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RHAMNUS PENTAPOMICA AS A NEW SOURCE OF TANNIN

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Abstract. *Rhamnus pentapomica* was obtained from Kohat District for studying its tannin content. The different portions of the tree, i.e. wood, bark and leaves, were examined.

The importance of tannins has increased considerably in the present time, due to their numerous uses in the leather industry, manufacture of ink, preservation of fishing nets, plastic industry and in the manufacture of ion exchange resins. Besides, tannins are widely used in deep oil-well drilling, for control of the viscosity and the water loss of drilling fluids. It has also been reported that the use of tannin in the preparation of tannin-formaldehyde glue for use in plywood industry and for adhesives has proved very successful.[1,2] Although 'Syntans' (synthetic tannins) are extensively used at the present time, they lack certain properties necessary to produce heavy leather, so that the importance of vegetable tanning materials is not seriously affected. (An exception to this is a new and recently developed Syntan, shich has got the required properties, but its cost is high.[3])

There are at least 300 varieties of tannin-bearing plants in the world. In Pakistan, very few plants have so for been used for the extraction of tannin. Goran and the mangrove of Sunderban forests are the chief sources of tannin in East Pakistan,[4] while Babul (*Acacia arabica*) is the main source in West Pakistan.[5] To meet the increased requirements of tannin for local industry, greater quantities of tannin have to be imported. Shortage of quebracho and chestnut in the international market, due to indiscriminate exploitation and blight disease, have caused great difficulties in obtaining the imported vegetable tanning materials.[6] Thus the necessity for examining new tannin-containing species within the country is evident.

Rhamnus pentapomica (local name Sheraoni) is found abundantly in Kohat, Hazara, and Rawalpindi regions of West Pakistan.[7] In the present study, the tannin contents of this plant have been studied.

Materials and Methods

Samples of *Rhamnus pentapomica* were collected from the hill tract of Gumbat, District Kohat. The bark, leaves and wood of the tree were collected separately from four different trees. The samples were dried in shade, cut into small pieces and powdered.

Method of Extraction. A weighed quantity of sample with 4–5 times its weight of water was repeatedly heated on a water-bath. After complete extraction of tannin the combined extract was concentrated and finally dried at low temperature.[6] For classification of tannins found in different parts of the tree, the standard qualitative tests were employed.[8]

Determination of the Percentage of Tannin. The tannis, were determined by the 'shake method' of hide powder.[9] Briefly, a dilute tannin solution, which is adjusted to approximate tannin content, is shaken with lightly chromium-tanned hide powder. Evaporation of the filtrate gives the proportion of nontannin which is present in the original solution. The total solids are measured by direct evaporation of a second portion of tannin solution. The difference between nontannin and total solids gives the amount of tannin present.

TABLE 1. TANNINS PRESENT IN THE LEAVES OF *Rhamnus pentapomica*.

Experiments	Observation	Inference
1. Lead acetate test	Dirty brown ppt	Flavotannin present
2. (i) Formaldehyde test (solution of the material +HCHO+HCl concd)	Brownish ppt	Flavotannin present
(ii) Filtrate from above+iron alum+sodium acetate	Colour changes to bluish pink	Gallotannin present
(iii) Filtrate from (i)+urea; boiled	Bulky white ppt	Gallotannin present
3. Iron alum test	Greenish black ppt	Flavotannin present
4. Bromine-water test	Orange ppt	Flavotannin present
5. Solution+HNO_2+HCl (dil)	No indication	Free gallic acid may be present
6. Solution+HNO_3+HNO_2	Slight ppt	Ellagic acid absent
7. Fehling's test	Positive	Sugar present
8. $FeCl_3$ test.	Greenish black colour	Mixed tannin eprsent

Results and Discussion

Table 1 gives the results relating to leaves of *Rhamnus pentapomica*. Similar results, with slight variation of colour, are given by the extracts of the bark and the wood. In the case of the wood, the presence of gallotannin was detected only by test 2(iii). However, test 2(ii) did not give the desired coloration. The bark extract gave positive results for all the tests. The presence of flavotannin, in the various extracts, was more marked than that of the gallotannin. The latter type of tannins were indicated only slightly.

Table 2. Analysis of the Different Parts of *Rhamnus pentapomica*.

Constituents	Wood (%)	Bark (%)	Leaves (%)
Total solid	19.5	26.3	32.1
Soluble solid	16.8	22.4	27.6
Insoluble solid	2.7	3.9	4.5
Nontannin	7.8	9.9	10.8
Tannin	9.5	12.5	16.8
Tannin–nontannin ratio	1.15	1.26	1.55

It is thus evident that mixed tannins (gallo and flavo) are distributed in the above three portions of *Rhamnus pentapomica*. Table 2 shows that tannins total solids, and tannin–nontannin ratio is higher in leaves than in wood and bark

Table 3 shows that extraction at 80-85°C is suitable, as far as the solubility of solid extract, colour and total solid yield are concerned. Higher solid percentage is obtained at 95–100°C but the solid so obtained is not easily soluble and hence the insoluble contents are high. Comparison of the colour of the extracts of different parts containing equal tannin percentage was made visually. It was found that the bark extract was brownish black, wood dark brown and leaves extract was brown. This observation shows the suitability of leaves tannin for use in the leather industry.

The pH values for various extracts at 0.5% tannin basis varied between 5.4–5.7. Generally the pH varies between 2.5–5.4 but higher pH values have also been reported.[10]

The reported values of the commercially known tanning materials have been compared with the tannin of leaves of *Rhamnus pentapomica* (Table 4). It is evident that the tannin percentage and tannin–nontannin ratio of the leaves of *Rhamnus pentapomica* are quite high but are lower than those of mangrove

Table 3. Analysis of the Extracts of the Different Parts of *Rhamnus pentapomica* at Various Temperatures.

Different portion	Extraction (°C)	Total solids (g)*	Soluble (%)	Insoluble (%)	Nontannin (%)	Tannin (%)	Tannin–nontannin ratio
Leaves	60–65	31.2	86.2	13.8	33.0	53.2	1.6
,,	80–85	32.1	85.9	14.1	33.4	52.5	1.5
,,	95–100	33.3	84.6	15.4	35.7	48.9	1.3
Bark	60–65	25.2	86.4	13.6	37.2	49.2	1.3
,,	80–85	26.3	85.2	14.8	36.6	48.6	1.3
,,	95–100	27.6	84.1	15.9	36.7	47.4	1.2
Wood	60–65	18.5	86.5	13.5	39.5	47.0	1.2
,,	80–85	19.5	86.2	13.8	40.0	46.2	1.1
,,	95–100	20.4	85.3	14.7	40.2	45.1	1.1

*Per 100 g of moisture-free portion.

Table 4. Comparison of Tannins of *Rhamnus pentapomica* Leaves with Common Tannins Reported in Literature.

Constituent	Chestnut wood (%)	Oak bark (%)	Hemlock bark (%)	Quebracho wood (%)	Mangrove bark (%)	*Rhamnus pentapomica* leaves (%)
Total solids	14.45	24.24	20.84	28.63	44.00	32.1
Soluble solids	13.08	21.77	16.76	23.77	37.28	27.6
Insolubles	1.37	2.47	4.08	4.86	6.72	4.5
Nontannin	5.31	9.28	6.59	3.12	8.78	10.8
Tannin	5–8	10–14	8–12	20–23	20–40	15–18
Tannin–nontannin ratio	1.46	1.34	1.54	6.61	3.24	1.55

bark and quebracho wood.[11] The tannin/nontannin ratio, which is of great importance to the industry, should generally be above 1 and preferably 2.[6] In the present study the tannin–nontannin ratio of the leaves and the bark is 1.55 and 1.26, respectively.

From the high pH value and low tannin–nontannin ratio, the low astringent nature and slow penetrating power can be concluded. This results in high fixation value and hence its suitability for heavy leather is evident.[11] The disadvantage of high pH value which imparts dark colour to the leather can be overcome by blending with acid tanning materials such as myrobalan and chestnut extracts.

It has been observed that slight fermentation of the extracts takes place with the deposition of some sediment when kept for more than 5 days. The deposition of sediment is minimum in the wood extract. This indicates the presence of gallotannin and reducing sugar.[6] It has the advantage that the loss of tannin due to fermentation is very low.[11]

In view of the above findings, particularly the high tannin percentage, reasonably good tannin–nontannin ratio together with the availability of the plant in fairly large quantities, *Rhamnus pentapomica* is considered suitable for commercial use in leather and other associated industries. It can also be blended with other tanning materials.

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References

1. M.B. Rahman and S.M. Imam, Pakistan J. Forest, **7**,145 (1957).
2. W.E. Hills, *Wood Extractives* (Academic Press, New York, 1962), p. 193.
3. A. J. Panshin, E. S. Harrar, J. S. Bethel and W. J. Baker, *Forest Products* (McGraw-Hill, New York, 1962), second edition, p. 509.
4. M. Qudrat-i-Khuda, A.K.M. Moslem Ali and A. Samad, Sci. Res., **11,** 81 (1965).
5. M.N. Malik and A.A. Khan, Pakistan J. Forest, **17,** 371(1967).
6. M.B. Rahman and S.M. Imam, Pakistan J. Forest, **9,** 1 88(1959).
7. R.N. Parker, *A Forest Flora for the Pujnab with Hazara and Delhi* (Government Printing Press, Lahore, 1956), p. 85.
8. *Thorps Dictionary of Applied Chemistry* (Longmans, London, 1954), fourth edition, p. 395.
9. M.A. Rahman and M. Ikram, Pakistan J. Sci. Ind. Res., **5,** 28 (1962).
10. *Wealth of India, Industrial Products* (C.S.I.R., New Delhi, 1960), part V, p. 219.
11. R.E. Kirk and D.F. Othmer, *Encyclopedia of Chemical Technology* (Interscience, New York, 1954), Vol. XIII p. 579.