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CHEMICALS FROM DOUGLAS-FIR BARK

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In the fall of 1947 the Oregon Forest Products Laboratory began investigating the chemical composition and utilization of western tree barks. One of the first barks investigated was that of Douglas-fir. Other barks that have been examined or are now under study are ponderosa pine, sugar pine, lodgepole pine, Jeffrey pine, Port Orford cedar, incense cedar, western red cedar, white fir, and grand fir.

Some of this work has been carried on jointly with the Department of Chemistry, Oregon State College.

DOUGLAS-FIR BARK CHEMICALS

Based on an annual cut of 6 billion board feet of Douglas-fir lumber in the states of Oregon and Washington and calculated on the basis that 20.8 cubic feet of bark having a specific gravity of 0.40 are available from each thousand board feet of logs, the potential annual supply of such bark is about $1\frac{1}{2}$ million tons. (The production of Douglas-fir lumber in the year 1950 was over 10 billion board feet.) The bark can be separated mechanically into cork, needle-like bast fibers, and a fine amorphous powder.

The cork is interspersed in the reddish-brown bark as light-colored layers varying in thickness from $1/32$ to $3/4$ inches. This Laboratory has found that Douglas-fir sawlog bark contains, by weight, from 25 to more than 50 per cent cork, 30 to 42 per cent of the short needle-like bast fibers, and 20 to 35 per cent of the amorphous powder. The cork particles contain approximately 40 per cent, the bast-fibers 20 per cent, and the amorphous powder 34 per cent of extractives. Sound whole bark contains from 25 to 30 per cent of extractives.

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Destructive distillation of the bark in an oven-type retort produces yields of approximately 45 per cent charcoal, 10 per cent tar, and 18 per cent combustible gas. This yield of charcoal is higher than that for wood, whereas the yield of tar and combustible gas is of the same order as that obtained from wood.

Most of our work thus far on bark components has been on the extractives. Three substances are present in Douglas-fir bark in commercially extractable quantities and have important potential industrial uses. These are tannin, wax, and the flavanone, dihydroquercetin.

Tannin

The tannin content of sound Douglas-fir bark, when determined by the procedure of the American Leather Chemists Association, varied from 7.5 to 18 per cent, based on oven-dry bark weight. The largest amount of tannin was found in the bark of young second-growth trees 57 to 70 years of age and the tops of older trees. The least amount of tannin was found in the bark of butt logs of old-growth trees. Bark, hand-peeled at a peeling plant, from poles and piling 32 to 43 years of age averaged 9.0 per cent tannin content.

In the conventional pole-peeling operation, the bark refuse contains about 50 per cent wood. Hence, this bark and wood mixture would average less than 5 per cent in tannin content which is considered too low for commercial extraction. In addition, the sapwood removed with the bark contains nontannin water-soluble substances, which lower the purity of the tannin extract.

Several bark samples, hand-peeled from logs in the woods soon after the trees were felled and then dried, were analyzed for tannin content during the past two years. This bark, up to 2 inches in thickness, has averaged quite consistently about $12\frac{1}{4}$ per cent tannin. In the commercial extraction of properly cured bark, a yield of 10 per cent based on the oven-dry weight of the bark,

may be expected. This tannin yield is about the same as that of eastern hemlock bark. Hence, from one ton of bark, 200 pounds of tannin may be expected in commercial extraction. This amount of tannin at 18 cents per pound amounts to \$36.00 per ton of bark. Assuming a tannin recovery of 10 per cent, $1\frac{1}{2}$ million tons of bark would produce about 273,000 tons of powdered extract containing 55 to 60 per cent, or about 150,000 tons of actual (100 per cent) tannin.

Cost estimates for producing a pound of 100 per cent eastern hemlock tannin were obtained from industrial firms during the past year. Exclusive of raw bark costs and based on a 10-year plant amortization period, the estimated costs of leaching the bark (about 1.5 cents) and evaporating the liquid extract to a dry powder (about 3.5 cents) total between 5 and 6 cents per pound of actual tannin. Including the cost of eastern hemlock bark at \$17.00 per ton (8.5 cents per pound of actual tannin), the total estimated cost of producing one pound of actual hemlock tannin is between 13.5 and 14.5 cents. Douglas-fir bark at \$2.00 per ton would give a raw material cost of 1 cent per pound of actual tannin. Excluding bark drying costs, the cost of producing one pound of actual Douglas-fir tannin would be between 6 and 7 cents.

The tannin in Douglas-fir bark is easily extracted with hot water. In the conventional counter-current process, leach water temperatures up to 200° F. may be used without converting the tannin to insoluble phlobaphenes. The total extraction time, with five leaching tanks in series, may be 15 hours, with 80 to 90 per cent recovery of available tannin. Several factors, particularly bark particle size and method of grinding, affect the rapidity and completeness of tannin extraction.

A light-colored tannin is produced when the aqueous extract is concentrated to about 50 per cent solid matter in a vacuum dryer and subsequently dried to a powder form in a spray or a vacuum drum dryer. The powdery extract from well-cured bark will contain from 55 to 60 per cent actual tannin and 40 to 45 per cent nontannins.

The annual consumption of vegetable tannin in this country is estimated to be about 150,000 tons of actual tannin, of which about 70 per cent is imported. Quebracho tannin from Argentina is imported in the greatest amount. The chief source of domestic vegetable tannin is chestnut wood in the Appalachian area. A blight has killed most of the chestnut forest, and estimates indicate that this source of tannin may be exhausted before 1960.

Douglas-fir tannin compares favorably with quebracho tannin for all of the major industrial uses, and it has been used for many years in leather-making at the tannery at Dallas, Oregon. Dr. Tu at the B. D. Eisendrath Memorial Laboratory, Racine, Wisconsin, concluded from his tests on Douglas-fir bark tannin extract, made during the year 1950, "that Douglas-fir bark is comparable to quebracho tannin. The leather produced was full, firm and had an agreeable light tan color. The tannin fixation, shrinkage temperature and other characteristics of the leather all revealed that Douglas-fir bark tannin resembles quebracho tannin." He found that it could be blended with other tannin extracts. In his opinion, "from the technical point of view, Douglas-fir bark extract could be developed very well into a satisfactory domestic tannin extract."

About 40 to 50 per cent of the tannin consumed in this country is used by the petroleum industry for controlling the consistency of oil-well drilling muds. During the past year, two industrial laboratories have reported that Douglas-fir bark tannin compares favorably with quebracho tannin for this use.

The Bureau of Mines' Laboratory at Tuscaloosa, Alabama, is interested in finding a material that will be beneficial for the concentration of low grade iron ores. Their tests on Douglas-fir bark tannin extract, made during the past year, indicate that it is as efficient as quebracho tannin for this purpose.

Hence, it appears that a market for Douglas-fir tannin is available and all that remains is to produce it economically on a commercial scale. In this connection, there is an important problem that requires consideration. Douglas-

fir tannin, like all other bark tannins, is quickly destroyed by enzymes, molds, fungi, and insects when the bark is wet or left on logs in the woods under conditions favoring attack by biological agents. To obtain the maximum yield of tannin, the bark must be removed from the logs soon after the tree is cut, and then it must be properly cured. Experiments conducted over the past two years have shown that a relationship exists between drying or curing methods and tannin yield and quality; improperly cured bark contains less tannin than well-cured bark. There is also the possibility that dihydroquercetin is converted to tannin during curing and storage of the bark.

The lumber industry on the West Coast does not on the whole practice bark salvage or debarking before sawing the logs into lumber. Bark that has been stored in millponds or left on logs lying in the woods will be low in tannin content. In order to obtain good tannin bark it will be necessary to debark the logs soon after felling the trees, possibly by debarkers at the mills, and to dry the bark in dryers before storage. The drying operation could be most economically done in a bark dryer at the tannin extraction plant. An analysis for the tannin content of one lot of bark removed with a hydraulic barker from logs ranging from 16 to 24 inches in diameter gave a $12\frac{1}{4}$ per cent yield of tannin by weight.

Some of the advantages of debarking sawmill logs are:

- (1) A saving in lumber scale of at least 5 per cent.
- (2) The sawyer has a better opportunity to inspect the log before starting breakdown into lumber.
- (3) There is a ready market for the clean barked slabs at pulp or hardboard mills.
- (4) There is less maintenance on saws and conveyor systems.
- (5) Logs barked on land do not contribute to stream pollution.
- (6) There is a reduction in accident and fire hazards in a bark-free plant.
- (7) The bark has value.
- (8) The general opinion of those experienced with debarking operations is that "debarkers are the coming thing for sawmills."

~~WAX~~

The second group of Douglas-fir bark extractives of potential commercial value includes the waxes. Douglas-fir bark contains on the average about 5 per cent of a light-colored wax soluble in hexane or petroleum-type hydrocarbon solvents. In addition, it contains about $2\frac{1}{2}$ per cent of a brown-colored wax soluble in aromatic type solvents or in chlorinated hydrocarbon solvents. The total wax content of the bark taken from Douglas-fir sawlogs in the Willamette Valley has averaged quite consistently about 7.5 per cent. The cork fraction in the bark contains the most wax; sometimes this amounts to about 13 per cent of the oven-dry weight of the cork. The wax can be solvent-extracted from wet or dry bark; drying of the bark prior to wax extraction is unnecessary. Wax extracted with benzene or trichlorethylene from wet bark is usually red-colored, for a little of the tannin may be removed along with the water from the wet bark.

In the Laboratory's experimental batch extractor, approximately 90 per cent of the wax was extracted from Douglas-fir bark with benzene in three hours with nearly complete recovery of the solvent by steaming the extracted bark residue.

The color of the crude benzene-extracted wax from dry bark is light brown to reddish-brown. Approximately two-thirds of the benzene-soluble wax is soluble in hexane.

The melting point of the Douglas-fir bark waxes is about the same as that for beeswax. They, however, are harder than beeswax but not as hard as carnauba wax. The chemical composition of the hexane-soluble wax was found to be about 60 per cent lignoceric acid, 20 per cent lignoceryl alcohol, and 20 per cent ferulic acid. Small amounts of sterols are also present.

The ferulic acid is a very reactive aromatic acid and, as far as is known, Douglas-fir wax is the only vegetable wax that contains an aromatic substance of this nature. This material gives the wax many interesting and unique properties.

It affords the organic chemist many opportunities to modify the properties of the wax. Ferulic acid itself may be converted into vanillin, a familiar substance.

During the past year this laboratory has had requests from a large number of companies for one- to ten-pound samples of the wax. For most important industrial uses of the wax, it would be desirable to raise its melting point, increase its hardness, and increase its solvent-retention properties. A simple, cheap means for accomplishing this now has been found. The melting point can be raised to exceed that of carnauba wax; in fact, the melting point can be increased as much as 50° C. Improvement in hardness and increase in solvent retention are also obtained. These properties are desirable when the wax is to be used on floors and for polishes.

Douglas-fir wax gives a clear, high gloss to wood surfaces. The hardened wax is easily applied and requires very little rubbing to give a highly lustrous polish. Douglas-fir wax also has the unique property of being easily emulsified. This is desirable when the wax is used for liquid polishes. We believe that the necessary changes desired by potential wax users have been accomplished and that the wax will find many large-volume uses.

This country imports all of its carnauba wax requirements, a major proportion of its candelilla wax, and about 70 per cent of its beeswax requirements. Carnauba and candelilla are high cost waxes. Calculated on the basis that a 5 per cent yield of hexane-soluble wax is obtainable from Douglas-fir bark and assuming that it will sell for the price of beeswax, the potential value of the wax from one ton of dry Douglas-fir bark is \$50.00.

It has been reported that it costs from \$6.00 to \$7.00 to solvent extract a ton of oil meal in a continuous-type extractor. It would appear that the cost of extracting a ton of Douglas-fir bark should be somewhat comparable.

No estimates have been placed on the potential value of the hexane-insoluble wax. This wax has a more complex chemical composition than the hexane-soluble wax containing lignoceryl alcohol, hydroxy palmitic acid, lignoceric acid, glycerol, a reddish-brown phenolic acid, and unsaturated hydroxy acids. The hydroxy acids in this wax are esterified to the phenolic acid and also to each other in an etholide-type linkage. The wax has a marked similarity to the "suberin" in cork. It has desirable properties and potential commercial value. The yield of this wax from Douglas-fir bark amounts to approximately $2\frac{1}{2}$ per cent or 50 pounds per ton of dry bark.

The properties of three modified hexane-soluble wax products as determined by the National Bureau of Standards are given in Table I. The Bureau mentioned that "these waxes have properties which may make them useful as replacements for waxes that are now on the market; however, such replacement would depend upon consumer acceptance."

Table I.

Properties of Modified Hexane Soluble Waxes

Sample	Penetration (mm)*	Softening Point**	Acid Number	Saponification Number
1.	0.3	78° C.	70	161
2.	0.7	86° C	77	129
3.	0.7	98° C	76	160

* 5 sec. - 100-g. weight at 25° C.

** Ring and ball method Federal Specification P-W-158.

Dihydroquercetin

The third chemical of commercial importance occurring in Douglas-fir bark is dihydroquercetin. This is a white crystalline compound that belongs to the group of organic compounds known as "flavonoids." Yields of more than 7 per cent have been obtained from some bark, the largest concentrations being found in the cork fraction of the bark. Some Douglas-fir cork has been found to contain more than 20 per cent by weight of dihydroquercetin.

Some flavonoids possess the pharmacological properties characteristic of the so-called vitamin P, are beneficial in the treatment of frostbite and fragility of blood capillaries, and are excellent antioxidants for the prevention of rancidity in fats and oils. Tests also are underway to determine their effectiveness for the treatment of radiation burns. The flavonoids differ in their abilities to accomplish the desired results when used for these purposes.

The naturally occurring yellow coloring matter, quercetin, has a high degree of activity for several of these uses. Rutin, a glucoside of quercetin, now is commercially extracted from buckwheat for the pharmaceutical trade and sells for about \$15.00 a pound. Both of these materials appear to be nontoxic.

During the past year we have prepared and sent many samples of dihydroquercetin to laboratories for evaluations of its potential usefulness. Our tests and those of industry have shown that dihydroquercetin is an excellent antioxidant for the prevention of rancidity of food products. It compares favorably with propyl gallate, which is now used for this purpose. Dr. DeEds in the U. S. Department of Agriculture Laboratory at Albany, California, has reported that dihydroquercetin and quercetin are beneficial for the treatment of frostbite injury. Other clinical tests are still in progress. At this time, it appears that large-scale important uses for dihydroquercetin will develop. The current prices for rutin, quercetin, and related flavonoids make the production of dihydroquercetin from Douglas-fir bark appear very attractive.

Quercetin

Dihydroquercetin differs chemically from quercetin only in that it has two more hydrogen atoms in the molecule than quercetin. Dihydroquercetin is converted into quercetin quite easily by treatment with bisulfite solutions. For example, approximately 90 per cent conversion to chemically pure quercetin is obtained by simple refluxation of dihydroquercetin in 5 to 20 per cent aqueous solutions of sodium, potassium, or ammonium bisulfite; over 50 per cent conversion is effected with dilute solutions and over 85 per cent conversion is effected with concentrated solutions within one hour. Quercetin is insoluble in hot bisulfite solutions whereas dihydroquercetin and tannins are relatively soluble. It is not necessary, therefore, to start with pure dihydroquercetin in order to obtain pure quercetin. The quercetin separates from the above hot bisulfite solutions as bright yellow crystals with a melting point of 316 to 318° C. On the other hand with calcium bisulfite liquor such as used in the commercial pulping of wood, dihydroquercetin forms a yellow, insoluble calcium complex of quercetin. This material separates as a fine, impervious crust, which adheres tenaciously to the sides of the container. The above reactions offer an explanation for the fact that difficulty is experienced in pulping Douglas-fir chips with calcium bisulfite liquor, but not with ammonium bisulfite liquor.

Recent analyses in this laboratory of Douglas-fir bark obtained from operators of sawmills are given in Table II. The logs from which these samples of bark were taken had not been stored in water. The data show that a yield of 146 to 200 pounds of tannin, 130 to 204 pounds of wax, and 80 to 152 pounds of dihydroquercetin may be expected from a ton of sound sawlog bark. In the conventional hide powder method for tannin analysis, at least a part of the dihydroquercetin appears as tannin. Therefore, an overlapping in the yields of these two water soluble constituents occurs.

Table II. ANALYSES OF DOUGLAS-FIR BARK FROM SAWLOGS
(Percentage based on oven dry weight of bark)

Source	Tannin	Wax	Dihydroquercetin
Rockport, California	8.8	6.5	6.0
Taos, New Mexico	13.6	9.2	7.6
Fall Creek, Oregon	7.3	10.2	4.0
Molalla, Oregon	8.1	8.0	5.5
Corvallis, Oregon	10.0	7.4	6.0
British Columbia*	7.0	8.3	4.7

* Logs stored in fresh water 90 days and in salt water 20 days.

TANNIN EXTRACTING EQUIPMENT

The following paragraphs include a suggested list of equipment that would be required for a commercial tannin extraction process using Douglas-fir bark.

Bark dryer

Adequate bark drying equipment can be fabricated locally. The Combustion Engineering Corporation, Chicago, Ill., manufactures a grinder-flash drying combination mill. A 6-unit, single-conveyor dryer producing 2 tons of dry bark per hour, manufactured by Proctor and Schwartz Company, Philadelphia, Pa., costs \$22,000

Bark grinders

These could be of the hammer-mill type, but a mill giving a shaving action is preferable.

Bark leaching tanks

These are circular wooden tanks varying from 10 to 18 feet in diameter and from 10 to 17 feet in height. They are generally equipped with a rotating arm to discharge the spent bark through a 2-foot square opening in the bottom of the tank. The bark is extracted with hot water, countercurrently, in a series of 4 or 5 tanks.

Evaporators

A 100-ton per day bark extraction plant, using about 7.0 pounds of water per pound of dry bark for leaching, will require an evaporator that has the capacity to evaporate about 53,000 pounds of water per hour. This evaporator requires 17,000 pounds of steam per hour and 700 gallons of recondenser cooling water per minute. The cost of this size evaporator, including pumps and interconnections, is about \$150,000.

Initial temperature of the tannin liquor on the first stage may be 200° F or less. Temperature of the final stage should be approximately 125° F. These temperatures are within the safe limits for Douglas-fir tannin extract.

Spray dryers

Prices for installed dryers are as follows:

1. For a 10-foot dryer with a production capacity up to 12 tons of dry extract per day, the cost is about \$45,000.
2. For a 14-foot dryer with a production capacity between 12 and 26 tons of dry powder per day, the cost is \$70,000.
3. For an 18-foot dryer with a production capacity of from 26 to 38 tons of dry powder per day, the cost is \$95,000.

SUMMARY

Douglas-fir bark contains potentially useful organic chemicals in commercially extractable quantities for which good markets exist. It is believed, from work done during the past two years on integrated extraction processes, that all of these chemicals may be produced from sawlog bark, and the extracted bark residue can still be used further for fuel, as soil conditioners, in destructive distillation, or for the mechanical separation of cork, bast fibers, and other bark products.

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