quantity so as to give 20.0% pure tannins on pelt weight. In case of heavy leather (buffalo hide), the quantity of solids was increased to 37.0% pure tannins on pelt weight. Tanning was performed in small shakers as well as in small rotary drums (Purpex). Fat-liquoring was done with sulphated cod-oil (pH 6.0) at the rate of 4.0% on pelt weight, after keeping tanned pieces for two days in float for better fixation of tannins.

Modification of Tanning Process. To see if leather of lighter shade could be obtained, the tanning procedure was slightly modified in one case by treating the pickled sheep pelt pieces for 30 minutes with 1.0% solution of sodium bisulphite before tanning with (a) 1.0% sulphited pine solids and (b) mimosa solids, without giving any float.

Solvent Tannage. To avoid excessive deposition on the grain side in case of tanning with unsulphited chir-pine solids, solvent tannage was tried by dehydrating pickled sheep pelt piece with alcohol and then running it in alcoholic solution of unsulphited chir-pine solids.

Heavy Leather Tannage. For tanning heavy leather, pieces of pickled buffalo pelt were treated for 30 minutes with 1.5% solution of 'Hypo', bringing their pH to 5.0, and then tanned with 0.5% sulphited chir-pine solids.

Physical Tests of Leather. Shrinkage temperature of leather strips (1.3 × 7.6 cm) was measured, before fat-liquoring, in water at pH 3.0 to 3.5 (15).

Estimations of Tensile Strength and Elongation were performed in Timber Physics Laboratories of the Pakistan Forest Institute. Strips (3.1 × 15.2 cm) were cut from tanned leather and then shaped like dumb bells with narrow portion of the specimen being 1.3 cm wide (15). Elongation was measured simultaneously with the determinations of tensile strength by measuring the distance between the clamps holding the test piece (15). The values were worked out as percent elongation on application of load.

Solids obtained with 1.0% sulphitation of chir-pine bark, during extraction, had high (47.0 to 48.6%) tannins. Maximum Tans/Non-tans ratio, depicting astringency, was found in case of solids prepared through 90 minutes extraction without sulphitation. The next higher values (1.28 and 1.21) were obtained in case of solids obtained with 1.0% sulphitation for 60 and 90 minutes durations, respectively.

Colour readings of solutions, taken on Lovibond Tintometer, are presented in Table 2.

Solutions prepared with sulphited pine solids had moderate red and blue colour units. Leather obtained by tanning with 1.0% sulphited solids was, overall, lighter in shade and is likely to be acceptable in commerce.

Results and Discussion. Analytical data of solids, obtained by extraction of chir-pine bark for different durations with and without sulphitation, is presented in Table 1.

Table 1

Tannin Content of Oven-dry Solids

Sulphiting (%)	Extraction (Mts)	Total solubles (%)	Non-tans (%)	Tannins (%)	Tans/ Non-tans (ratio)	Purity of tannins (%)
0.0	30	87.1	52.9	34.2	0.65	39.3
	60	84 4	46.1	38.3	0.83	45.1
	90	80.1	27.4	52.7	1.92	65.7
0.5	30	73.8	49.5	24.3	0.49	32.9
	60	75.2	43.2	32.0	0.74	42.5
	90	83.6	38.4	45.2	0.85	54.0
1.0	60	86.4	37.8	48.6	1.28	56.2
	90	85.8	38 8	47.0	1.21	54.6
2.0	30	89.1	52.3	36.8	0.70	41.3
	60	89.2	49.5	39.7	0.80	44.5
	90	68 9	41.7	27.2	0.65	39.5

Table 2

Colour Readings of Tannin Solutions

Sulphiting (%)	Duration of extraction (Mts)	Colour readings in Lovibond Tintometer Units		
		Red	Yellow	Blue
0.0	30	27.2	6.7	5.3
	60	26.9	7.7	4.4
	90	22.5	4.9	3.1
0.5	30	29.9	4.9	3.8
	60	26.9	8.1	4.8
	90	30.2	7.9	6.1
1.0	60	21.7	6.6	2.0
	90	19.8	3.1	0.9
2.0	30	28.4	9.4	4.0
	60	29.9	9.9	3.4
	90	27.5	9.2	4.3

Tanning Trials. Trials on tanning of pickled skin and hide pieces were carried out with pine and mimosa solids. Trials 1-3 and 4 and 8 were made in shaker and drum, respectively. Trials 6 and 7 were made on delimed pelts, in drum. Details are summarised in Table 3, below:

Table 3

Tanning Experiments

Tanning; Trial No.	Tanning material	pH of float at start	pH of float at end	Progress of tanning
1	2	3	4	5
	(A) Tanning of pickled sheep pelt			
1.	(*a*) Unsulphited pine solids given in one instalment	2.8	—	Almost half penetration in 6 hrs. No further progress in next 18 hrs. Excessive deposition on grain side. (Expt. abandoned)
	(*b*) Mimosa solids given in one instalment	3.5	—	Almost half penetration in 6 hrs. Almost 3/4 on leaving overnight.
2.	(*a*) Unsulphited pine solids given in one instalment	3.5	3.5	A little more than half penetration in 4 hrs. pH of float which shifted to 4.1 was readjusted to 3.5 Almost 2/3 penetration in further 18 hours. Full penetration on leaving overnight, in float.
	(*b*) Mimosa solids given in one instalment	3.5	3.5	A bit more than half penetration in 4 hrs. Full penetration in further 18 hrs.
3.	(*a*) 1.0% sulphited pine solids given in one instalment	3.5	3.5	Almost 2/3 penetration in 2 hrs. Slight progress in further 2 hrs. No progress in next 6 hrs. pH of float which had shifted to 4.2 was re-adjusted to 3.5 Full penetration in next 6 hrs.
	(*b*) Mimosa solids given in one instalment	3.5	3.5	A bit more than 2/3 penetration in 4 hrs. Full penetration on leaving overnight in float.

1	2	3	4	5
4.	Unsulphited pine solids given in two equal instalments	4.0	4.4	With half of the required quantity of solids about 1/3 penetration in 60 mts. By giving rest of the solids about 2/3 penetration in further 2 hrs. Full penetration on leaving overnight in float.
8.	2.0% sulphited pine solids given in 3 equal instalments at 30 mts. intervals.	4.0	4.2	About 1/3 penetration in 60 mts. Full penetration on leaving overnight in float.
	(B) Tanning of delimed sheep pelt			
6.	1.0% sulphited pine solids given in 2 equal instalments.	4.8	5.0	Almost 2/3 penetration in 30 mts. On giving second instalment full penetration observed in next 60 mts. Fullness and grain improved on leaving overnight in float.
	Tanning of del med goat pelt			
7.	1.0% sulphited pine solids given in 2 equal instalments	4.8	5.0	Almost 2/3 penetration in 30 mts. After giving second instalment of solids full penetration in next 90 mts. Fullnes and grain improved on leaving overnight in float.

In general, it appeared that the rate of penetration of unsulphited chir-pine tannins was quite low. This might be due to low solubility as well as some deposition of these tannins on the grain side. Since on sulphitation the solubility of tannins increases (11, 19), the rate of penetration also advanced.

On tanning sheep pelt pieces, by modified procedure, with mimosa and 1.0% sulphited chir-pine solids, full penetration of chir-pine tannins was achieved by leaving the pelt overnight in drum; whereas in case of mimosa tanning full penetration took comparatively much shorter time. Pre-tanning treatment of sheep pelt with 1.0% solution of sodium bisulphite resulted in leather of much lighter shade on tanning with 1.0% sulphited chir-pine solids.

By adopting solvent tannage much faster penetration was observed i.e., about two-third penetration in 2 hours. Of course, leaving the piece overnight in liquor gave better

leather. However, the pelts, following tanning, were to be kept immersed in water for 8 to 10 hours to allow partial regaining of normal form. Even after this treatment the leather obtained still remained quite thin.

Buffalo hide pieces, on tanning with 0.5% sulphited chir-pine solids (pH of float 5.5), took five days to acquire almost two-third penetration. At this stage the pH of float had shifted to 5.0. By adjusting the pH to 3.0, full penetration was achieved in subsequent two days. This trial indicated that heavy leather can be produced by tanning buffalo hide, in delimed state, with chir-pine solids. Optimum pH of float lies in the vicinity of 3.0.

Tests on Tanned Leather. Various standard tests were made to evaluate the final qualities of leather as given below:

(*a*) Shrinkage temperatures, estimated for different tanned pieces, are given in Table 4.

Table 4

Shrinkage Temperatures of Tanned Pieces

Tanning Trial No.	Material investigated	Shrinkage temperature (°C)
2	Pickled sheep pelt tanned with:	
	(*a*) Unsulphited chir-pine solids	85.0
	(*b*) Mimosa solids	82.0
3	Pickled sheep pelt tanned with:	
	(*a*) 1.0% sulphited chir-pine solids	87. 0
	(*b*) Mimosa solids	85.0
5	P ckled sheep pelt treated for 30 mts. with 1.0% solution of sodium bisulphite and then tanned with:	
	(*a*) 1.0% sulphited chir-pine solids	87.0
	(*b*) Mimosa solids	81.0
6	Dilimed sheep pelt tanned with: 1.0% sulphited chir-pine solids	87.0
7	Delimed goat pelt tanned with: 1.0% sulphited chir-pine solids	89. 0
10	Pickled sheep pelt dehydrated with alcohol and then tanned in alcoholic solution of unsulphited chir-pine solids.	89.0
Control	Untanned sheep pelt	45.0

Shrinkage temperature of proteins is the point, expressed in temperature units, at which the increasing disruptive tendencies surpass the diminishing cohesive forces (15). Most of the tanning processes increase the shrinkage temperature of collagen. In case of vegetable tannins it increases with an increase in fixed tannins, degree of tannage etc. Thus it gives not only true measure of tanning but also an insight in true linkage mechanism. It is, therefore, overwhelmingly suggested as a criterion for tanning involving crosslinkage of polypeptide chains (16).

Table 4 indicates that shrinkage temperature of chir-pine tanned leathers was higher than that of leather produced by mimosa tanning. These values sugeest that crosslinkage of chir-pine tannins, with collagen of pelts, was a bit better than that of mimosa tannins.

(*b*) Tensile strength and elongation percentage of tanned leather pieces is given in Table 5.

Table 5

Tensile Strength and Percent Elongation

Tanning Trial No.	Material tested	Load (Kg)	Elongation (%)	Tensile strength (Kg/cm^2)
4	Pickled sheep pelt tanned with un-sulphited chir-pine solids	40.82	54.70	207.31
6	Delimed sheep pelt tanned with 1.0% sulphited chir-pine solids	47.62	39.78	325.70
7	Delimed goat pelt tanned with 1.0% sulphited chir-pine solids	53.52	36.55	313.56
8	Pickled sheep pelt tanned with 2.0% sulphited chir-pine solids	37.65	61.45	185.30
Control	Pickled sheep pelt tanned with mimosa solids	45.36	62.62	230.57

Since strength of fibres depends on existance of strong lateral cohesion between macro-molecules, the ruptuer of fiber must involve rupture of transversal cohesive bonds between individual macro-molecules (16). Tensile strength is considered, therefore, a valuable criterion for judging quality of leather (15). For summer shoes the minimum parameter is recommended as 2.5 Kg/cm^2, in case of leather for lined shoes, and higher for unlined shoes (2).

Leather produced by tanning sheep-skin with 1.0% sulphited chir-pine solids had superior tensile strength of 325.70 Kg/cm^2 which surpassed even the value imparted by mimosa tanning.

Elongation percentage of leather is an indication of quality and is direct measure of properties which make it particularly adapted to certain uses. If it is more, probably the leather is weak; if less, the leather might have started hardening and becoming brittle(15).

Elongation of leather, obtained by tanning with 1.0% sulphited chir-pine solids, was 39.8%, while that for leather produced by tanning with unsulphited chir-pine solids was 54.7%. This indicative value also appeared to be favouring tanning with 1.0% sulphited chir-pine solids.

Conclusion. (1) Chir-pine bark solids can be utilized for tanning leather for the production of both light as well as heavy leather.

(2) Delimed pelts took lesser time in achieving full penetration as compared to pickled pelts.

(3) Sulphiting, during extraction, increased the solubility and, consequently, the rate of penetration of chir-pine tannins.

(4) Chir-pine solids, prepared with 1.0% sulphitation, appeared to be best for tanning purposes as they had higher tannin content and astringency as compared to solids prepared with other degrees of sulphitation. Solutions prepared with these solids were also of lighter colour.

(5) Extraction of chir-pine bark at higher temperature (94-96°C) appears to have resulted in extraction of chir-pine resin which is sometimes found sticking to the bark. This also tends to block the passage of tannins to the interior of pelts and help in excessive deposition on the surface.

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