Opportunities to Use Bark Polyphenols in Specialty Chemical Markets

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Current forestry practice in North America is to transport pulpwood and logs from the harvest site to the mill with the bark on the wood. Approximately 18 percent of the weight of logs from conifers such as southern pine is bark. The majority of this bark is burned as hog fuel but its fuel value is low.[1] When compared with natural gas at an average of $2.50/MBTU or electricity at 3.5 cents/KWH, burning wet bark has a gross fuel value of about 1.2 cents/lb on a dry weight basis. Considering the cost of transport as well as the capital and maintenance costs of boilers, processing bark for fuel is a costly business and seems to be practiced only to avoid a large solid waste management problem. One must not lose sight of the fact that one must handle nearly two lbs of wet bark to recover that 1.2 cents. In addition, concerns about air quality, especially increasingly stringent limits on particulate emissions, has stressed the ability of hog fuel boilers to meet regulatory requirements. We need to find ways to produce higher value products from bark.

It is instructive to remember that tree barks were the source of high value specialty chemicals in the past. In the early American colonial days, quercetin-3-*O*-rhamnoside, a bright yellow compound easily obtained from red oak bark, led export trade to Europe where it was valued as a yellow dye.[2] From 1900 to WWI, the United States Leather Company, making vegetable tannins from eastern hemlock bark, was ranked in the top ten capitalized companies in the United States. Eastern hemlock forests concentrated from New York to Pennsylvania were harvested for the bark while the wood was often left to rot.[3]

During the 1950's and 1960's major efforts were made by forest products companies such as ITT Rayonier[3] and Weyerhaeuser Company[4] to develop specialty chemical markets for a wide range of products obtained from western hemlock and Douglas-fir barks. Although ITT Rayonier had plants operating in Washington and British Columbia in the 1960's, they were closed just prior to the energy crisis of the early 1970's. Other notable efforts by New Zealand Forest Products and Bohemia Lumber Co were timed better with the energy crisis but were not successful. Wattle tannins from South Africa and quebracho tannins from South America have dominated the vegetable tannin market and the lion's share of this material is still used in leather manufacture.[5] Nevertheless, the oil crisis of the early 1970's alerted the forest products industry that it can be impossible to purchase the phenol needed in their wood adhesives no matter what the price.[6] A wide array of tannin-based adhesives was developed using wattle tannins in South Africa where access to petrochemicals was limited.[7] The stimulus of the oil crisis also coincided with major advances in analytical equipment, particularly Nuclear Magnetic Resonance (NMR) spectroscopy, to spur major research efforts in the area of condensed tannin chemistry in the 1970's and 1980's.

It is not possible in the space here to adequately summarize that very active, world-wide research effort[8-11]. Rather, we will summarize some of the work we have done, together with collaborators from around the world, in our Southern Research Station effort selecting work that might be of the most direct help to the forest products industry in developing processes for using bark as a source of specialty phenolics. The mission of our work at the Southern Research Station is to obtain fundamental information on the structure, reactions, conformation, and complexation properties of flavonoids such as the condensed tannins. Our effort includes developing specialty chemicals as well as helping to define the environmental significance of these polyphenols. Much of the work we have done has not been cited in this review, but we should be happy to provide additional materials to any readers requesting additional information.

Polyflavanoids (Figure 1) make up about half of the dry weight of most tree barks. These phenols are distinctly different from wood lignins in that they are extremely reactive compounds and carry three chiral centers that typically are consistent in absolute stereochemistry within a plant genus. The polyphenols most commonly found in tree barks are 5,7-dihydroxyflavans. The properties of the 5,7-dihydroxyflavans are different from 5-deoxyflavans in wattle or quebracho tannins that carry only a 7-hydroxyl on the A-ring. The polymeric 5,7-dihydroxyflavans tend to be linear and of a higher molecular weight than the 5-deoxyflavans are typically angular at the terminal unit and usually of lower molecular weight.[12,13] Another very important difference between these two classes of polyflavanoids is that the interflavanyl bond in the 5,7-dihydroxyflavans is labile to either mild acid or alkaline conditions.[14] Acid-catalyzed cleavage of the interflavanyl bond is used both as an analytical tool to define the structure of the polymers and as a method to make flavanyl derivatives for specialty chemical uses.

There are also important differences in the way these two classes of polymers react with aldehydes[15] and hydroxybenzyl alcohols.[16] The 5,7-dihydroxy flavans react extremely fast with formaldehyde to produce water insoluble materials whereas the 5-deoxyflavans in wattle or quebraco extracts are more controllable. This feature of conifer bark tannins together with the fact that, with the exception of the oil crisis period, phenol has been comparatively cheap in North America, much of the work we have done has been directed to use of tannins as substi-

tutes for resorcinol.[17] The vicinyl di- and tri-hydroxy substituted B-rings of polyflavanoids offer potential for use in products related to metal complexes.[18] Compounds with a pyrogallol hydroxylation pattern have exceptional anti-oxidant properties.[19] We will be putting more emphasis on the properties of the B-ring in future.

A primary objective when starting our work in the early 1970's was to obtain a better understanding of the structure of tannin polymers isolated from southern pine bark. The 13C NMR spectra of purified polymers were consistent with a procyanidin polymer in which the chain extender units were of a 2,3-*cis*-3,4-*trans* and the terminal unit 2,3-*trans* stereochemisty.[20] An important feature of the work on southern pine bark tannins was the finding that there is heterogeneity in the location of the interflanyl bond[21] but that the extent of chain branching is small.[22] The molecular weights of these compounds proved to be much lower than commonly thought with about 10 to 15 flavans units as usual for the 5,7-dihydroxyflavans.[23] Most other conifer bark tannins are of a similar structure.

When considering a bark chemicals business, it is important to consider other potentially competitive sources of tannins. Wattle and quebracho tannins dominate the vegetable tannin business today. We found that pecan nut pith, the membrane material between the meat and hard shell that is a sizable resource in the Southern United States, is an exceptional source of tannin. These tannins are 3,5,7,3',4',5'-hexahydroxyflavans of 2*R* absolute stereochemistry. Both 2,3-*cis* and 2,3-*trans* chain extender units are present but the terminal unit seems to be exclusively 2,3-*trans*. The molecular weight of pecan pith is about the same as or slightly lower than that of a conifer bark tannin. The most important feature is the fact that these tannins can be recovered in high yields (close to 40% of dry tissue weight) and the extracts contain only very small amounts of carbohydrates.[24]

Even though the condensed tannins in a broad spectrum of plants have now been described, it is important to note that new sources of tannins with unusual chemistry can still be found. The tannins in the bark of guamuchil (also called madras thorn) that grows in Mexico and can be used to make excellent leather is a case in point.[13] C NMR spectra suggested that these tannins were previously unknown 2,3-*cis* 5-deoxy flavans, similar to wattle tannins but with a different stereochemistry. Because the interflavanyl bond in these compounds resist cleavage, it was necessary to resort to synthesis in order to prove the absolute stereochemistry of the chain extender and terminal units but we now have finally proved the structures of a whole series of 2,3-*cis* profisetinidin dimers and trimers.[25] This work is mentioned both to encourage natural products chemists to keep searching for new polyphenols in different plants and also to emphasize the importance of a strong R&D element in any bark chemicals business. New commercial sources of polyphenols can come up at any time.

In addition to taking care in selection of the resource, it is also important to carefully select the conditions used for extraction. Although we originally had concerns about extraction with sulfite ion to increase yields and water solubility of the product, we found that reaction of the 5,7-dihydroxyflavans with sulfite ion mainly involves cleavage of the interflavanyl bond with the formation of flavan-4-sulfonates. Sulfonation at C-4 appears to limit opening of the pyran ring so diarylpropanol sulfonates are obtained only from the terminal catechin unit.[26] Sulfonation of the aromatic rings is limited unless reaction conditions are severe.[27] From the standpoint of preparation of an intermediate for adhesive development, the most important feature of these flavan-4-sulfonates is that under mildly alkaline conditions desulfonation with formation of a reactive flavanyl quinomethide occurs.[28] Therefore, the final product contains little if any sulfonic acid functionality and the products are insoluble in water.[29]

Because these compounds readily suffer rearrangements and oxidation in alkaline solution,[30-31] it is important to use care in subjecting these compounds to high pH. Unfortunately, in an effort to increase extract yields, there have been numerous examples of the isolation of a polymer with little residual reactivity. Much higher extract yields can be obtained by extraction with strong bases, but the condensed tannins suffer rearrangement reactions that destroy the phloroglucinolic ring essential to reactivity in adhesive formulations. Even though these reactions have been thoroughly documented,[14,30-32] it is still often seen that the desire for higher extract yields apparently drives attempts to use alkaline bark extracts in development of tannin-based adhesives. Use caution in attempting to do that.

With the exception of the time of the oil crisis in the early 1970's, the price of phenol and phenolic resins for wood adhesives has remained relatively low.[33] Unless one has an exceptionally rich source of tannin or a tannin-based adhesive that offered substantial benefits in properties that would allow premium prices, it seems that it would be difficult to compete with phenol-formaldehyde resins in North America. Because tannins react with benzyl- alcohols or formaldehyde much the same as resorcinol and resorcinol sells for approximately $ 2.00/lb in the United States, we have concentrated our efforts on trying to substitute tannins for resorcinol.

One sizable market for resorcinol is in wood laminating adhesives. In cooperation with Dr. Roland E. Kreibich we have developed a number of approaches to using tannins in lumber end jointing adhesives.[17,24,29] The most recent work in this area was directed to bonding wood of high and widely ranging moisture contents.[24] We demonstrated tannin-based adhesives for end-jointing green, wet, or dry, or importantly any combination thereof, that can meet the basic strength and durability requirements for structural end-joints. When used to bond hardwoods such as aspen, bond strength is high but the wood failure is low.

However, for many applications, it would not seem necessary to meet all requirements for structural end joints in laminated beams. A similar technology has been developed using alkaline hydrolyzates of proteins from soybeans.[34] Whether tannin-based adhesives can compete with these Soybond adhesives depends to a large degree on relative prices of tannins and protein.

Adhesives formulated for bonding of cord to rubber also represent a sizeable market for resorcinol-based adhesives. In cooperation with Dr. Gary R. Hamed, we demonstrated that we could substitute tannins from various plant extracts for resorcinol in the resorcinol-formaldehyde-latex (RFL) adhesives used to bond polyester or nylon cord to styrene-butadiene rubber.[35] An important feature of the tannin-substituted RFL adhesives seemed to lie in increased toughness of the adhesive, a feature of importance to manufacture of rubber belts as well as tires.

If one can avoid the cost of extraction and use the total biomass of high tannin content materials as a raw material for adhesive formulation, prospects for substitution of phenol in wood adhesives seem more favorable.[36] Following on the work of Mistsunaga and co-workers,[37] we have explored the reactions of catechin under sulfuric acid-catalyzed phenolysis.[38] Opening of the pyran ring with substitution of the C-2 carbocation by either phenol or even the phloroglucinolic A-ring is the main reaction involved with catechin. More work needs to be done to learn about the reactions of oligomeric and polymeric proanthocyanidins. However, this product does seem to have potential to accelerate the cure speed of phenolic resins used in oriented strand board or plywood adhesives. Here whole bark might replace phenol at about 35 cents/lb.

Opportunities to exploit the complexation of tannins with metal ions have only just begun to gain attention. Tannin-aluminum complexes are important in vegetable tanning of leather.[5,18] The literature on this subject is growing rapidly and I cannot provide a thorough review on this topic for you now. We have collaborated with Dr. Peter E. Laks in the development of tannin-based wood preservatives using complexation of the tannin with copper ion, and those products are effective wood preservatives.[39] Scalbert and his collaborators have recently expanded on this theme and have done some extremely interesting work on the complexation of tannins with iron as an explanation for the mechanism by which tannins provide natural resistance to fungi that must rely on phenol oxidase enzyme activity.40 Readers interested in this topic are encouraged to contact Dr. Scalbert for his most recent results.

Currently, most of the interest in condensed tannins lies in their anti-oxidant properties and human health through diets containing high tannin content. The very successful 18th International Conference on Polyphenols, appropriately held in Bordeaux France in 1996, concentrated to a large extent on the "French Paradox" where people with exceptionally high fat diets also have an unusually low incidence of heart disease because of their use of red wines and fruits containing high tannin content.[41] Extracts from the bark of *Pinus pinaster* and grape seeds are sold throughout the world as over the counter anti-oxidants. These compounds are also active against some cancers.[42] An enormous amount of the effort on tannins now being directed to the health benefits of high tannin diets in Europe and the consumption of green tea in Asia.

We have begun some exploratory studies to investigate the potential for use of tannins as industrial anti-oxidants.[43] For most applications it is necessary to modify the structures to make them soluble in hydrophobic polymer systems. While making a fatty thiol derivative solves that problem, we must also find ways to improve thermal stability so that these derivatives can withstand the high temperatures encountered in processing of thermoplastics.

Much of the commercial and ecological significance of tannins lies in the propensity of condensed tannins to form complexes with proteins. Therefore, we have devoted much of our effort to obtaining an understanding of the shapes and flexibility of these molecules and how they form complexes with proteins, either in the formation of leather from raw animal skins or in their activity in stopping extra-cellular enzymes associated with micro-organism including bacteria and viruses. This effort has gone on for over 15 years and it is impossible to provide an adequate review in the space allotted here. However, a review of that work should appear in print soon.[44]

I want to take time to mention two recent works. After many years of effort to define bond lengths and angles of a number of flavan-3-ols through crystal structures, molecular mechanics using a number of different force fields, molecular dynamics and search methods, and NMR experiments, we were finally able to fully assign the NMR spectra of two phenolic dimeric procyanidins in water, the solvent of biological interest. We were able to explore the effect of changing from an organic solvent to water on the preferred shape of of these molecules. When in water, these compounds prefer to be in a comparatively compact high energy state that seems to be stabilized by hydrophobic interaction.[45] In organic solvents, these compounds exist in two different conformations that are only loosely held because they exchange in the short time course of an NMR pulse and acquisition sequence.

Similar preference for hydrophobic association and/or hydrogen bonding to amino nitrogen has been proposed as the primary driving force directing the complexation of polyflavanoids to polypeptides. However, in our NMR experiments on the mixtures of catechin or dimeric procyanidins with various polypeptides containing proline, we found that the aromatic protons on either the A- or B-ring of the flavanoid and the most conformational accessible protons in the polypeptides stayed close to each other and there was not a strong preference for interaction with proline.[46] Even though much more work will be needed to

paint an accurate picture of tannin- protein complexation, we are beginning to make some progress that might help both in developing new uses for bark and in helping to explain the biological significance of these compounds.

In closing, we should go back to consider why all the advance in our understanding of the chemsitry of tannins has not yet resulted in a significant commercial enterprise in North America. Location of a processing plant close to concentrations of the resource is one of the critical parts of the requirements for success. Here, the forest industry holds an advantage over most other agricultural crops because large amounts of bark are available at most pulp mills or many horizontally integrated forest products processing complexes. It is also critical that a bark processing plant be located immediately adjacent to a wood processing plant that can accept spent extracted bark residues and any chemical processing wastes that might occur. This also argues strongly for placement of such a plant immediately adjacent to a pulp mill.

A second aspect that has been critical has to do with business culture. A mismatch in business culture is the primary reason that there has not been more success in use bark as a source of specialty chemicals on the part of the forest industry. Management must be skilled in small-volume, high-value, widely-diversified businesses. Specialized technical and marketing skills directed to a wide range of specialty chemical and pharmaceutical markets are needed. There must be an especially heavy investment in research and development. In contrast, most of the forest products companies in North America are large-volume, commodity-oriented business. It would seem that partnerships between the forest products and specialty chemical businesses would be required to match the resource with the business culture needs.

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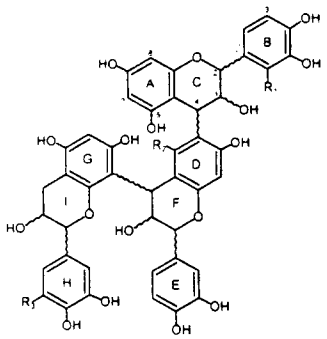
Figure 1. Proposed Basic Structure of Conifer Bark Tannins



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