Tannin Content of some Hokkaido Materials.

By

Prof. Lloyd Balderston, Ph. D.

A number of Hokkaido plants have been examined at this laboratory with respect to their tannin content. Through the kindness of Professor Niisima, Director of the Hokkaido Government Forest at Nopporo, the following samples were furnished from the forest:—

Quercus grosseserrata	Mizunara
Quercus glandulifera	Konara
Castanea pubinervis	Kuri
Salix Caprea	Bakkoyanagi
Juglans Sieboldiana	Onigurumi
Carpinus cordata	Sawashiba
Alnus hirsuta	Keyamahannoki
Alnus japonica	Yachihannoki
Cercidiphyllum japonicum	Katsura
Magnolia Kobus	Kobushi
Magnolia hypoleuca	Hōnoki
Prunus Ssiori	Shiuri
Picrasma quassioides	Nigaki
Kalopanax ricinifolium	Sennoki

In each case samples were furnished from three portions of the trunk. The following samples were furnished from the College forest:—

Pinus densiflora	Akamatsu
Pinus Thunbergii	Kuromatsu
Taxus cuspidata	Onko

Samples collected from logs brought in for the new buildings of the University:—

Abies sachàlinensis	Todomatsu, Akatodo
Picea jezoensis	Yezomatsu

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Picea Glehni	Akayezomatsu
Fraxinus mandshurica	Yachidamo

Samples sent by Nippon Hikaku Kaisha, Ikeda :—

Quercus dentata	Kashiwa
Quercus grosseserrata	Mizunara

Samples collected in Sapporo :—

Larix leptolepis	Karamatsu
Salix purpurea	Koriyanagi

Samples collected at Zenibako and Kotoni by Mr. Shimidzu :—

Rosa rugosa	Hamanasu

The method of analysis used was that of the American Leather Chemists' Association. The central feature of the method is the use of chromed hide powder, which is shaken with a water infusion of the material. The amount of soluble matter thus removed from the infusion is estimated by difference, and is called tannin. The hide powder used was American Standard, made by the Standard Manufacturing Company, of Ridgway, Pennsylvania. Its moisture content was about 13%. It was of such acidity that 10 grams of the air-dry powder, digested in boiling water for 5 minutes required about 10.5 cc. of tenth-normal caustic soda to neutralize it to phenolphtalein.

Details of the method are as follows :—The material is ground so that the whole sample will pass through a seive of 20 meshes per linear inch, well mixed and stored in a glass container with stopper to prevent change of moisture content. Ten grams of this sample are dried for 16 hours at 95 degrees C. to determine moisture. From 20 to 80 grams are extracted with hot water in an apparatus so arranged that the extract may either be withdrawn as fast as formed, or returned to the boiling vessel. The steam is condensed and the resulting water drips on the material and percolates through it. The first 500 cc. are collected outside in 2 hours, when the connections are changed and the extraction continued with 500 cc. of water under a reflux condenser for 14 hours longer. The purpose of removing the first 500 cc., which contains much the largest part of the tannin, is to avoid loss of tannin due to prolonged heating.

When the extraction has continued a total of 16 hours, the flame is extinguished, and the liquid which is then in contact with the material is withdrawn and tested for tannin, by means of a solution of 1% gelatine and 10% NaCl, in water. Any precipitate is assumed to be due to tannin, and the extraction should be repeated. In no case was

tannin found at this point in the work. The infusion thus prepared is cooled to 20 degrees C., and made up with distilled water to 1000 cc. It should contain not less than 3.75 nor more than 4.25 grams of tannin. If on completion of the analysis the strength of the solution appears too high or too low, the extraction should be repeated with another portion of the sample, the proper amount to be used being calculated from the result of the first analysis.

The necessity for limiting the strength of solution so closely is due to the fact that unless the proportions of hide powder and tannin are closely controlled the amount of matter taken up by the hide will vary.

One hundred cc. of the infusion, pipetted into a thin glass dish 3 inches in diameter with a flat bottom are evaporated and dried at 95 degrees C. to determine total solids extracted from the material. Another portion is filtered and 100 cc. evaporated to determine soluble solids, that is, solids soluble at 20 degrees. Since filter paper absorbs some tannin, it is necessary to tan the filter to be used. Those employed were made by the Toyo Filter Paper Company, number 3, 15 cm. in diameter. This grade of filter has been compared with the Swedish paper prescribed in the official method, and found to be superior to that. To about 80 cc. of the infusion, 1 gram of purified kaolin is added, the mixture well stirred, and poured quickly on to the pleated filter. The filtrate is returned to the filter at frequent intervals for an hour. The liquid is now carefully removed from the filter in such a manner as not to disturb the kaolin, and a fresh portion of the infusion poured in. As soon as the filtrate is clear, a fresh dry vessel is placed to receive it, funnel and receiving vessel being covered to prevent evaporation.

In order to determine soluble non-tannin substances, 200 cc. of infusion are shaken 10 minutes in a stoppered bottle with wet chromed hide powder prepared as described below. The liquid and hide are thrown on a linen cloth which has been thoroughly washed to remove soluble matter, and squeezed to separate as much as possible of the liquid, which is now stirred with 2 grams of kaolin and filtered, the filtrate being returned until it comes clear. Of this filtrate 100 cc. are evaporated and dried as with total and soluble solids. The weight of this residue must be corrected on account of the dilution of the infusion by the water of the wet hide powder. The corrected non-tannin weight, subtracted from the weight of soluble solids, gives the tannin in 100 cc. of infusion, and this is easily expressed as a per-

centage of the air-dry material, and also of the water-free material.

The preparation of the hide powder is as follows:—Fifteen grams of air-dry powder are weighed for each determination to be made, with an excess of five grams to be used in determining water in the wet hide powder. The whole is wet with ten times its weight of water, shaken up, and then for each gram of hide powder 1 cc. of a 3% solution of chrome alum is added. The vessel is then allowed to stand over night or shaken continuously for one hour. The wet mass is now placed on a muslin strainer and squeezed to about 75% water; then mixed with distilled water, 15 cc. for each gram of hide powder, and allowed to stand 15 minutes; then again squeezed and soaked 15 minutes. After four washings, it is squeezed to 73% water as nearly as possible, and weighed out in portions of 46 grams for each determination. Each such portion adds about 34 cc. of water to the 200 cc. of infusion with which it is shaken.

The difference between total solids and soluble solids is called "insolubles," consisting of various materials soluble at 100 degrees, but not at 20 degrees.

All values in the following table are percentages calculated on waterfree basis. The last column shows the number of separate determinations on which the average values are based.

The apparatus employed does not hold more than 80 grams of material, so that percentages of tannin below 5% are to be considered as approximation only, since these analyses did not conform to the official method.

Analyses of Hokkaido materials with respect to tannin contents.

Material	total solids	soluble solids	insolubles	non-tannin matters	tannin	number
Quercus dentata.....bark	26.74	21.83	4.91	10.55	11.28	3
wood	15.94	14.14	1.80	7.24	6.90	1
Quercus grosseserrata .....bark	20.04	18.49	1.55	9.28	9.21	6
wood	5.04	4.76	0.28	2.06	2.70	1
Quercus glandulifera.....bark	11.12	10.63	0.49	6.22	4.41	2
wood	5.68	5.52	0.16	3.63	1.89	1
Castanea pubinervis .....bark	13.77	13.12	0.65	7.13	5.99	2
wood	11.02	10.59	0.43	3.93	6.66	1
Salix Caprea .....bark	19.04	16.64	2.40	8.41	8.23	1

Material	total solids	soluble solids	insoluables	non-tannin matters	tannin	number
Salix purpurea .....bark	32.73	30.56	2.17	23.07	7.49	1
Juglans Sieboldiana .....bark	14.86	13.54	1.32	7.81	5.73	1
wood	8.18	7.68	0.50	3.99	3.69	1
Carpinus cordata .....bark	11.93	11.39	0.54	5.68	5.71	1
Alnus hirsuta .....wood	4.78	4 39	0.39	3.42	0.97	1
bark	8.50	7.40	1.10	5.90	1.50	1
Alnus japonica.....wood	4.31	3.97	0.34	3.36	0.61	1
bark	5.35	5.07	0.28	3.68	1.42	1
Cercidiphyllum japonicum. bark	13.30	12.13	1.17	7.13	5.00	1
Magnolia Kobus .....bark	22.13	18.01	4.12	15.67	2.34	1
Magnolia hypoleuca .....bark	17.02	15.37	1.65	12.30	3.07	1
Prunus Ssiori.....bark	16.13	14.92	1.21	9.63	5.29	1
Picrasma quassioides .....wood	5.84	5.68	0.16	4.65	1.03	1
Kalopanax ricinifolium ...bark	13.10	12.76	0.34	9.25	3.51	1
Pinus densiflora.....bark	18.18	15.06	3.42	8.72	6.34	1
Pinus Thunbergii .....bark	18.91	12.63	7.28	6.77	5.86	1
Taxus cuspidata.....bark	27.94	25.30	2.64	15.71	9.59	1
Larix leptolepis .....bark	16.06	14.53	1.53	6.06	8.47	1
Abies sachalinensis .....bark	15.87	14.68	1.19	12.61	2.06	2
Rosa rugosa .....root bark	43.43	36.18	7.25	12.66	23.52	1
Picea jezoensis .....bark	20.62	17.81	2.81	8.78	9.03	3
Picea Glehni .....bark	37.10	31.64	5.46	12.43	19.21	4
Picea Glehni .....inner bark	49.63	43.96	5.67	19.63	24.33	1
outer bark	32.17	23.70	8.47	8.53	15.17	1
Picea jezoensis.....inner bark	24.54	22.62	1.92	12.22	10.40	1
	15.23	12.16	3.07	4.64	7.52	1
Quercus grosseserrata..inner bark	26.41	24.65	1.96	12.40	12.05	2
outer bark	11.20	9.71	1.49	5.05	4.66	2
„ „ large tree ...inner bark	22.00	20.52	1.48	9.80	10.72	2
outer bark	9.62	7.50	2.12	4.08	3.42	2
extreme outer bark	4.12	3.88	0.24	2.78	1.10	1

Reducing sugars were determined by the usual method in the barks of *Quercus dentata*, (2.1%), *G. grosseserrata*, (2.6%), and *Picea Glehni*, (3.1%). *Abies sachalinensis* bark has from 7 to 10% of a balsam, much like Canada balsam, whose refractive index at 18° is 1.504.

Fraxinus mandshurica showed about 27% total solids, but the quantity of tannin was too small to be estimated with any certainty by the official method.

Beside these Hakkaido materials, a sample of Camachile bark, *Pithecolobium dulce*, was received from one of the Pacific islands recently placed under the control of Japan. This was examined by S. Sawayama in 1918 and by K. Nakagawa in 1919. Its analysis is as follows: Total solids, 42.87; soluble solids, 34.86; non-tannins 9.71; tannin, 25.09. This tree is a native of Mexico, introduced long ago by the Spaniards into the Philippines and other Pacific islands. The bark is extensively used in the Philippines, and makes leather of first class quality.

Of the Hokkaido materials examined, the following appear worth further consideration:—

1. *Salix purpurea*, Koriyanagi. When the annual crop of twigs for the kori industry is stripped, many tons of the bark are destroyed in Sapporo every spring. Because of the high percentage of non-tannins, liquors made from this material alone penetrate slowly. It should be used in connection with some other material low in non-tannin, like quebracho or mimosa. Leather made with this willow bark alone is of very good quality but rather dull in color.

2. *Salix Caprea*, Bakkoyanagi. This is in every respect a very good material, and if there is any supply of willow timber available, the bark should be utilized.

3. *Taxus cuspidata*, Onko. The bark is so thin that the yield from a tree is small, but the percentage of tannin is high enough to make it worth saving.

4. *Picea jezoensis*, Yezomatsu. The bark of this large and valuable timber tree is thick, and the total yield of tannin per tree is therefore fairly high. The quality of leather produced is good, but it is somewhat stiff and the color quite dark. It is a very promising material for heavy leather making. Great quantities are wasted every year. The most important material for heavy leather making in Germany and Austria is the bark of the Fichte, superior to this in no essential respect.

5. *Picea Glehni*, Akayezomatsu. This is also a large tree. Its wood is scarcely distinguishable from that of *P. jezoensis*. With possibly one exception, (*Pinus halepensis*), this bark is richer in tannin than that of any other coniferous tree which has been investigated. It is rather thin, so that the tannin yield per tree would probably be hardly greater than from *P. jezoensis*. The quality and color of the leather produced are very satisfactory. The color is lighter and brighter

than that of the product from either of the Hokkaido oaks. In flexibility, "feel" and toughness, as well as softness, this leather is of very high grade, and for light weight leathers the bark of Akayezo-matsu seems superior to any other tannin material native to Japan. It is very important that extract factories be established to utilize the bark of the two species of Yezomatsu, both from the timber used in paper making and from that brought in for lumber. The two sorts should be worked up separately, as the extract from *P. Glehni* would probably be worth considerably more than the other. The quantity of bark now being wasted in Hokkaido is probably sufficient to supply the needs of all the tanneries operating in Japan at present.

6. *Rosa rugosa*, Hamanasu. In spite of the high percentage of tannin in the root bark of this shrub, it has no commercial importance for leather making because the roots are so small. The color of the leather is rather dark.

7. *Quercus dentata*, Kashiwa. This is the material most extensively utilized for tanning in Japan. It is shipped south both as crude bark and as extract, liquid and solid. It yields leather of good quality, being especially suitable for heavy leather making.

8. *Quercus grosseserrata*, Mizunara. This is not much inferior to *Q. dentata*, and is used to some extent in extract manufacture. Its wood is extensively used for lumber and great quantities of both species of oak are used for firewood, and the bark ought to be utilized. It can be peeled easily in April, May and June, but from wood cut in the winter it can only be removed by chopping, or by a troublesome and expensive steaming process. Since labor for cutting the wood is most available in winter, it would seem necessary in order to save the bark to go to the trouble of chopping it off. It might be possible, however, to cut down the trees in the spring and have the bark peeled off, and then allow them to lie until winter to be cut up into saw-logs and firewood. In this way only a small part of the total labor would be demanded at the time of year when farm operations are in progress.

9. *Larix leptolepis*, Karamatsu. The bark of this tree is probably equal in quality to that of the Yezomatsu, and when supplies of larch timber are available, the bark should be made use of.

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