UTILIZATION OF DOUGLAS-FIR BARK

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FOREWORD

Although basic research on bark utilization has been underway for many years, with numerous significant results, the work has not yet produced an economic outlet for the major part of the bark accumulating at wood products manufacturing plants in the Northwest. With environmental quality control limiting burning--generally the cheapest and most feasible bark disposal method--interest in developing economic uses has grown.

To give scientists entering the field a "leg up," Dr. J. Alfred Hall was commissioned to prepare this technical review of Douglas-fir bark uses. Dr. Hall was formerly director of the Forest Service's Forest Products Laboratory at Madison, Wis.

Acknowledgment is made to Weyerhaeuser Co. for permission to reproduce bibliographies on quercetin and dihydroquercetin as well as making available several reports and copies of patents; also to Miller Freeman Publishing Co. for permission to reproduce plates published in October 1942 issue of *West Coast Lumberman*.

Many of the abstracts shown as quotes in this report have been simplified by Dr. Hall for the purposes of the subject being discussed.

Mention of companies or products by name does not constitute an endorsement by the U.S. Department of Agriculture.

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CHAPTER I

SUMMARY AND CONCLUSIONS

The Douglas-fir region produces annually about 1.5 million tons of bark that must be disposed of some way. Existing outlets are taking substantial quantities of bark, but cannot effect much reduction in the pile of waste bark.

Increasing public demand for abatement of air pollution, e.g., from "wigwam burners," makes imperative exploration of all possibilities of commercial use of Douglas-fir bark.

The physical and chemical makeup of old-growth Douglas-fir bark is unique and lends encouragement to increased attempts to find uses for it.

USES OF WHOLE BARK

Power fuel.--There are indications of expanding use of bark for generation of power, especially for the forest products industries and metropolitan or smaller municipal areas.

Domestic fuel.--As for domestic fuel, it appears that existing equipment is capable of making satisfactory briquets of Douglas-fir bark, similar in usefulness to the well known "Presto-Log." Increasing use of planer shavings for other purposes than compressed fuel may encourage use of bark for domestic fuel in the form of pressed logs.

Pyrolysis and charcoal manufacture.-- Charcoal can be made from Douglas-fir bark by conventional methods of dry distillation, and some production of charcoal briquets from bark has begun rather recently, but with no recovery of the products of distillation. The yield of charcoal from Douglas-fir bark is considerably higher than from wood.

Considering the chemical composition of Douglas-fir bark, I suggest that research be conducted on pyrolysis under reducing conditions, at relatively low temperatures and under high vacuum in order to recover possibly valuable products. Such recovery might make pyrolysis of bark quite profitable.

Board and tile manufacture.-- Much work has been done on the use of barks for board and tile manufacture, or in molding compounds for various uses. Most of this work has been done in Europe where appreciable quantities of board are made from various barks.

As for Douglas-fir bark, work has been done mostly in taking advantage of the plastic and thermosetting properties of the raw material without additives. Some commercial production of boards containing large proportions of bark has been carried out, and some continues.

Suggestions are made for further research in the field of use of Douglas-fir involving use of the basic, known, chemical features plus additives, in attempts to improve the usefulness of the bark or its physical fractions. As old-growth fir is exhausted, the use of second-growth bark, with lower content of cork, will bring about changes in technique.

Agricultural use.--Dr. W. B. Bollen of the Pacific Northwest Forest and Range Experiment Station estimates that about 100,000 tons of bark per year are used for agricultural purposes in the Pacific States. Dr. Bollen's extensive work in the field gives the basis for proper use of bark as mulch or soil improver and amendment, with much fine data on proper use of nitrogen with bark.

Present unsystematic marketing of raw, ground bark is expected to develop into better organized production and specific uses on specific soils. Various additives and methods of improvement are cited and discussed. Suggestions are offered for treatment of dry bark with anhydrous ammonia and subsequent heat treatment with formaldehyde to produce a product with bound nitrogen in slowly available form.

A review of the considerable amount of related literature dealing with other barks is presented.

PHYSICAL FRACTIONATION

An historical survey is given of the many efforts to develop and market products based on physical separation of the bark into its principal fractions: cork, fiber, fines.

The surviving industry producing these fractions is at Longview, Wash.(Weyerhaeuser Co.). The patents involved are listed and discussed, along with the multitude of uses suggested.

Twenty years' experience by Weyerhaeuser Co. in producing and marketing the physical fractions have resulted in a continuing business of modest size. One of the best markets has been for fines in drilling muds. Considerable success has also been obtained in fields of use for the cork fraction. The fiber fraction has been found quite satisfactory for wide use in reinforcing certain plastics, especially when further refined by chemical means.

A major difficulty in the field of marketing physical fractions has been uneven demand. Physical fractionation as the basis for a multiproduct business might give greater flexibility.

WHOLE-BARK EXTRACTS

More work has been reported on extracts from whole hemlock bark than for Douglas-fir. A large amount of effort is reported on combinations of "polyphenolic extracts," with formulations for use in resins. Water extracts and various alkali extracts, along with various condensing agents, are described. Also, uses of extracts for drilling muds, tanning agents, etc., are listed.

Some of this work has led to successful businesses, mostly applied currently to hemlock but with appreciable inroads being made by Douglas-fir.

The usefulness of crude aqueous or alkaline extracts of whole bark might be expanded by better knowledge of their actual chemical composition.

GENERAL CHEMISTRY OF DOUGLAS-FIR BARK

In spite of the expenditure of much manpower and money, the general chemistry of Douglas-fir bark remains unsatisfactory from the point of view of a basis for successful diversified chemical industry. The raw material is highly variable, according to age of tree, height in the trunk, and probably site.

Good information is available on the nature of the wax and cork fractions, although the nature of the "phenolic acid" component of the latter is still open to much questioning. This class of materials, the phenolic acids, comprises most of the fines fraction and is a component of the fiber fraction, both products of physical separation.

Dihydroquercetin is the only specific pure chemical thus far obtained in quantity, and its markets are limited.

WAX

Wax is obtained by solvent extraction of whole bark and from the cork fraction after treatment with alkali.

During the 1950's, considerable interest was shown in Douglas-fir bark wax for commercial development. Decreasing use of the natural waxes, along with economic problems of a single product industry based on bark, have caused failure of any commercial production. Earlier indications of combined production of wax, tannin, and dihydroquercetin were not realized.

The composition of the wax is reasonably well known, not offering any physical superiorities over other better known natural waxes. In the future, if demands for natural waxes increase, or costs of production of Douglas-fir bark wax decrease by virtue of a multiproduct industry based on bark, wax by direct extraction and by hydrolysis of cork might become important.

CORK

The physical cork fraction has been rather well characterized, except for the phenolic acid content. It contains dihydroquercetin in considerable percentage (mostly over 15 percent). Wax content varies from 5-10 percent. The hydrolyzed wax (alkali) yields an array of hydroxy acids and unsaturated fatty acids, along with around 40 percent of phenolic acids.

Much more work should be executed to determine:

(a) The nature of the phenolic acids from cork.
(b) The mode of combination of these with the wax acids.

ALKALI EXTRACTS

The voluminous work on various alkali extracts and their proposed uses is reviewed. Much of the work, especially by Weyerhaeuser Co., led to a pilot scale operation and some attempts to market various fractions for various purposes. The concept of solvent extraction of wax components from the alkaline extract was developed. But, with the exception of limited success in invading the drilling mud field, little of lasting value seems to have been accomplished.

Again, it seems clear that much more intensive work in the basic chemistry of Douglas-fir bark must be done before accurate guides can be developed for commercialization.

FIBER

The crude fiber fraction of the bark, physically separated, averages around 40 percent. The older trees have bark of lower fiber content, the younger ones, higher. In future processing of young-growth bark, the recovery of values from the fiber should be increasingly important.

The fiber is left as a residue from alkaline extraction. Chemically, after exhaustive refining, it appears to be similar to ordinary wood fiber but differs from it widely in physical form. This purified fiber amounts to around 22 percent of old-growth bark.

The principal survivor among products of "alkaline extraction" is the refined fiber. This product is meeting with considerable success as an ingredient of various resins for improving strength and other properties.

Attention is called to the fact that much time and effort of the nature of "industrial service" was expended in order to achieve even the limited success of bark fiber.

TANNIN

The chemistry and uses of tannin from Douglas-fir barks are surveyed. Aside from drilling muds, no large commercial uses for tannin extracts from domestic barks are at present important. Leather manufacture, in general, uses imported tannins or chemical processes.

The tannin from Douglas-fir bark belongs to the general class of "condensed," "catechol," or "phlobatannins," according to the nomenclature preferred.

Like other vegetable tannins, there may be uses that can be developed, either through processing with other substances or splitting into component molecules of usefulness and economic value.

But, in the form of crude tannin extracts or concentrates, the material does not appear attractive unless it can be made cheaply as a byproduct of a multiproduct industry.

DIHYDROQUERCETIN AND QUERCETIN

Dihydroquercetin is distinguished as the only pure chemical compound that has been made from Douglas-fir bark in commercial amounts. The derivative, quercetin, is easily obtained. Much work has been done on uses for both compounds without developing markets that warrant large-scale production.

If such uses ever develop, an excellent source is available in Douglas-fir bark, especially in the cork fraction of old-growth bark.

"PHENOLIC ACIDS"

This term has been accepted as including a great number of substances abounding in barks, generally characterized as having more phenolic and carboxyl groups than lignin. Since these substances were measured as "lignin" in conventional lignin analyses, they were long considered as lignin until much work showed that their constitution was quite different. Much effort has been expended in the general field, and an appreciable proportion of it was done on Douglas-fir bark. No attempt was made in this report to review more of the voluminous work than that on Douglas-fir and a little on hemlock and redwood.

The rather high content of these materials, especially in the fines physical fraction of Douglas-fir bark, and the promising chemical reactivity of the material and many fractions derived from it, render it quite attractive as a source of chemicals, especially phenols and phenolic derivatives for possible use in the plastics and adhesives. Even though pure substances may not be obtained except at prohibitive costs, the possibility of reactive and standardized mixtures is encouraging.

The fundamental difficulty is the fact that, with all the effort expended, the true constitution of the phenolic acids still eludes us.

The key to utilization of this important bark fraction is in the obtaining of thorough understanding of its nature. Also, a principal factor in basing a successful multiproduct industry on Douglas-fir bark lies in ability to utilize the phenolic acids fraction.

The task of unraveling the chemical puzzle will be long, tedious, and costly. But, a long-range program, adequately financed and staffed with capable chemists of mature postgraduate caliber, should be able to do the job.

Previous efforts to use this material in processes based on inadequate knowledge of the true chemical nature of the compounds concerned have been, for the most part, failures. There are not likely to be any quick successes. But if the necessary research is accomplished, we can have some answers that will determine whether a successful industry can or cannot be based on this part of the bark.

ADHESIVE COMPOSITIONS

Seventeen patents and many published articles covered in this report deal with methods for producing adhesive compositions from Douglas-fir bark. Most of the work reported has been in the field of adhesives for plywood, laminated lumber, particleboard, and other types of resins. Most of the effort has been expended in empirical experimentation, doubtless with results that were encouraging. But the industries concerned have become more sophisticated over the years, and requirements now are for adhesives and resins of standardized and predictable properties. The preparation of such materials from Douglas-fir bark does not seem impossible but has not been done.

With future increase in bark from younger growth, the percentages of potential phenolic materials will increase.

CHAPTER II

INTRODUCTION

Although really accurate figures are not available, it appears that about 1,500,000 tons of Douglas-fir bark per year produced in the Douglas-fir region are not used for any purpose. This figure includes bark removed from logs in manufacture of lumber and veneer and not used for fuel or sold for any use. In short, it has to be burned as waste or disposed of otherwise.

Use for various agricultural purposes is large and expanding but, because of transportation costs, is not expected to consume much of this huge pile of bark. Efforts have been and are being made to use this material in various ways; for charcoal, compressed for domestic fuel, in making artificial boards, etc.

Worldwide, much work has been put into utilization of bark in general, but a large proportion has only a general relation to the specific problem of Douglas-fir bark. This bark is unique in both its physical and chemical structure, as well as the availability of a huge supply.

It seemed desirable to collect under one cover reports of work applicable directly to Douglas-fir bark in order to facilitate later studies in the field of its utilization. Also, it seemed appropriate to include such work on other coniferous barks as might be reasonably closely related to the central problem. Therefore, I have covered physical and chemical work, uses of whole bark, physical fractions, and chemically prepared fractions.

I have interpolated my own comments on the reports of work presented and my suggestions for future work in the hope that these may encourage and aid further efforts to solve the basic problem. Most available economic data have been omitted because they are obsolete.

CHAPTER III

ANATOMY

In cross section, starting at the center of the tree, the following general anatomical divisions occur: pith, wood (xylem), cambium, and bark (phloem). Some of the cells in the bark form a **cork cambium** called the **phellogen**. This cuts off more cells to the outside than to the inside; the outer cells are called **phellem**. The cells on the inside of the cork cambium are called the **phelloderm**. Taken together, these three layers constitute the **periderm**. This and associated nonfunctional phloem constitute the outer bark or rhytidome.

Rhytidome is a term derived from the Greek word meaning wrinkle and refers to the appearance of the outer bark when it consists of layers of cork alternating with layers of tissue cut off by the cork (Esau 1965, p. 338-339).

In general, the trees lay on the same number of growth rings of phloem as of xylem. But the subsequent history of bark in older trees is one of physical and chemical changes.

The most complete description of the structure of Douglas-fir bark is given by Chang (1954):

> GENERAL FEATURES
>
> Bark, mostly thick to very thick but highly variable in different localities, usually about 1 to 2 inches thick in thin-barked trees, about 5 to 6 inches, sometimes up to 1 to 2 feet thick in old or thick-barked trees. Outer surfaces of young trees rather smooth, grayish, slightly broken into scales and appearing brownish underneath; bark from old trees rather rough and broken into deep furrows with small scales that are mostly connected, grayish brown on outer surface.
>
> Periderm in old or thick-barked trees well developed, rather thin in thin-barked trees or young stems; variable in cross section from fine lines to very broad bands, sometimes up to about one-half inch wide, composed of 15 or more layers of periderm cells and usually mingled with some comparatively narrow bands or lines; light creamy yellow in color, in contrast to deep, rather brilliant-brown secondary phloem tissues on cross and longitudinal sections; fibrous, with diffuse fibers visible to naked eye. Inner bark about one-eighth to one-fourth inch thick, lighter in color than outer bark; only diffuse fibers and parenchyma cells distinct under lens.
>
> MICROSCOPIC STRUCTURE
>
> Periderm usually composed of 2 to 3 layers of phelloderm, a layer of phellogen, and broad phellem variable in number of cells and formation of layers. Phellem cells mainly thin walled and uniform in thickness but occasionally with layers of, or sporadically distributed, thick-walled cells which were probably transformed from phelloderm; rectangular to nearly square in cross section, about 30 to 50 microns in tangential dimension and about 50 to 90 microns in radial dimension; often at least 30 cells in a layer. The last-formed phelloderm cells comparatively thick walled and mingled with parenchyma cells of secondary phloem; simple pits distinct in those cells in outer bark rhytidomes. Phelloderm and phellem often contain 'resinous' substances; small crystals observed in phellem cells.
>
> Sieve cells rather regularly arranged in cambial region, 2 to 6 cells, mostly about 3 cells in a radial row, interspersed by parenchyma cells; sieve cells in outer part of inner bark mostly obliterated and indistinct; active sieve cells about 20 to 30 microns and about 50 microns in radial and tangential dimensions, respectively, in cross section; length variable in different specimens, from 1.5 to 4.5 millimeters, mostly from 2.5 to 3.7 millimeters. Sieve areas usually partially crowded, not evenly spaced; alined mostly in single rows on radial surface of sieve cells, occasionally with pairs or a few cells close together vertically, and at a small angle to vertical axis of sieve cells . . . .
>
> Fibers differentiated rather early and often only 15 cells away from cambium; solitary or sometimes 2 to 3 in small groups but without definite pattern, diffuse and rather crowded at certain locations; more or less circular and slightly irregular in cross section; about

> 50 microns in diameter and 600 microns to 1.5 millimeters long, mostly about 1 millimeter, tending to be longer in inner bark than in old outer bark. Cell walls thick with distinct lamellate layers and a very narrow lumen; simple pits rather distinct.
>
> Parenchyma cells appear singly or 2 to 3 in short radial multiples in more or less discontinuous tangential lines, rather continuous lines in region close to cambium . . . . Individual cells about 100 to 200 microns high with flat to more or less rounded end walls; containing abundant 'tanniferous' substances and crystals with rectangular lateral faces.

Grondal (1942) published an excellent article on Douglas-fir cork which will be covered more fully in the chapter on physical fractionation. His photomicrographs of anatomic features are included in the appendix.

> ...Deep cork formation occurs at a relatively early age in the life of the tree, and the phellem of the secondary periderm often functions for many years, producing anastomosing lunes of cork in which annual growth layers are usually clearly visible to the unaided eye. Between the lunes of straw-yellow cork, which in the very thick bark on the butt logs and stumps of large trees are in the form of very wide tangentially disposed bands, are areas of dark red, dead phloem tissue. The bast fibers in this tissue are slender, elongated, thick-walled and brittle. . . .
>
> The dead phloem tissue is hard and inelastic. It contains large, but as yet quantitatively undetermined amounts of tannin and other extractives. [Refer to Benson 1915, 1917.] Somewhat empirical experiments indicate that, when ground to a powder, this material may be used in plastics, as well as for the production of tannic acid, but from the standpoint of cork recovery, it presents a major problem.

During World War II, considerable interest was generated in Douglas-fir bark as a source of cork, since Mediterranean cork was in short supply. This interest was the cause for Grondal's work. During the same years, the Forest Products Laboratory did work along similar lines, summarized in an unpublished report by Arthur Koehler.[1/] In this report is another brief discussion of structure:

> Douglas-fir in the Pacific Northwest has next to the thickest bark of any native species, being exceeded in this respect only by the giant sequoia and closely seconded by redwood. The bark at the base of large trees in western Oregon and Washington sometimes is as much as 12 inches thick, but decreases in thickness rapidly upward . . . . In the drier interior of the country, the trees are smaller and the bark is thinner, although it may be 3 or 4 inches thick in butts of logs and stumps in the Inland Empire region.

[1/] Arthur Koehler. Utilization of Douglas-fir bark. USDA Forest Products Laboratory, Madison, Wis. 1945.

The bark of Douglas-fir, like that of other species of trees, consists of an inner live portion, the phloem, which is about 1/8 to 1/2 inch thick and contains no cork, and an outer dead portion which varies greatly in thickness and consists of alternating layers of corky fibrous tissue. The corky layers range in thickness from 1/2 inch or more on butt logs in the Pacific Northwest to almost paper thinness on top logs throughout its region of growth. The fibrous layers range mostly from 3/16 to 1/16 inch in thickness.

The cork in the bark consists of typical thick-walled, more or less isodiametric cells much like that of Mediterranean cork. The fibrous tissue consists of moderately thick-walled, sharply pointed fibers containing more or less dark, gummy material from which a coffee-colored extract is readily soluble in cold water and more so in hot water.

CHAPTER IV

USES OF WHOLE BARK

FUEL

In the two "Bibliographic Series, No. 191" (Roth and others 1960), and "No. 191, Supplement 1" (Roth and Weiner 1968) published by the Institude of Paper Chemistry, there are 163 references on the use of bark as fuel. As would be expected, most of these have to do with the bark from pulpwoods, drying, comminution, methods of burning, either alone or in mixture with other fuels. Since most Douglas-fir bark is produced at sawmills and plywood mills, most of these references have only indirect relationship to the general problem.

In the future, as supplies of old-growth Douglas-fir diminish, and young growth becomes an important pulp species again, burning of Douglas-fir bark for power in pulpmills may become important.

Many years ago, John Rue and E. P. Gleason (1924) of the U.S. Forest Products Laboratory gave the following heat values for barks from various pulpwoods:

Species	B.t.u. per pound
Hardwood	9,410
Lodgepole pine	9,386
Douglas-fir	10,820
Ponderosa pine	9,275
Jack pine	9,870
Balsam fir	8,970
Spruce	9,590

Dry wood has a heat value of about 8,000 B.t.u.'s per pound.

Historically, there has been a major shift in the composition of the manufacturing wastes in the industries operating on Douglas-fir. About 25 years ago, the Northwest pulp industry, mostly operating on hemlock, spruce, and true firs, began to bark its logs hydraulically and chip whole logs. It was evident that barking Douglas-fir logs before sawing into lumber or peeling for veneer could produce bark-free slabs that could be chipped and made available to the growing kraft pulp industry.

This became a regular practice over the years, and Douglas-fir bark became the principal waste of lumber and plywood manufacture. Even trimmings, edgings, shavings, and sawdust began to go into pulp, increasing the percentage of bark in the waste.

In earlier years, before the days of cheap electric power, many plants used their mixed wood and bark to generate their steam for direct power, for electric power, and for operating dry kilns. Widespread electrification plus, in many cases, substitution of gas or oil for wood increased the waste pile that had to be burned to get rid of it.

In the big, integrated plants, especially those involving pulpmills, the problem of waste disposal was not as serious as in the smaller sawmills and veneer and plywood plants. Enormous steam requirements called for use of all available industrial waste for fuel, often supplemented by oil or gas. Sometimes, careless operation caused excessive fly ash and smoke in the vicinity of some plants in certain kinds of weather.

A serious factor in burning bark for fuel is its usually high water content. This arises from river or sea estuary driving and storage, storage and handling in millponds, and, in some cases, hydraulic barking.

This same problem of water in bark fuel plagued the pulp industry for many years, and much literature deals with methods of reducing water content of bark to raise its heat value. The old "Dutch ovens" are still used in many places, especially in the larger power plants. These depend, in effect, upon moving hot gases from combustion through the stream of wet fuel being fed to the furnace, evaporating part of the water and making fuel more easily burned and thus raising its heat value.

Hence, the economics of using Douglas-fir bark for fuel has several factors, some of which have a technological basis. Although there are undoubtedly other factors, some of them may be about as follows:

1. Costs of collection at consuming point.

   In general, transportation of bark by truck may run around 4 to 5 cents per ton-mile. Clearly, the size of bark chunks, packing, and water content will affect the amount of dry fuel contained in a unit of raw material and, thus, cost of hauling.

2. General composition of bark, depending on age of trees, location on trunk, and other factors.

   Bark varies widely in its physical makeup, according to age of tree, location up the trunk, elevation, aspect, and probably other factors.

3. Water and dirt content and costs of reducing it.

   Dry, clean log storage and a dry barking process yield drier bark, but it may contain more dirt. Hydraulic barking or wet storage may reduce dirt and increase water content.

4. Costs of comminution to suitable size.

   The "Dutch oven" is not very selective as to size of chunks or particles. But, for more sophisticated use for power, more uniformity in size is desirable.

5. Costs of controls and mechanisms for insuring clean combustion, with low smoke and fly ash production.

   Low production of smoke and fly ash requires controls to achieve.

A recent article by Verner J. Adkison[2/] gives some good information with respect to the general problem in the upper Willamette Valley. Quoting from Adkison:

> Many of the efforts to burn bark have been in old Dutch ovens with high stacks for increased draft. Natural drafts through the grates were usually hand-controlled and the fuel was batch-loaded into the firebox by drop chutes. The larger part of the fuel was incinerated in the stack, and was characterized by a large plume of black smoke across the landscape . . . .
>
> Modern boiler plants in Eugene and Springfield that are doing a good job are designed with the burning of bark in mind . . . with combustion control systems, metered fuel cells, forced drafts, and induced fans, coupled with mechanical fly ash collectors and smoke indicating devices.

Adkison draws the general conclusion that, in that area, use of bark for power is sound economics and cites several supporting reports.

Whether bulk use of bark for steam, heat, or power generation in the Northwest can become reality is a question of importance and worthy of economic study.

Technology for installations capable of clean burning exists. Gaseous products of combustion should be far less of a nuisance than those from oil for they would carry no SO_2 and much lower concentrations of CO and hydrocarbons. So, some improvement in the general problem of air pollution in metropolitan areas might be expected from proper use of bark for steam. Bark presses have been designed, capable of reducing water content to below 50 percent.

DOMESTIC FUEL

The revolution in fuels used for power generation, following World War II, was duplicated in the field of fuel for domestic heating. Prior to the war, hogged fuel was a widely used material in the Northwest. It was fed by automatic stokers into basement furnaces for hot air or steam heating. About the only present descendant of this era is the Presto-Log, widely manufactured and distributed, mostly for fireplace fuel.

[2/] Unpublished paper presented at the meeting of the Pacific Northwest International Section of the Air Pollution Control Assoc., Vancouver, B. C., Nov. 21-22, 1968.

This product originated around 1933 (Bowling 1933). It was designed to use planer shavings for the most part, and still does. The process compresses the wood at about 15,000 to 20,000 pounds per square inch, to a density of about 1.3. The product, a cylinder about 12 inches long by 4 inches thick, weighs about 8 pounds. Presently, it retails for about 10-12 cents per unit, and the fuel thus costs about $0.0125 per pound or $25 per ton. It yields about 8,250 B.t.u.'s per pound.

For purposes of comparison of heat values, the following tabulation may be of value:

	Approximate B.t.u.'s per pound
Coal	From 10,000 to 15,000
Peat	About 10,000
Lignite	About 11,000
Charcoal	12,000 to 14,000
Wood	8,000
Fuel oils	12,000 to 14,000
Natural gas[3]	24,000
Douglas-fir bark[4]	10,000+
Presto-Logs	8,250

The above figures suggest that Douglas-fir bark might well be considered as the basis for a domestic fuel if it could be processed profitably into some such convenient form as Presto-Logs, or pillow briquets, or extruded cylindrical briquets. It could probably not compete with oil or gas in fuel value per dollar at present prices but should compare well with Presto-Logs in cost per ton. Increasing use for particleboard or pulp of the wood waste that has gone into Presto-Logs may point some interest in the direction of bark.

The chemical composition of Douglas-fir bark indicates that it would probably be self-binding if compressed while hot. The production of a good board or tile at the Oregon Forest Products Laboratory (Burrows 1960b), compressed without additives, is strong indication that this is true.

An adequate product must meet several requirements, aside from cost of production:

1. It should withstand moderate exposure to high humidities without disintegration.
2. It should be tough enough to be handled in transportation or at the point of use without crumbling. Mixture with wood fiber might help.
3. It should hold together during burning as a charcoal briquet does. Other properties, such as odor and smoke during burning must be inoffensive.

There are many possible roads of development, but a few things are clear. The raw material must be ground and mixed, probably to about the size of the product marketed as "Agricultural Bark." It must be dried to somewhere around 8 or 10 percent moisture content (ovendry basis). The raw material might be ground or chopped wet and then dried.

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[3] Figures furnished by Northwest Natural Gas Co., based on 60 pounds per cubic foot of liquid gas.

[4] Rue and Gleason (1924).

There are several forms in which a product may be designed for domestic fuel: pillow form briquet, cylindrical briquet (e.g., 1 inch by 1 inch), extruded rods, logs similar to Presto-Logs, etc. The potential market and its needs will determine the form.

There is little information published on the applicability of any such forms to Douglas-fir bark itself, but some work has been done that is at least suggestive.

Only a few years after the development of the Presto-Log machine, Jefferson B. Rodgers (1936), a graduate student in agricultural engineering at the University of Idaho, carried out a rather large experiment in cooperation with Wood Briquettes, Inc., of Lewiston, Idaho. This company was a subsidiary of Potlatch Industries, who held the machine patents.

Rodgers put about 25 types of material into the logs produced by the machine but included only one bark, redwood. However, he concluded that quite satisfactory logs could be made from everything he tried if it was dried to below 8 percent moisture content. He suggested some modifications in grinding (hammer mill) material for pressing and small changes in design of the pressing die.5/

As far as is known, there are no present commercial developments of Presto-Logs based on bark. Brown Co. (New Hampshire) produced them for a while but discontinued the operation as uneconomical.

Rodgers states that, with some materials, better bonding was obtained if the material was mixed with wood.

At Oregon Forest Products Laboratory, the work of Burrows (1960b) on hardboard indicated difficulty in press release unless the platens were cooled before release. Presto-Logs are cooled before release.

An article by Walter W. Letts (1951a) appeared in a report of a conference on wood fuel at Philadelphia. And in another, Letts (1951b) discussed a patented method of producing briquets from sawdust and other forest wastes, including pulpwood bark. The material produced was being marketed under the registered name of "Letts Burnets." It consisted of small cylinders, 1-1/8 inches in diameter, broken into short lengths. Apparently it was an extrusion process. A brief description is given by Reineke (1964):

> . . . operating on a multiple piston system. Eight or 16 extrusion tubes produced stoker-size briquets 1-1/8 inches in diameter and several inches long. The pressure faces of each piston, or ram, had a dimpled center and scalloped radial grooves, the imprints of which improved the interlocking of successive charges of material, so that there was less tendency for the briquet to break up into small disks. The product was satisfactory, but production ceased on retirement of the developer.

A letter from Sandy Hill Corporation, which manufactured the Letts press, is in the appendix. The machine may be of basic interest and is apparently worthy of consideration for development.

5/ Personal communication from Mr. Reinmuth, of Potlatch Industries, in charge of "wood briquettes," states that they have had little success in pressing bark.

A letter from Dr. John Rowe at the Forest Products Laboratory in Madison, Wis., (September 17, 1969) describes a fuel briquet obtained by him from the Japanese Forest Products Laboratory in Meguro, Tokyo, Japan. This product is an extruded continuous rod about 2 inches in diameter, with a small hollow core, about three-eighths of an inch, being manufactured commercially in Hokkaido from spruce and fir bark. Production in 1964 was 5,000 tons. The product is made on a continuous press at the rate of 1 meter per minute. Bark is pressed at 8-9 percent water content at 400° C. and 70 kg. per cm.^{2} for a residence time of one-half minute. A letter from the Government Forest Experiment Station, Meguro, Tokyo, Japan, giving up-to-date (1969) information, is reproduced in the appendix.

As of May 18, 1970, Oregon Timber Products Co. at Albany, Oreg., had, in early stages of operation, a plant for production of fuel briquets from ground Douglas-fir bark. The proposed product is made by continuous extrusion as a cylinder about 2.75 inches in diameter, with a hollow core about 0.62 inch in diameter. The briquets for distribution may be cut to any length, but plans are to market 13-inch sticks.

The four briqueting machines are made by Nisshin Company, Ltd. (see letter from Mr. Yonezawa in the appendix), and are rated to handle 124 tons of bark per 24-hour period. Auxiliary equipment includes grinding, screening, and drying machinery.

According to preliminary information, the moisture content of the material fed to the press must be between 5 and 15 percent in order to prevent possible fire or blowing.

Attention may be called to an interesting article by Millstein and Mørkved (1960). The article deals with spruce bark, but the methodology of experimentation offers some good ideas. An abstract is quoted from "Bibliographic Series, No. 191, Supplement 1, Institute of Paper Chemistry" (Roth and Weiner 1968, p. 113):

> Lab. expts. were designed to study the relationship between mfg. variables (temp., moisture content, adhesive used, etc.) and the quality of briquets made of sawdust or bark of spruce (*Picea excelsa*) or pine (*Pinus sylvestris*) at a const. pressure of 1000 kg/cm.^{2}. A gen. quality improvement with increasing temp. (from 20 to 100°C.) was obtained up to moisture contents of 15-16%. The opt. moisture content was 10% at the lower and 8% at the higher temp. .... Briquets made from spruce bark alone showed a good quality over a wide range of temp. and moisture content. Full-scale investigations showed that bark with moisture contents up to 50-60% (based on o.d. wt.) can be ground continuously in a hammer mill to a particle size comparable with sawdust, dried in a flue-gas (suspension) drier, and pressed into fuel briquets in a 20-ton plunger extrusion press. Spruce bark in particular gave good briquets and when mixed with sawdust, made an efficient binder. The quality of briquets contg. pine bark resembled that of sawdust briquets. In gen., bark required a slightly lower power consumption than did sawdust.

All things considered, the following points seem clear:

1. Bark is available in quantity.
2. It probably can be processed into a form of high density briquet suitable for domestic fuel.

3. Drying to below 10 percent moisture content, and grinding (hammer mill) are essential steps before compressing.
4. A fairly high temperature in compression seems desirable; probably higher than that reached in Presto-Log manufacture.

Increasing demand for sawdust and planer shavings for pulp manufacture and particleboard indicates steadily decreasing supplies of wood waste. Perhaps there is here a field for bark utilization.

PYROLYSIS

The literature on pyrolysis of bark is not abundant. Probably the reason for this lies in the general availability of wood for manufacture of charcoal and the ease of conversion of wood into lump charcoal compared with the granular and friable, such as charcoal produced from barks. Lump charcoal was about all there was in the older days of charcoal making, and the comparatively simple methods used left no incentive to use bark.

Also, barks in general accumulate dirt which appears as ash in charcoal. For backyard barbecues this is unimportant but, for industrial use, it usually is a disadvantage. Briqueted charcoal for domestic use apparently could be quite satisfactory when made from bark.

The old process of making charcoal from wood is prehistoric. Former large-scale industrial production in large plants, with recovery of the products of distillation, has not survived. There are many small plants and some big ones in the United States today still producing charcoal for domestic or industrial use, mostly ground and formed into briquets. Recovery of byproducts is rare in this country. Production of charcoal from bark is quite small, in spite of the fact that, in general, the yield from bark is considerably higher than that from wood.

A brief discussion of the use of barks in charcoal manufacture is given on pages 649-652 of Browning's "The Chemistry of Wood" (1963).

In general, most reported work has dealt with conventional procedures borrowed from the technology of wood pyrolysis. An exception is an article by Euler, Hasselquist, and Lo̎or (1947). This article deals with making the raw material acid or alkaline, producing distillation decomposition products of wax and phlobaphenes.

Another suggestive article (Browning 1963, p. 652) deals with conversion of the bark of *Betula verrucosa* at 500° C. The tar from this distillation is reported to include a large neutral hydrocarbon fraction, containing mostly aliphatic and alicyclic compounds.

A report by Bergström (1957) gives data on various methods of wood distillation and yields of conventional recovery products and presents a complete bibliography of his reports to 1957. Little attention is given in this report to bark, but yields from bark of pine, spruce, and birch, distilled by conventional methods, are tabulated on page 123. Yields of charcoal are higher than from wood of the same species.

Bergström stated:

> The tar from pine and spruce bark is very thick and granular and solidifies when the water is removed. The noncondensable gas obtained during charring of pine bark contained, after cooling down, a light yellow powder which gradually was deposited in the pipes of the distillation apparatus as a yellow sticky mass.

No further mention of investigation of the chemical nature of this substance was made.

Work is reported on vacuum distillation of tar and hydrogenation. Products listed are: lubricating oils, phenols, tar for rubber compounding, etc. Also reported is work on heating wood with $Ca(OH)_2$ at 270° C. in water and under pressure. Water-soluble products and oils are formed with a solid residue consisting of the calcium salts of organic acids.

Water-soluble products and oils can be obtained from this residue by destructive distillation. The water-soluble products are mostly alcohols. The oils contain phenols, hydrocarbons, and higher alcohols. Appreciable yields were obtained of acetone, methyl ethyl ketone, and higher ketones.

This work was on wood, by conventional methods. It might be of considerable interest to investigate the lime technique on bark.

The report includes interesting reference to hydrogenation of wood but without reference to publications. Apparently, the hydrogenation was carried on at 430° C., with Cu, Ni, Co, and other catalysts. Bergström also states:

> Experiments in production of liquid fuel showed that the wood, when heated under suitable conditions at 270° C. with wood tar only, and also with other oils, could be changed into liquid form without catalysts and without hydrogen gas.

A footnote to this article:

> The publications of Kolningslaboratoriet are grouped together in Products from Wood,' Series I, parts 1, 2 and 3, and in Series II, parts 1, 2, 3, 4, 5, 6, 7, 8, and 9. A more comprehensive List of Publications is given in 'Products from Wood, Series II, Part IX.
>
> Unpublished works have been collected in 45 volumes and kept at Kolningslaboratoriet.

PRODUCER GAS

During World War II, shortages of petroleum for motor transport led to considerable work on the substitution of wood or charcoal for this purpose. A great deal of motor transport in Europe, especially in Germany and Sweden, used the process. In general, the fuel was the old "producer gas" made by interaction of carbonaceous material and water vapor at comparatively high temperatures, a process yielding a mixture of CO, hydrogen, and a little methane. Charcoal was the preferred base material, since wood produced tarry, acidic distillates in addition to the fuel gas, necessitating scrubbing devices ahead of the motor. About 700,000 gasogens were reported in use in Europe in 1942.

Much work was carried out in the United States and other allied countries on this general process, although it did not become necessary to use it to any appreciable extent.

The work at the U.S. Forest Products Laboratory was summarized in 1951 by Miller. Canada had done earlier work on the subject (Jenkins and Guernsey 1936).

It is of historical interest to note an article by George S. Wilson on this subject in 1917. This article gives much engineering data, based on the use of "hogged fuel" at 0.5 cent per cubic foot.

The Russians have apparently continued experimentation and developmental work on the use of wood or bark as power fuel, with most orientation toward production of "gasified wood" for use as fuel for power generation at steam plants.

An article by Lyamin (1965) was abstracted by the Institute of Paper Chemistry (Roth and Weiner 1968):

> Samples of softwood bark (moisture content 21.5, 25, 48 percent) were gasified in an experimental 'LTA apparatus,' and analyses were made of the fuel gas (purified in a scrubber, tar-separator, and condensation trap). The yield of gas from bark was 25-30 percent higher than from wood. The overall gasification efficiency was about 78 percent. Tar from bark differed widely in composition from that obtained from wood.

That article and several others refer to the "LTA apparatus" or the "Lyamin furnace." It appears that the only one revealing some detail about the apparatus is by Lyamin and Bolśhakova (1959), but it was not abstracted at Appleton.[6] It describes the LTA apparatus, the initials probably referring to "Leningrad Technical Academy."

A rather poor plan is presented. Yields of tar, gas, and calorific values are given. It is proposed that removal of tars, etc., increases the availability of the moist gas for use as fuel in internal combustion engines. Missing are data concerning the mixture of air, water and other gas fed through the generating furnace.

The following abstract of a paper by Kromina and Tischenko (1965) may throw a little light on the subject:

> Thermolysis of wood in a gas generator or a gas-generating furnace differs essentially from the process of dry distillation (due mainly to better heat-exchange conditions and gasification in a continuous flow of gas *containing up to 15 percent H*) and resembles decomposition in vacuo in a reducing medium. Because of rapid entrainment of decomposition products from the low temperature zone by the flow of gas, nonvolatiles and substances of low volatility reach the gas-scrubbing equipment. As a result, the wood gasification tars, especially the soluble tars, differ in their composition from dry distillation tars.

In the article by Lyamin and Bolśhakova (1959), no data are given on the actual temperature of pyrolysis. The temperature of air admitted to the generator is given as 13° C.; "gas temperature in gaso-generator orifice [entrance or exit?] 92° C. to 116° C." None of the articles abstracted give data on pyrolysis temperature.

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[6] Copies of original articles by Lyamin (1965) and Lyamin and Bolśhakova (1959) are on file at Pacific Northwest Forest and Range Experiment Station, Portland, Oreg.

In a subsequent article, Kromina and Tishchenko (1966) discuss gasification of bark in the "Lyamin furnace."

Soluble tars from wood and bark differed considerably in composition, the total yield being much less from bark. But the soluble tar from the bark contained more phenols than that from wood (7 percent: 4.14 percent).

About all that can be said with certainty about the above reports is that the process apparently involves a low temperature pyrolysis in a stream of air containing hydrogen, scrubbing or condensing volatiles, or doing both and using the resulting gas for fuel either for furnaces or internal combustion motors.

A U.S. patent issued in 1965 to Warren I. Lyness (assigned to Buckeye Cellulose Corp.) is of interest:

Small pieces of bark, lignin, or sawdust are pyrolyzed at 20-100 mm. Hg. and at 150°-500° for 5 minutes to 4 hours while passing through the bed of material formic acid vapor mixed with an inert gas such as N, CO_2, or superheated steam. The yield of the liberated compounds of low-molecular weight, especially guaiacol, vanillin, and catechol, is greatly increased, and the yield of charcoal is correspondingly reduced. However, I was informed April 17, 1970, by Buckeye Cellulose Corp. that they have not used this patent.

Only one publication (Kurth and Ratnam 1950) dealing with pyrolysis of Douglas-fir bark has appeared. The authors carbonized bark cubes (about 1 inch) in a retort heated by a muffle furnace. Temperature of carbonization was measured with a thermocouple in the mass. Provisions were made for separating and estimating condensable and non-condensable products.

Fourteen runs were made with temperatures from 745° F. to 910° F. at various lengths of time. Charcoal yield at 910° F. and 2.5 hours was 42 percent of the weight of the charge. Naturally, at lower temperatures the yield was higher.

Beyond the usual determinations of yields of volatile products (methyl alcohol, acetic acid, acetone), the presence of phenols up to 6.7 percent of the bark was shown. Also, the presence of a long-chain acid, possibly lignoceric, was demonstrated.

Probably the most important result was demonstration that Douglas-fir bark gives a yield of charcoal possibly 35-40 percent higher than Douglas-fir wood. In spite of this fact, little charcoal has been made from Douglas-fir bark.

At the present time, a firm in Medford, Oreg., is reported to be producing charcoal from a mixture of bark and sawdust. This firm is preparing to manufacture its product into briquets in the near future. At Springfield, Oreg., Kingsford Chemical Co. started manufacture of charcoal from fly ash. It is now using mostly sawdust and bark in unrevealed proportions to make briquets. Both plants apparently pyrolyze in a conventional way.

There appears to be small economic prospect for recovery of volatile distillation products from charcoal manufacture from either wood or bark by conventional methods of pyrolysis.

But, from hints in the literature, one may hypothesize that something might be done in destructive distillation of Douglas-fir bark under conditions designed to recover products of thermal decomposition in usable form.

It will appear later in this report that Douglas-fir bark can be roughly separated by physical means into three fractions: fiber, cork, and fines.

The fiber fraction is largely carbohydrate and lignin, and could yield charcoal in about the same way as wood. But, as will appear, the fiber is becoming useful for purposes much more valuable.

The cork fraction has a quite different chemical composition as compared to the other two, but a large proportion apparently consists of the "phenolic acids," combined with long-chain aliphatic acids and alcohols.

The "fines" fraction, separated by physical means, will carry portions of the other fractions, but will be very largely composed of the "phenolic acids." As will appear, these are bodies of poorly determined chemical nature, but certainly quite different from ordinary lignin, probably of flavonoid polymers in a higher state of oxidation.

If it were desired to find out if any part or all of the bark could be made to yield products of pyrolysis of useful nature, it seems to me a beginning should be made on the fines fraction. This would avoid mixture of products from cork and fiber with those from fines, which may be expected to be quite different from the other two fractions.

An apparatus might be designed to provide for:

1. Operation under reduced pressure in the entire system, probably around 20 mm. or less.
2. Pyrolysis chamber so arranged as to give accurate and controlled temperatures from, say, 300° C. to 600° C.
3. Pyrolysis to take place in a reducing atmosphere. (Vide: Russian use of hydrogen. Lyness' use of formic acid.)
4. Very rapid removal, condensation, and refrigeration of products of distillation.

The objective of the experimentation should be removal of products of pyrolysis from the zone of pyrolyzing temperature as rapidly as possible, thus preventing interreaction of expected very reactive substances. In ordinary wood pyrolysis, there is an exothermic reaction that begins when the wood is hot enough to initiate exothermic decomposition of cellulose. The products of thermal decomposition undergo another exothermic reaction in the vapor phase according to some evidence.

I have found no evidence, positive or negative, with regard to an exothermic reaction in bark but suggest that pyrolysis be carried out at temperatures below that required to start the process in wood.

Possibly a fluidized bed process could be designed that could accomplish this end. Possibly the fines fraction could be suspended in a high boiling stable material, liquid at operating temperatures, recycled as a means of carrying the fines into reaction and the carbon out. I recall experimentation in Madison, Wis., on carbonization of wood in a bath of "Wood's metal." Maybe that will not work but it could be tried.

If encouraging results can be obtained in a laboratory apparatus, one could proceed to pilot scale operation and think about pyrolysis of whole bark. But the early work should be carried out as straight research to find out facts upon which a process might be based.

BOARD AND TILE MANUFACTURE

Apparently, only one venture into commercial manufacture of a hardboard containing large percentages of Douglas-fir bark has been attempted--that by the Oregon Lumber Co. at Dee, Oreg., in the 1950's.

In Europe, various barks are used, either for all or part of the furnish for artificial boards.

Blossfeld (1961) reported that, in East Germany, 20,000 tons of spruce bark are used annually in the manufacture of wood particleboard. Presumably, a mixture of bark and wood is used, as is often the case.

Machacek and Martykan (1962) reported on the results of their work in Czechoslovakia on use of bark in making insulation board. Procedure and machinery for preparing the bark and producing board are described. The board produced was from bark of softwoods, but satisfactory operation of machinery could not be attained without addition of wood fiber to the furnish. Generally, enough wood fiber was contained in the bark from mechanical barking to give satisfactory results. Most of the preparation and manufacturing procedure described in this work does not depart much from conventional insulation board processes in this country.

The board produced was reported to have these properties:

Density	360 kg./m.^{3}
Flexural strength	4-6 kg./cm.^{2}
Water absorption (24 hr.)	40 percent
Compressibility (5 kg./cm.^{2})	9 percent
Heat insulation	0.07 kcal./m./hr.

Suggested uses were:

1. Roof insulation of panel houses.
2. Heat- and sound-insulating layers under wooden floors.
3. Middle layers of crosspieces.
4. Vertical and horizontal insulating elements in industrial and agricultural buildings.

A pilot plant started in 1959-60 was successful; and in 1962, design was completed for a plant with annual capacity of about 230,000 m.^{2}, to be introduced in a lumber mill that uses a barking process.

A few observations reported in this work may have general applicability to the question of manufacture of board from conifer bark.

1. Bark fiber is apt to be brittle and breakable and to felt poorly. [Douglas-fir bark fibers seem to have greater strength.]

2. Bark, with some wood fiber, gave good boards.

3. Paraffin was added in emulsion form to the extent of 2 percent of the dry solids in the furnish. The wax content of Douglas-fir bark should make this unnecessary.

This article refers to several unpublished reports by the staff of the "Wood Research Institute," indicating high interest in the general problem of bark utilization, both from hardwoods and softwoods, wastes from pulp and tannin manufacture.

Similar results had been reported in Canada (Clermont and Schwartz 1948). This work was also aimed at production of insulation board from what was mostly pulpmill bark waste. The amount of ether-soluble material in the bark had a proportional sizing effect.

Anderson and Runckel (1950) reported the successful production of hardboard from Douglas-fir sawmill waste containing from 15-45 percent bark.

The wax content of the bark was reported to serve as the water-repelling agent in a wet process hardboard, eliminating the necessity of adding sizing agents.

A mill using this process was built by the Oregon Lumber Company at Dee, Oreg., with a capacity of 120,000 square feet per day of 0.25-inch board. A flowsheet of the process was presented (Anonymous 1952a). The process in use at Dee was patented in 1957 by Lighthall and Anderson in Canada.

The plant was operated for a number of years on this basic process by the Oregon Lumber Co. and later by Hines Lumber Co., which took over Oregon Lumber Co. When U.S. Plywood Corp. acquired the Dee plant, the process described above was discontinued and replaced by one using all wood. Reasons given included:

1. Bark did not stay mixed well with ground fiber in the furnish tank. This was cured by more vigorous stirring.
2. The board was low in paintability. This was cured (or might have been) by a thin coating of resin.
3. Bark fibers made the surface prickly. Light sanding remedied this.
4. Color was too dark.
5. Dirt and sand in the bark caused trouble.

The process used slabs from the sawmill, chipped and fiberized in an Asplund Defibrator. In the beginning, it was attractive because the raw material was cheap and the wax content of the bark component gave good properties. However, within a few years, the growing market for pulp chips made removal of the bark before sawing slabs economically attractive, and this removed unbarked slabs as a source of raw material for hardboard.

In fact, at present, probably the best way to consider a mixed bark and wood board is to remove the bark, prepare the wood fiber and bark components separately, and blend according to board properties desired. A large number of references in the bibliographies of the Institute of Paper Chemistry (Roth and others 1960; Roth and Weiner 1968) indicated this to be true for coniferous species.

When the Dee process was developed, use of bark made additives unnecessary and thus saved money. Because of the change in demand for pulp chips, this advantage probably disappeared in spite of the fact that the technical properties of the mixed board were good. Further, because of variable chemical composition of the bark and the variable amounts included in the furnish, production of board of standard uniformity must have been difficult. But the matter of suitability of Douglas-fir bark alone for board and tile manufacture still attracted interest, because the chemical composition of the bark indicated strong possibilities for producing good sheets of molded boards or tiles.

Clark Heritage of Weyerhaeuser Co. indicated (U.S. Pat. 2,697,081, 1954a) the preparation of "a thermo-setting composition of selected Douglas-fir bark components and phenol-formaldehyde resin." In a subsequent patent (U.S. Pat. 2,697,082, 1954b), he claimed to control the flow properties of a low resin, bark-filled, molding compound by incorporation of predetermined quantities of the cork fraction. It will be observed that the objective in these patents was a molding compound rather than a board. Several other attempts have been made with western redcedar, redwood, and other barks.

Perhaps the most comprehensive studies in use of whole Douglas-fir bark in making boards or tile were reported by Burrows (1960a; 1960b). The orientation here was quite different; viz., toward dry process hardboard or particleboard made without any additives. The study was designed statistically to study effects and interactions of:

1. Particle size
2. Moisture content (12, 16, and 20 percent)
3. Pressing pressure (150, 300, and 450 pounds per square inch)
4. Type of overlay (none, 60-pound kraft, and 1/10-inch veneer)

There were 324 boards made under various conditions, and physical data were recorded. A pilot run was also made in the Cascades Plywood Corp. plant, Lebanon, Oreg. (now U.S. Plywood Corp.).

In the laboratory, good boards resulted. In the pilot plant, considerable difficulties were encountered, especially "blows" and sticking in the press. Burrows (1960b) reports that these were corrected by cooling before removal from the press. He ascribed these troubles to too high a moisture content and too high a content of bark fines, but no clear evidence is adduced that these were the basic reasons. It seems possible that evolution of CO_2 by thermal decarboxylation might have taken place. If so, the inclusion of too much "fines" would have made it worse.

Burrows' (1960b) conclusions were:

> 1. A board product containing essentially all bark can be manufactured without additives. Douglas-fir bark contains constituents which, under proper conditions of heat and pressure, will self-bond sufficiently to form a panel. [This is not enough. Considerable speed in operation is requisite for commercial success, and this process is slow.]
>
> 2. Physical properties of barkboard can be altered significantly by changing pressing procedure and by applying overlay materials. Moisture content of the mat can influence properties somewhat; particle size has little effect on properties. Physical properties are generally comparable to those of commercial particleboard and hardboard. Specific gravity and thickness of barkboard range between those of wood particleboard and hardboard. [It is suggested that work be done

> using simple additives to react with phenolic hydroxyls, carboxyls, and/or aliphatic hydroxyls known to be present. The objective might be better properties, higher press speeds, simpler unloading and cooling.]
>
> 3. With some modifications, a manufacturing system for wood particleboard could be used to make barkboard. Major modification would be a press capable of being heated and cooled rapidly. [But this is indeed a major change and is bound to slow things.]
>
> 4. Analysis comparing cost of manufacturing wood particleboard to estimated cost of manufacturing barkboard indicates that manufacture of barkboard is practical. [Needs reanalysis.]

In this work, the material was hammer milled, dried in the laboratory to about 12 percent, screened to -4 + 10, -2 + 10, and -2 + 20. It appears to me that these fractions are not very comparable, especially when mat moistures of 12 percent, 16 percent, and 20 percent were used. Cork and fiber fractions of the bark do not grind very well, even when dry. Perhaps work on more completely separated physical fractions would be profitable. Perhaps chemical treatment of the fines fraction--for example, before mixing with the other fractions and pressing--would give better bonding and no blows, even with removal hot from the press.

There are present, at least theoretically, components of phenol-based resins as well as polyesters. It might be possible to produce more reaction points by incorporating oxidizing agents.

Mild alkali treatment liberates "phenolic acids" that are apparently combined in the untreated bark. Why not try that, then mild acidification to get more reaction?

The carboxyls, plus some carbonyls, dry, should react with anhydrous ammonia, yielding amino groups to react with formaldehyde.

A raw, coarsely chopped bark might serve as filler in a thick panel, covered with two sheets of 1/4-inch plywood, similar to Heebinks' "pulp chip" panel at the U. S. Forest Products Laboratory.

The phenolic fraction, mostly in the fines and hydrolyzed cork, might be a basis for preparation of an adhesive of **controllable** properties for use as a binder. A further suggestion for possible improvement in board properties was given by Lehmann (1968):

> Several variables influencing the process of molding whole-bark-extended compounds (primarily Douglas-fir bark) into a deep-draw cup mold were studied. Douglas-fir bark exhibited reasonable flow properties without the addition of any binder for simple shapes; however, 10 percent resin had to be added to achieve satisfactory flow for deep-draw molding. Temperature of the bark was important in producing good flow, and cooling of the mold was necessary to prevent blistering. A supplementary study of the use of whole Douglas-fir bark in combination with thermoplastics for injection molding suggests that whole Douglas-fir bark can be added as an extender to certain injection molding compounds except where color clarity is critical.

AGRICULTURAL USE OF DOUGLAS-FIR BARK

The barking of Douglas-fir saw logs and veneer logs made available large quantities of bark, mostly but not entirely free from wood. Attention soon became attracted in the Northwest to the possible use of this abundant material in agriculture as soil improver or mulch, raw or untreated, and sometimes with nitrogen added in some form. During the past 20 years, and at an accelerated rate in the past few years, use of Douglas-fir bark for these purposes has grown until it amounts to a large annual tonnage. In general, this widespread use has been without correspondingly widespread knowledge of how best to use the material.

Dr. W. B. Bollen (1969, p. 1) gives the results of a 1968 questionnaire to county extension agents and sawmills. A conservative estimate of use of bark for agricultural purposes in the Pacific States is given at 100,000 tons per year. "Peat moss" or "moss peat" is reported as being marketed in the United States at an annual rate of 500,000 tons.

Bollen points out the reduced availability of sawdust, wood shavings, and chips and the possibility of bark for many agricultural uses formerly served by these materials (mulches, soil conditioners, animal bedding, etc.)

The literature on general use of organic wastes in agriculture is indeed voluminous and impossible to cover in this report. Nor can attention be given to the widely scattered work on many barks and woods, so we shall focus on Douglas-fir bark and some other subjects that involve general principles applicable to that subject.

A generalized publication by Franklin E. Allison (1965) gives extensive results in the general field but with scant reference to Douglas-fir bark. However, this publication carries a reasonably good bibliography. Insofar as it touches problems common to Douglas-fir bark and other material, results are comparable to those of Bollen and his coworkers.

Douglas-fir bark is available in the West, in bulk or in bags, under various brand names, raw or treated with addition of nitrogen, composted in various ways, mixed with hemlock or other barks, or of Douglas-fir bark alone. A rough measure of costs is given by the price of bulk ground bark in Portland, delivered at $15 per unit (200 cubic feet). When bagged, the cost goes to $0.80 to $1 per 2 cubic-foot bag. If the product is improved by addition of nitrogen, the price goes higher. Clearly, delivery to points distant from place of origin adds cost.[7/]

There is little system in the present market. Fineness of grinding, inclusion of wood fragments, moisture content are only a few of the variables met. It may be expected that systematic preparation and marketing of Douglas-fir bark for agricultural use will be future developments, and that such publications as those of Bollen and coworkers will influence such developments to a great degree.

[7/] The chemistry of organic nitrogen in soils, forms, reactions, assimilation by plants, and the innumerable interactions of the soil microflora with nitrogen, is basic to the intensive study of soil amendment by bark. Perhaps the most complete modern review is "Soil Nitrogen" (1965), published by the American Society of Agronomy, Madison, Wis. Edited by W. B. Bartholomew and Francis E. Clark.

Toxicity

There have been and still are many popular beliefs concerning relative merits and disadvantages in use of various forms of wood wastes and bark, either as mulches or soil amendments. Bollen (1969, p. 13) states:

> A former belief that tannins, resins, and other wood extractives have a toxic effect on plants when wood residues are added to soil has been found largely erroneous. We have learned from research that any "toxicity" noted after bark or other wood products are used on or in the soil is most likely due to a nitrogen deficiency that can easily be remedied by adequate fertilization.

That there are substances in some other western barks and woods that may exert negative influences on plants is reviewed by Bollen (1969, p. 17). But extensive work in his laboratory fails to show deleterious effects due to Douglas-fir bark.

A publication by Bollen and Lu (1969), dealing with the tannin of Douglas-fir bark and its fate in soils, supplements the above. In this experimentation, the workers used a "tannin" extract from bark after removal of waxes, flavonoids (such as dihydroquercetin), and phlobaphenes. It is to be observed that the "tannin" fraction may have included "phenolic acid" complexes.

The authors suggest that, because of the moderate decrease in nitrification effected by tannin, leaving bark on forest soils should lower nitrate production and decrease nitrate in water supplies in forest streams. This matter may also have significance in agricultural use.

Bollen (1969, p. 13) refers to previous work by Aspitarte (1958), who found that Douglas-fir bark tannin liquor, equivalent to 2,000 p.p.m. carbon, was 33 percent decomposed in 60 days in Willamette silty clay loam. Wax was only 17 percent decomposed and -20 mesh cork, 8.5 percent.

Grinding and Screening

The difference in composition of the various physical fractions of Douglas-fir bark and the influence of grinding and screening procedures in manufacture will doubtless have considerable influence upon its behavior in or on the soil.

Bollen (1969, p. 15) points out that Douglas-fir bark, ground to pass a 16-mesh screen, can be mechanically separated into the following percentages of different fractions:

Cork	-16 +35 mesh, 25 percent
Bast	-35 +170 mesh, 25 percent
Fines and dust	-170 mesh, 50 percent

This last fraction consisted of broken cork and bast plus parenchyma and sieve cells. When it is considered that such distribution will vary according to the age of the bark, the fineness of grinding, and moisture content, the variability of the material is emphasized. The known wide differences in chemical composition of the physical fractions, which will appear in later discussion, determine the wide differences in behavior in the soil. Bollen points out that cork (-60 mesh) decomposed most rapidly; bast (-35 +170 mesh), next in order; fines (-170 +250 mesh), third; and dust (-250 mesh), least.

Use as Mulch

Bollen (1969, p. 18) suggests that bark for use as mulch might well be a screened grind, ranging from one-half inch to fines, with the majority of the particles ranging from one-fiftieth to one-eighth inch (approximately 32 to 6 mesh). This portion of his bulletin (p. 18-22) gives an excellent treatise on the use and value of the bark in mulching, with many valuable suggestions based on his extensive experimental work. The addition of nitrogen in some form is recommended, with reasons and results spelled out. In discussing nitrogen addition to bark for mulch, he pointed out that, since relatively little bark is in contact with the soil at any time, little additional fertilizer nitrogen is required until plant roots extend into the mulch.

Soil Conditioning

When bark is to be incorporated into the soil, addition of supplemental nitrogen becomes important. The bark is now mixed with the soil, in contact with the plant roots. Bollen (1969, p. 25) recommends 10 or 20 pounds of nitrogen per ton of bark to bring the C:N ratio to near 50:1. Explicit directions are given to obtain maximum value in improving the tilth of heavy soils by utilizing the high cation exchange capacity of the bark, its decomposition to humus, improved water penetration, and better aeration. For sandy soils, increased humus content and water-holding capacity are achieved.

Ammoniation and Composting

Bollen (1969, p. 4-6) treats of nitrogen requirements of bark; the sources of nitrogen such as ammonia, nitrates, ammonium salts, vegetable refuse, manure and sewage sludge; and the process and value of composting.

Various bark composts are on the market. Ivory and Field (1959) reported on the preparation and marketing of white fir bark and its popularity in culture of orchids.

Bollerslev (1968) reported on the process employed at Emmett, Idaho, by the Boise Cascade Corporation. Species of bark processed are ponderosa pine, grand fir, Douglas-fir, spruce, and larch. In this process, the hammer milled bark (half-inch screen) is sprayed with aqueous ammonia (20 percent) and composted at 135° to 150° F. It is ready for market in about 90 days in winter--a little longer in summer because of less heat loss from the frozen surface in winter.

Bollerslev reports that all of Boise Cascade's soil conditioners are now a fine grind, screened to eliminate wood and fines. He reports production of 150 tons per day. Private reports to the writer state that it is being shipped to the east coast.

A more recent article (Sullivan 1970) on the operations of Boise Cascade Corp. reported production at Emmett as up to 350 tons per day, using all bark produced at Emmett. About 40 percent is going into "chunk bark."

Bollen and Glennie (1963) reported on the use of fortified bark, and Bollen (1969, p. 4-5) gives a condensed report on the use of ammoniated bark, describing both spraying with aqueous ammonia and treatment of the wet bark with anhydrous ammonia. "Ammoniation also softens the needlelike bast fibers of Douglas-fir [bark] so that they lose much of their objectionable handling properties." As would be expected, because of the differing chemical composition of the physical fractions of Douglas-fir bark, it was found that fibers, cork, and fines absorbed anhydrous ammonia in different amounts. Bollen points out the desirable feature of ammoniation in that it introduces both quickly and slowly available nitrogen.

Other workers have reported on fortifying and treating sawdust and bark for soil conditioning: Voigt, Brenner, and Wilde (1949) and Davey (1953) described use of anhydrous ammonia on sawdust; Isomäki (1967) summarized recently started work in Finland; Burton (1959) reported on the use of redwood bark as a trickling filter in sewage disposal plants; and Allison and Klein (1961) compared rates of decomposition of 10 kinds of woods and barks.

In 1957, the Armour Research Foundation, in cooperation with Canadian Forest Products, Ltd., reported on a method of converting bark to a soil builder (Anonymous 1957a, 1957b). The process is reported as involving grinding and condensing the tannin by addition of formaldehyde. This was followed by acidifying with hydrochloric or sulfuric acid, heating to complete the condensation, and washing and drying. The product was reported as improving moisture-holding capacity of soil, serving as a base for fertilizer, and controlling the rate of absorption of plant food from the soil. I found no reports as to commercialization of the process.

This appears to be a variation on various processes of reacting bark with formaldehyde, mostly for adhesive compositions.

Ornamental

At present, several companies are producing lump forms of various barks for ornamental use in home gardens or elsewhere. In general, these are of low agricultural significance, although eventually they will be incorporated into soil.

They are made from selected pieces of thick bark, coarsely subdivided by mechanical means, and smoothed and rounded by an abrasive process; e.g., tumbling. The fines produced may appear as agricultural bark.

Discussion

In the extensive study carried on in this part of this report, it has been surprising to find only one reference to the work of Maillard in France, as early as 1912. In "Soil Nitrogen" (Bartholomew and Clark 1965, p. 119), a brief paragraph is devoted to his work. Basically, Maillard (1912, 1917) thought he demonstrated the formation of "melanoidins" and humic substances by the reaction of the reducing sugars and similar substances with amino groups. Subsequent work along these lines is discussed in "Soil Nitrogen," especially methyl glyoxal-amino condensations.

Many years ago (1926), when I worked on the manufacture and properties of concentrated orange juice for the California Fruit Growers Exchange, our principal problem was the darkening of orange concentrate. This was a 72-percent-solids syrup. On aging at room temperature, it turned brown, eventually evolving carbon dioxide in spite of being sterile.

In work never published, I was able to show the reaction was between reducing sugars and amino acids. One of the principal reactors was ascorbic acid or vitamin C.

Later, working on aging of tobacco for Liggett & Myers, I found the same type of reaction responsible for the darkening of leaf tobacco. Since the rate and amount of darkening was proportional to amino N concentration, the idea of accelerating the process by increasing amino N arose. This I did by treating dry tobacco leaves (about 2 percent moisture) with anhydrous ammonia in vapor phase. Upon subsequent humidification (about 12 percent) and exposure for a few days to humid and warm air, the tobacco was aged quite well.

This little history suggests the possibility of treating **dry** or nearly dry Douglas-fir ground bark with anhydrous ammonia in vapor phase. The presence of carboxyl groups and probably carbonyl groups, and certainly phenolic groups, in the phenolic acids should bring about the binding of considerable NH_3 in the form of amide or amino groups. Further reaction should take place with the free carbonyls of sugars and pentosans, uronic acids, and possibly lactones. Probably also, depending on fineness, NH_3 would be adsorbed.

If any considerable amounts of N are thus bound, subsequent treatment with formaldehyde and heat should bring about condensation with amino groups and formation of materials with slowly available N.

Preliminary treatment of the bark with an oxidizing agent--probably in the wet condition--and subsequent drying, might create other points for reaction with gaseous ammonia. Such a product, subsequently fortified with quickly available N should have valuable properties in supplying nitrogen, both quickly available and slowly available over a long term.

This suggested procedure might be found especially applicable to the bark fines because of their high content of phenolic acids and the necessity of sometimes separating them in ground bark manufacture.

Dr. Bollen told me that work had been planned but not carried out on the nature of the nitrogen combined and adsorbed by Douglas-fir bark.

In the publication by Bollen and Glennie (1963), table 2 indicates that even treating the wet bark with gaseous ammonia gave 1.68 percent N, of which 0.66 was in amide form.

Related Patents

Several patents in related fields are abstracted by the Institute of Paper Chemistry (Roth and others 1960; Roth and Weiner 1968):

Santmyer (1957) states "Nematodes and other parasitic worms in soils are controlled by the application of chlorinated quebracho bark." This suggests chlorination of the cork-wax fraction of Douglas-fir bark for production of possibly biodegradable insecticide.

McCully (1960) describes a method of preparing a resin-bearing material, the resin having ion-exchange properties. The method comprises mixing previously untreated bark of 1-20 percent tannin content (e.g., Douglas-fir or hemlock bark) in particulate form with aqueous formaldehyde, heating at a rate of 2° to 10° C. per minute from room temperature to 75° to 95° C., and then acidifying the mixture to pH_1 with continued heating to complete the resin formation.

A second patent by McCully (1965) suggests further improvement. A resin of use as a soil conditioner is prepared by mixing a moist tannin-containing bark in particulate form with crystalline urea, heating the mixture, adding aqueous formaldehyde and acidifying to pH_1 with rapid heating up to at least 75° C. at 2° to 10° per minute to effect resin formation on the bark. The bark can be hemlock, Douglas-fir, etc.

CHAPTER V

PHYSICAL FRACTIONATION

As has been indicated in the section on "Anatomy," Douglas-fir bark is especially noteworthy because of the reasonably well-defined zones of cork, fiber, and fines. This structure is characteristic of old-growth bark. Younger trees have bark lower in cork and higher in fiber and fines, with the last carrying a higher content of tannin than in old bark.

The earliest published recognition I found of the possible industrial significance of this unique structure is an article by Guy C. Howard, chemical engineer, of Seattle, in 1923. Mr. Howard obtained U.S. Patent No. 1,455,762 for a process of recovering cork and other products from Douglas-fir bark. The process consisted of grinding and screening the bark to separate cork granules or flakes from the pulverized fibrous constituents.

Howard was interested primarily in the tannin content, but in his examination and experimentation on Douglas-fir bark came to the conclusion that much greater potential values lay in the physical fractions. Quoting from his article:

> Cork cells are common to most kinds of bark but in the Douglas-fir particularly--this cork component is a pronounced feature and constitutes a considerable percentage of the bark. It is a true cork and has the peculiar characteristics of structure that give to cork its well known properties. Fir bark will average around 33 percent of cork.

His discussion of Mediterranean cork, production and uses, concludes that Douglas-fir cork, associated with the fibrous constituent, can yield only a granular product that will not equal the best quality of Spanish cork but has properties and cheapness that make it a material of industrial value. Suggestions for its use include insulation and soundproofing in linoleums and floorings. Concerning fiber, he states:

> The fiber product of bark is a constituent which comes out in the process to the extent of around 33 percent by weight. It is a clean, reddish colored, fibrous material which is flexible when wet and dries to a strong fiber of papermaking qualities. Its market will be in the making of box board shipping containers, building papers and similar grades. Also for wall board, core stock for plywood, insulation products, and so forth.

These uses for fiber have not materialized for various reasons. The bark fiber has been found more valuable for other purposes, as will appear in the section on chemical fractionation. The physically separated fiber fraction is heavily encrusted with the phenolic substances and is structurally dissimilar to wood fiber, which is filling most of the suggested uses. Quoting Howard further:

> Associated with the cork is a considerable percentage of wax, equal or better than beeswax in quality and resembling it in appearance.
>
> The tannin content of fir bark will average around 6 percent by weight on the air dry bark. The inner or cambium layer of fir is richer in tannin than the outer layer. . . .
>
> Fir tannin has been used commercially to tan leather but its quality is not fully recognized in the trade although it is regarded as similar to the hemlock product.
>
> Bark is being used as both a domestic and industrial fuel, but its possibilities as a domestic fuel for Pacific Coast cities in competition with coal have not been touched. In the process under discussion the fuel value serves simply as a means of utilizing that portion of the bark not marketed in other forms.
>
> Bark can be recovered . . . by debarking the log enroute to the sawmill by passing it over a set of rossing rolls in combination with suitable disc guides. . . . .
>
> Chemical procedures are a mental hazard to many people, hence a mechanical process is preferable if it will secure the same result. Fortunately, in this instance, it will and the necessary treatment involves only mechanical operations carried out in standard types of equipment. Roughly, this consists in drying the bark to a suitable condition, subjecting it to progressive and classified grinding and screening operations in conjunction with dust arrestor equipment to collect a fine mesh product. This effects the segregation of the bark into cork, fiber, wax and tannin products, and a residual product suitable as fuel. The cork comes out because of its greater resistance to grinding and the fiber product represents a portion that has not been pulverized by the operation. . . .
>
> The matter is now in the same position as any other pioneering project previous to its being established commercially save that the basic conditions essential to its success are all favorable and its feasibility is almost self evident.

The somewhat optimistic views expressed were not to be realized. Howard was well ahead of his time for nobody in the lumber industry was willing or prepared to undertake the type of production and marketing problems involved. Yet, Howard's process, with refinements and more sophisticated equipment, did actually develop into a small industry. But principal outlets for cork and tannin and wax decreased over the years as other materials took over the functions formerly served by these fractions. Mr. Howard later became famous as the inventor of the process for manufacture of vanillin from sulfite waste liquor.

Shortly after the outbreak of World War II, attention began to be given to Douglas-fir cork to replace, in part, unavailable Mediterranean cork. In 1942, Bror Grondal reported on work on the problem at the University of Washington. At this time, the United States was using about 200,000 tons of Mediterranean cork per year, but this use has dropped to about half that at present.

Grondal estimated that the State of Washington, at that time, could produce about 100,000 tons per year. He did much work on selection and grading of bark, drying, grinding, screening, etc., with primary emphasis on the cork fraction.

The raw cork had satisfactory insulating properties but contained tannin and "other extractives" causing rapid corrosion of iron and steel in the presence of moisture. Extraction of the crude material with a weak ammonia solution and washing removed these materials and improved the physical structure of the cork cells by expanding them. Although the material produced, combined with a synthetic resin, was thought to be useful for many purposes, there was no commercialized production.

Shortly after the war, Weyerhaeuser Co. (then Weyerhaeuser Timber Co.) carried out extensive experimental and pilot plant work at Longview, Wash., evidently with the intention of creating a multiproduct industry based on Douglas-fir bark. An important contributing factor was the growth of plywood manufacture and improved methods for removing the bark from peeler logs before starting the peeling of veneer.

Ray Hatch, of Weyerhaeuser Co. (Pulp Division), received a patent (1948) on cork preparation. Hatch's patent deals with hammer milling, screening, and abrading in a rod mill, primarily to recover cork.

A month later, Pauley (1948), in the Research Division of Weyerhaeuser Co. at Longview, Wash., received a patent on preparation of cork and fiber. The bark was hammer milled, partially dried, screened to remove fines, finely comminuted in a ball mill and screened. The fractions were "coarse cork, fine cork and pure [sic] bast fiber. The fibers vary from 0.016 to 0.051 inch in length and from 0.0016 to 0.0055 inch in diameter." It will be noted that this process was designed to recover fines, cork, and fiber.

A year before the issuing of the patents described above, Elliot Marple (1947) had described the line of "Silvacons" being produced at Longview. This report described use of these products in thermosetting plastics and in cold molded plastics.

> Silvacon 508 was described as consisting of bast fibers; for use in increasing strength of plastics.
>
> Silvacon 383 consisted primarily of cork flakes up to one-fourth inch in size. This material was recommended as a resin extender when mixed with other Silvacons.
>
> Silvacon 490 was a "fine, amorphous powder, reactive with alkali and other chemical reagents, and used in plastics only when mixed with other Silvacons."
>
> Silvacon 412 was a combination of cork and fiber.
>
> Silvacon 472, "the most versatile of the products, is a combination of cork, lignified fiber and powder."

In subsequent advertising, various fractions and mixtures of fractions were marketed under numerical designations for a wide range of uses. They were all grouped under the generic term, "Silvacon." None were pure fractions in the chemical sense.

They were recommended for use in the following:

- Drilling muds, for regulation of properties (mostly powder)
- Phenolic molding compounds, as filler and floor improver
- Adhesive extenders especially in plywood
- Rubber products, as an aid in processing and as an ingredient
- Foundry sand as an ingredient
- Vinyl products and flooring
- Thermoplastic resin extension
- Asphalt products and coatings
- Magnesite cement composition

Many attempts to find uses in other fields were made, and some were successful. Naturally, the company is reticent with respect to sales for various uses, modifications of process, etc., but a few conclusions are warranted.

Production of physical fractions of bark still continues on an industrial scale at Longview. A principal difficulty has been uneven sales of fractions, the fines having found the largest market in drilling muds. After some 24 years, the conclusion is probably warranted that the operation is profitable.

In the earlier phase of operation, the yield of fractions was approximately:

- Fiber rich, 30 percent
- Cork rich, 20 percent
- Powder rich, 50 percent

At present, operations are reportedly aimed at "ornamental" bark, with other fractions as byproducts.

It is of interest to note patents by Anway (1948, 1952), one of which antedates those issued to Hatch and Pauley:

> Bark containing from 30 to 80 percent moisture is washed and tumbled to remove sand, rotted bark, sawdust and like material, ground in a hammermill, dried to a moisture content of 15-25 percent in a heated airstream, passed through a ball mill, and then over a series of screens; in this manner, the bark yields 4 percent 14-mesh and 15 percent 28-mesh cork, 18 percent 48-mesh fibers, and 63 percent 48-mesh powder. The bark powder contains lignin and waxlike materials which impart to the powder a plastic character and, therefore, it is suitable for molding compositions.

Nothing further appears to be on record concerning this patent.

Grondal and Dickinson (1953) obtained a patent that appears to have been rather basic, but no information is available on licensing under this patent.

Collins and Williston (1958) (of Weyerhaeuser Co.) obtained a patent on a process of cork production that embodied some small variation. The impure 1/2-inch pieces (maximum) were passed through a differential speed roller mill in which controlled shearing action broke up the cork aggregates and removed the phloem (powder) without reducing the cork particle size. Further refining was obtained by additional steps of milling and separation.

Heritage, of Weyerhaeuser Co., obtained a patent in 1959 that may be regarded as a more sophisticated version of the above and, with regard to the subsequent development of the industry, rather basic:

> Bark is reduced to a moisture content of less than 30 percent by weight, grinding to a mixture of particles having maximum cross-sectional dimensions of less than 0.5 inch and including cork particles, cork containing aggregate, parenchyma particles, and fibers (sclerenchyma) encrusted with parenchyma tissue; screening out most of the cork particles and aggregates, milling the remaining material, screening the milled material to separate a concentrated fiber fraction; abrading this fraction to remove encrustations on the fibers; entraining the abraded material in an air stream, and fractionating out the fiber in an air separator.

Van Beckum and Miller (1962) obtained a patent that describes another method of cork recovery, in which the bark in the form of particles is treated with high-pressure steam and then exploded (as in the Masonite process), subsequently effecting a size classification. As far as known, this was not reduced to practice.

USES OF PHYSICAL FRACTIONS

The usefulness of the various fractions, either alone or in mixtures, has been the subject of numerous articles and patents.

Silvacons--General

Beginning in 1947, quite a flow of general articles dealing with the Silvacons appeared. They were, for the most part, based on information contained in Weyerhaeuser's Bulletin No. 10-A (see Appendix) of the "Silvatek Products Division," which had been created to handle the business of bark products along with some others.

The long list of uses represents the enthusiasm for the potentialities of the products that then reigned. It is perhaps unfortunate that the sales effort, especially the use of "product engineers" trained for the very wide array of industries covered, was not made available. Thus, many of the uses envisioned were not developed to a great degree. Also, as the years went by, great changes in technology changed processes and products. For example, the uses for the cork fraction then announced have been greatly reduced by increased use of various plastics and foamed plastics for purposes than satisfied by cork.

In addition to Weyerhaeuser's Bulletin No. 10-A, other articles dealing with the newly marketed Silvacons were published, some of which were: Anonymous (1947a); Arnst (1948); Van Beckum (1949, 1952); and Weyerhaeuser Timber Co. (1949a, b).

In 1962, R. A. Waldron, of Weyerhaeuser, delivered a paper, titled "The Development and Marketing of Industrial Products Derived from Douglas-fir Bark," at the 16th annual meeting of the Forest Products Research Society in Spokane, Wash. No copy of this paper is available, but the following is taken from an abstract of the preprint:[8]

> There have been many problems involved in their market development work. Their uses [Silvacons] and some of the marketing problems are discussed. Problems:
>
> (1) The selection of personnel with suitable characteristics for working with the technical people encountered and with the wide backgrounds needed.
>
> (2) Developing of whole new techniques for an industry that may utilize Silvacons.
>
> (3) Competition with cheap local products of similar types and many others.
>
> Despite these problems it is felt that a modest success has been made in the development of markets for these industrial products.

This statement came 20 years after the start of research and development leading to Silvacons.

Drilling Muds

Although most of the reports of patents and developmental work subsequent to 1947 can be classified according to specific physical fractions, some are general and many deal with more than one fraction. For example, Nestle (1952) says: "A water base drilling mud contains a seasoned or weathered crude oil; a mixture of the cork, bark-fiber, and bark-powder fractions of Douglas-fir bark; and sodium carboxymethylcellulose." The field of drilling muds was to become important as an outlet for physical bark fractions and, later, for chemical fractions.

In 1960, a reasonably good discussion of the use of bark fractions and other materials in oil well drilling appeared (Miller and Van Beckum 1960). This article is a semitechnical discussion of the technology involved. "The two functions of chemical control [of mud properties] and lost circulation correction provide essentially the entire market for tree-derived products in oil well drilling fluids." The authors list a number of lignin and tannin preparations used.

Caraway (1954) tested 70 materials for use in drilling fluids. Best found included "Douglas-fir bark No. 1" (not otherwise identified).

Patents were granted to:

Heritage (1956b) "Well-drilling fluids."
Drilling mud of clay, sodium hydroxide and a "bark component" comprising cork, parenchyma tissue and sclerenchyma tissue of bark phloem.

Van Beckum (1956) "Oil well drilling fluid."
A composition containing 65 percent cork from tree bark and 35 percent fibrous material from trees is added to oil well drilling fluids to prevent "loss of circulation" or loss of fluid through fissures or cracks.

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[8] Supplied by Dr. Rowe of the Forest Products Laboratory, Madison, Wis.

Tronolone (1957) "Lost circulation."

> An additive for lost circulation comprises a mixture of equal weights of fibrous shredded wood, ground leather, and flaky Douglas-fir bark.

Several other patents dealing with drilling muds will be covered later.

Cork in Boards and Floor Tile

Heritage (1956a) also patented a process for using cork from bark along with parenchyma tissue in making boards or molded articles. The process applies to "the bark of many trees, particularly conifers" (not to Mediterranean cork). The cork and parenchyma tissue is used as a thermoplastic binding material for binding wood fibers or other wood particles for hot-pressed boards or molded products. "The cork component of bark flows with ease when subjected to heat and pressure." The patent describes board made from wood fibers mixed with at least 5 percent of the separated cork component or from 50 to 75 percent of the bark from coniferous trees. The mixture is pressed at 400 p.s.i. at 380° F. for from 5 to 60 minutes.

Two preceding patents by Heritage (1954a, b) had dealt with similar matters on a different basis. One dealt with a composition of "selected Douglas-fir bark components" and phenol-formaldehyde resin. The second described use of cork as a flow modifier in thermosetting phenol-formaldehyde molding compounds containing the bast fiber of bark.

In 1959, Burrows, of the Oregon Forest Products Research Center, published a bulletin describing a technique for making floor tiles similar to that used in making particleboard. His raw material varied from Weyerhaeuser's cork fractions to a cork prepared in the laboratory. He states that the Weyerhaeuser No. 388 was best on the basis of particle size and color.

He added 5 percent by weight of a butadiene-styrene thermoplastic binder to half of the tiles, and 5 percent diethylene glycol to the other half. The latter acted as a plasticizer. Numerous other variables were covered. His tile was three-sixteenths of an inch thick.

He reported that his tile was "about equivalent to, or better than, tile made from Mediterranean cork oak," and that "the estimated retail selling price of floor tile from Douglas-fir cork was favorable when measured against prices of other commercial flooring materials."

Unfortunately, these important experiments took place about the time that some radical changes were occurring in the field of floor coverings. The vinyl tiles, vinyl asbestos, etc., were making heavy inroads. Cork tile was becoming passé. To make matters worse, the thickness of the vinyl and other tiles was one-eighth inch or less, with stiffness of the floor being obtained from the underlayment. This created a better market for plywood and particleboard, but none for cork tile.

Cork in Shell Wads

King (1956) obtained a patent dealing with use of "flaked bark of Douglas-fir," a Silvacon, which is presumably one of the cork fractions. The material is coated with a "sulfur-free synthetic latex and dried before being compressed in molds to form expansible over-powder shot-shell wads of required sizes." Certain advantages are claimed: efficient gas seal, no disintegration on firing, symmetrical shot pattern.

Cork in Patching Veneer

In 1964, Christensen, of Weyerhaeuser, obtained a patent describing a preparation for patching voids in veneer core that consists of 35-65 percent by weight of "a coniferous bark fraction, this fraction being at least 60 percent by weight of bark cork mixed principally with sclerenchyma tissue." The rest of the mixture was 65-35 percent rosin or lime-treated rosin.

In 1965, Oita, of Weyerhaeuser, obtained a patent describing a process especially adapted to paper-overlaid, wood veneer laminates, filling voids in the veneer prior to the application of the paper overlay. The compound consists of "45-60 percent of a cork-rich coniferous bark fraction [e. g., from Douglas-fir bark], 5-10 percent of a tall oil derivative, and 22-50 percent of a pine wood resin [e. g., Vinsol]."

These patents, at least in principle, and with certain automatic machines for application, have been reduced to practice.

Further general references on the cork fraction include Little (1941), Friedman and Ezell (1942, 1943), Anonymous (1942), and Cooke (1943).

Fiber Fraction

With respect to the crude fiber fraction of Douglas-fir bark, separated by the physical processes described above, little is found in the literature. The fraction is complex and, apparently, the fiber content is much more useful when refined by chemical means. This type of fiber will be discussed later.

As previously mentioned, Bulletin No. 10-A (see Appendix) described the probable uses of Silvacons. George Cornwall, then editor of the "Timberman," also discussed them (Anonymous 1947b).

In 1953, Kiefer and Kurth of the Oregon Forest Products Laboratory at Corvallis published work on the chemical composition of the fibers. At this time, the physically separated fibers were being regarded as closely similar to wood fiber. Kiefer and Kurth's work demonstrated radical chemical differences as well as anatomical differences. They reported:

> About 35 to 48 percent of the air-dried bark is composed of short, spindle shaped bast fibers. These have been found to possess an outside wall or matrix of a reddish-brown phenolic acid which is soluble in dilute alkali solutions. The fibers have a high specific gravity, a thick layered or ring-structure cell wall and a cell cavity.

Subsequent work showed the chemical nature of the reddish-brown incrustant to be allied to that of the "powder fraction" and revealed the presence within the fiber structure proper of a small fraction of "true lignin." At this time, the application of standard procedures for wood analysis to this fiber was not very productive of clear results.

Slightly prior to the publication above, an anonymous contribution appeared in "Chemical Processing" (1951). This article discussed the use of Silvacon 412 in asphalt roof coatings. It is described as a fine, granular (28-200 mesh) natural plastic, with an approximate chemical composition given. "Available in unlimited supply... removes the threat of an asbestos-fiber shortage." No further published reference to this use can be found.

A process for preparation of a material for patching plywood sheets made from Silvacon 509 was patented by Jorgenson, Williams, and Miller (1959). The material included a "phenolic resin or the like, a resin hardener, a mineral filler and a 'nonswelling fibrous material' such as Silvacon 509." Extended usefulness of the fiber fraction apparently did not come until chemical processes were developed.

Powder Fraction

The fines or powder fraction produced by physical means found uses in adhesives and especially in drilling muds, although little reference is made in the literature to use of the specific fraction. Several patents on the uses appeared:

Van Beckum and Cook (1951) described an adhesive made essentially from "comminuted parenchyma tissue, bark powder derived from bark phloem, and an aqueous sodium hydroxide solution (20 parts tissue, 40 parts water and 4 parts of sodium hydroxide)."

Ayers and Bradley (1957b) referred to an adhesive previously described (U.S. Pat. 2,781,286, Feb. 12, 1957a) and described replacement of shell flour with bark phloem flour.

The next patent (Baxter, Schoening, and Preusser 1959) refers directly to Silvacon 490, describing use of a residue from wood hydrolysis, methylcellulose, and Silvacon 490 (a Douglas-fir bark phloem product) in compounding a phenolaldehyde adhesive for use in making plywood.

In 1961, Anderson, Breuer, and Nicholls described the use of Silvacon 472 (another powder fraction). Barks, including Silvacon 472, were extracted with hot aqueous sodium carbonate to provide extracts useful in bonding particleboards.

Whole-Bark Extracts

Although the powder fraction of Douglas-fir bark was being used during the period 1950-61 as glue extender for various purposes, no publications on the matter have been found.

On the contrary, considerable interest developed in use of extracts of whole bark.

A good beginning on the subject was offered by Herrick and Bock in 1958. This article deals largely with extracts of hemlock bark, but the principles developed are broad. There is a good discussion of formaldehyde-phenolic reaction in hemlock extract.

In general, polyphenolic bark extracts were combined with polymethylolphenol, either in dry form or as a 40- to 45-percent aqueous solution that is "quite stable at ordinary temperatures." The polymethylolphenol acts as a cross-linking and polymerization agent. Formulations containing 49 percent bark extract, 34 percent polymethylolphenol, and 17 percent filler (unspecified) are described as fast curing and producing acceptable exterior grade Douglas-fir plywood. There is a good bibliography on the general subject.

A little later Herrick and Conca (1960) described the use of resorcinol-formaldehyde resin for cold setting adhesive formulations for similar uses.

The following patents elaborate the general subject further but deal with extracts of whole bark rather than specific physical fractions:

Herrick and Bock (1959b) extracted bark [Douglas-fir or western hemlock] with ammonia and the dry extract reacted with sodium hydroxide. The resulting sodium salts are combined with the sodium salt of a polymethylolphenol for use as thermosetting glue for plywood, laminates, etc. They received a U.S. patent in 1962.

Herrick and Bock (1965) replaced the preliminary extraction with ammonia by extraction with sodium hydroxide. In the mixing with polymethylolphenol, resorcinol is added. This would have speeded up the setting of the adhesive, permitting shorter press times and probably lower press temperatures. The process is applied to "coniferous bark such as hemlock or spruce bark."

Herrick and Bock (1966) mixed a preformed resorcinol-formaldehyde condensate (volume ratio HCHO: resorcinol 0.5 to 0.8) with an alkali bark derivative in a ratio of condensate: derivative 0.5-4. This ratio could have been calculated only from the NaOH, since the composition of the alkaline extract could only be approximated.

In this patent, the patentees state again that the alkali bark derivatives can be a Na-substituted bark derivative formed by reacting a dry aqueous ammonia extract with NaOH in aqueous solution.

A patent to Williams and Baxter in 1960 is similar in general principle to Herrick's patents, with some variations. The comminuted bark was reacted with paraformaldehyde and an alkali. This is a departure from Herrick's procedures. For use, this material was compounded with a phenol-aldehyde thermosetting resin.

All the above patents dealing with adhesives, either from the powder fraction or whole bark, have in common the reaction of formaldehyde with phenolic hydroxyls, in tannins, phlobaphenes, or the phenolic acids, all of which would be extracted in part by alkali.

The alkali extracts also attracted the attention of the rubber chemists. Adams, Messer, and Howland (1951) made a thorough investigation of the use of several materials in producing master batches from butadiene-styrene copolymers and furnace blacks (carbon), the various materials being used as dispersing agents. They used proper mixtures of carbon black, the dispersing agent, and sodium hydroxide. Best results were obtained with "Marasperse LB" (a sulfite lignin product). Also used were Silvacon 490 (powder), "Tomlinite" (an alkali lignin), and several other bark extracts. Good results were reported in using up to 3.0 percent of the extracts.

Howland patented a related procedure in 1954.

Adams patented a process in 1951 (Canadian, 1956). In this process the alkali hydroxide solution of the "amorphous particles obtained from the highly parenchymatous tissues of the bark of Douglas-fir" is used as a dispersing agent. Previously discussed was use of the physical fractions in **drilling muds** as viscosity controls and sealants. Increasing use of various lignin byproducts of the sulfite pulp industry may have suggested the content of the following patents in which the concept of sulfited bark extracts is introduced. Again, in general, they deal with the phenolic content of the bark and the capacity of sulfurous acid to react with it.

Van Blaricom and Gray (Canadian, 1957) describes digestion of Douglas-fir bark with aqueous sodium sulfite or bisulfite, filtering and spray drying the product. This is described as "water-soluble sulfonate derivatives of polymeric phenolic compounds having a high phenolic and low methoxyl content." The product is useful as tannin substitute and viscosity regulator for drilling muds. In effect, the reaction was probably mostly with the phenolic acids, principal components of the bark powder fraction.

The same patentees obtained a U.S. patent in 1958 and a Canadian patent in 1959.

The temperature for digestion of the bark is given as 50-200° C., and the process uses ammonium, sodium, or potassium sulfite. The process of ion-exchange for separating the sulfited products from residual inorganic salts is described. The product is said to be useful as a drilling mud additive and "chemical intermediates."

A variation appears in the next patent in this field (Gray, Steinberg, and Crosby 1960). Douglas-fir bark, or other coniferous bark, was digested with an aqueous solution of sodium or potassium **sulfide** or hydroxide or mixtures thereof at "an elevated temperature to convert part of the water insoluble portion of the bark to a water soluble alkali metal derivative. The product is for use in drilling muds, etc." This appears to be designed to liberate combined phenolics by a technique similar to that used in alkaline pulping processes.

The next patents by Gray and Van Blaricom (1961; Canadian, 1963) add to previous ones by describing use of acid sulfites. The digestion of bark was carried out at elevated temperature with an aqueous acid solution of sodium or potassium acid **sulfite** for production of a drilling mud additive.

The same patentees had another variation (Canadian, 1960; U.S., 1960). The drilling mud additive was prepared by subjecting bark [e.g., Douglas-fir bark] to solvent extraction followed by digestion in an aqueous solution of sodium sulfite. Presumably, the idea here was to extract the free wax components, either to recover the wax or prevent its modifying the properties of the additive or both.

Herrick and Gray, in 1964, came up with a patent similar to the later patent by Herrick and Bock (1966).

In 1965, Hergert and others published an excellent summary of the above and much other work on western hemlock bark. This is a summary of the work of the research division of Rayonier, Inc., at Shelton, Wash., aimed at the production of their dispersant, "Rayflo," a product that has found wide use.

CHAPTER VI

GENERAL CHEMISTRY OF DOUGLAS-FIR BARK

Discussion of the chemical nature of Douglas-fir bark and the many attempts to develop chemical processes of utilization is complicated. This arises partly from two principal matters:

1. The chemical makeup of the whole bark is still uncertain, although a few facts are reasonably well understood.

2. Patents and developmental work were proceeding during progress of most of the work on basic chemistry and include considerable evidence of guesses that usually did not result in commercially successful processes.

The rising rate of interest in the chemistry of barks may be indicated by the distribution of the publication dates of the 251 references given in an excellent chapter on the subject in Browning's "The Chemistry of Wood" (1963):

Prior to 1940	24
1940's	38
1950's	117
1960's	72

Obviously, at the date of publication the 1960's were hardly begun.

In 1961, Gregory and Root, of Weyerhaeuser Co., published an interesting study on bark research in general. They made a statistical analysis of the literature under various headings, but here we are interested in the division, "Chemical Processes." They analyzed 172 references with the following results:

	No. of references
Water extraction	31
Aqueous alkaline extraction	32
Extraction with aqueous salts	18
Neutral solvent extraction	9
Solvent extraction with chemical cleavage	7
Pulping	45
Pyrolysis	7
Hydrolysis	4
Chemical modification	19

Under "Water extraction" were included processes for production of tannin and for various uses such as resin ingredients, dispersing agents (e.g., drilling muds), flotation agents, molding compositions, and natural dyes. Also included were the various flavonoid compounds (e.g., dihydroquercetin from Douglas-fir bark) and studies of their uses.

Under "Aqueous alkaline extraction" are included many processes involving both extraction and chemical cleavage. In Douglas-fir, the basic material involved is principally the indefinite group known as phenolic acids. Also included are numerous proposed processes for use of the various products.

"Neutral solvent extraction" is generally aimed at waxes, oils, fats, resin acids, dihydroquercetin, and related compounds.

Under "Chemical modification," the authors state that most of the literature is devoted to two areas: caustic treated bark for various uses and bark treated for agricultural use.

Various processes that combine mechanical and chemical processes for many proposed uses are covered.

The authors review the status, at that time, of the various processes of bark utilization in the West. They also give an excellent survey of the possibilities of and obstacles to preparation and marketing of both pure chemicals and mixed preparations from bark for industrial use.

> There are four general types of products that can be produced from bark. These are pure chemicals, mechanical fractions, crude chemicals, and chemical-physical mixtures.
>
> Unfortunately, our knowledge of the composition of bark raw materials and processing has not yet instigated a way to obtain high yields of pure chemicals at competitive prices.
>
> Barks of different species have individual characteristics which can be exploited. For example, Douglas-fir bark has a relatively high wax content. Redwood bark and Douglas-fir bark each have distinctive types of fibers. Other barks are rich in tannin and dispersing materials. Many barks contain phenolic substances which can be chemically modified to attractive ingredients for the manufacture of resins and plastics.
>
> Commercial success will come to the company that finds the optimum process to take advantage of the unique characteristics of its raw material bark and which converts substantially all its bark into a limited number of useful products.

I may add that, as among the many alternatives possible, a diversification of processes and products will provide the opportunity to meet changes in technology and requirements in the fields of consumption.

Our present task is to record and analyze the past progress in chemistry and chemical utilization of Douglas-fir bark with a view to possible future developments and unanswered questions, the answering of which may aid the solution of the general problem.

Reference has already been made to early publications calling attention to various potentialities in utilization of Douglas-fir bark (Benson 1915, 1917; Grondal 1942; and Howard 1923). As indicated, these early interests were largely aimed at tannin and cork. However, Howard (1923) called attention to the wax content, especially of the cork fraction.

During the 1920's and 1930's, Zellner and coworkers in Germany did much pioneering in the use of selective solvents to separate constituents of many barks. There is a long series of publications by Zellner's school, dealing mostly with hardwoods. Many compounds were isolated and identified, mostly by use of selective solvents and applicable purifying techniques. These publications appear in *Monatschefte* for those years.

Kurth and coworkers (1948) gave a good rough summary of the chemistry of Douglas-fir bark. In bark from trees 50 years to 250 years old, they found the tannin content varying from 7.6 percent to 18.3 percent. The highest content was in the bark from the top logs of trees 50-80 years old.

Using three solvents, petroleum ether, acetone, and water successively in that order, they obtained the following results:

	Extractives (bottom logs)		
	Petroleum ether	Acetone	Water
	- - - - - - - (Percent) - - - - - - - -		
Age of tree:			
50-80 years	4.76	17.14	7.14
80-110 years	5.47	16.48	9.14
110-250 years	5.00	16.4	7.20

	Extractives (top logs)		
	Petroleum ether	Acetone	Water
	- - - - - - - (Percent) - - - - - - - -		
Age of tree:			
50-80 years	3.54	13.70	14.75
80-110 years	3.98	16.10	9.61
110-250 years	3.84	12.60	11.50

About the only conclusion that can be drawn from this is that the composition of the bark varies with age and position on the trunk. Roughly, one can find indications, also, that wax, resin, and the like, in gross, are higher in the bottom logs. Later work by Kurth and his colleagues (Hergert and Kurth 1952; Kurth and Smith 1954) showed that waxy components are combined in the cork, and the cork content increases with age.

In fact, as the bark ages, tannins are degraded to phlobaphenes, sugars and related compounds decrease, flavonoids seem to increase, and so on.

Just to make matters a bit more complicated, let us consider the following pertinent excerpts on "cork formation" from DeZeeuw (1941):

> It has long been known that physiological drought and the usually high atmospheric temperature that accompanies this condition have considerable influence on the type of development and extent of cork formation in tree stems....
>
> The time involved is that when the lunes of cork that form under the initial periderm in the young stem invade the secondary phloem tissue, a situation that is evidenced by the roughening of the bark on the outside....
>
> In white pine *(Pinus strobus)* exposed stems began cork formation in 19.6 years; shaded stems required nearly 35 years....

If this effect is also found in Douglas-fir, there should be more cork in bark from old growth in southern Oregon, for example, than in the Olympic Peninsula or North Cascades. Perhaps Rocky Mountain Douglas-fir will be found to have higher cork content at ages comparable to west-side Douglas-fir. And, one might expect higher cork content on the south side of a trunk than on the north; from trees grown on the south slope than on the north.[9]

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[9] Dr. Rowe, at the U.S. Forest Products Laboratory, calls attention to the fact that the Mediterranean cork oak *(Quercus suber)* produces relatively little cork when grown in moist, cool climates. (Personal communication.)

In short, Douglas-fir bark is quite variable in its chemical composition, a matter of considerable importance from the point of view of engineering and economics.

We shall have to deal with wax and wax components, tannins, polyphenols, flavonoids and related materials, phenolic acids (perhaps physiologically related to tannins and flavonoids), cork (containing waxy components and phenolic acids along with flavonoids), and fiber. In only one case, dihydroquercetin, shall we find much in the way of assured yield of a pure chemical easily obtainable in useful form.

CHAPTER VII

WAX

Wax is present free in the ground bark and also combined in the cork fraction. The latter will be discussed under "Cork."

It has already been mentioned that the presence of wax in Douglas-fir bark was recognized early (Howard 1923). But it attracted little attention until the mid-1940's.

During World War II, the pressing need for industrial alcohol led to the building of a plant for production of alcohol by wood hydrolysis at Springfield, Oreg. The process, modified from the German process by Scholler, treated wood in the shape of "hogged fuel" with 0.5 percent sulfuric acid at 150° C. in a semicontinuous process. The sugar solution produced was drained off, purified, and fermented. The process is described by Harris and Beglinger (1946).

The lignin residue attracted interest because, eventually, peacetime economic success of the process was conceived to be largely in the finding of profitable uses for the lignin.

In the process of hydrogenation of this product, catalytic and under high pressure, workers at the U.S. Forest Products Laboratory found substances originating from wax components. The matter was investigated and reported by Clark, Hicks, and Harris (1947).

Extraction with benzene of the original, dried, hogged Douglas-fir waste, which contained approximately 30 percent bark, yielded 1.5 percent extractives. The authors reported they obtained "wax-like brown and black substances" consisting of "a mixture of long chain aliphatic acids, alcohols, esters, and unidentified materials." They reported the identification of behenic acid, lignoceric acid, and a C_{15} alcohol in the products of hydrogenation of the lignin residue.

Properties of the wax extracted from the hogged fuel, bark, and lignin residue are given. As would be expected, the wax from the lignin residue, having been subjected to rather violent chemical treatment, gave considerably higher acid value, lower iodine value, and much higher Reichert-Meissl number than the others.

A little later, Kurth (1947a) reported further on the subject. He studied the recovery of a petroleum soluble wax from the lignin residue produced by wood hydrolysis. This wax was described as similar to beeswax and also as resembling closely "an extractive from Douglas-fir bark." Kurth also reported that the wax content of bark was higher at the base of the tree, the converse of tannin, and that the chemical composition differed materially from the similar extractive from the wood.

Clark, Hicks, and Harris (1948) continued work on the residue from hydrolysis. The authors extracted with benzene and followed conventional methods for separating the components of the wax obtained. They were able to characterize saturated acids, C_{20}, C_{22}, and C_{24}, and oleic acid. Saturated alcohols, C_{20} and C_{22} were identified. In the "unsaponifiables" they found the saturated hydrocarbons, C_{22}, C_{24}, C_{25}, and C_{26}. (These are probably formed in the hydrolysis reaction.) From 8 kg. of the lignin residue, extracted with benzene, they obtained 1,695 g. of crude extract; the acid fraction, 1,112 g.; unsaponifiables, 297 g.

At the May 19, 1948, meeting of the Pacific Northwest Section of the Forest Products Research Society, Kurth gave a full resumé of his work on wax from wood-sugar lignin residue. Insofar as I can determine, this paper was not published but formed the basis for Kurth and coworkers' other papers on the subject.

In this paper, he described work on destructive distillation of the "lignin residue." It gave:

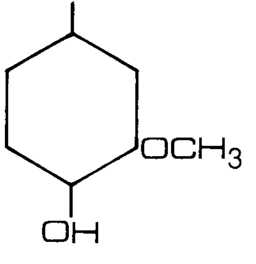
	Percent
Charcoal	55.8
Pyroligneous acid + dissolved tar	18.0
Insoluble tar	8.4
Combustible gas	10.3

The insoluble tar contained 25 percent lignoceric acid. The remainder consisted of phenols and hydrocarbons.

Kurth, Kiefer, and Hubbard (1948) had reported on the broad chemical composition of the bark. In 1950, Kurth and Kiefer reported further on the composition of wax from bark.

The wax was extracted with benzene and separated into portions soluble and insoluble in hot hexane.

The fraction soluble in hexane was reported to consist of approximately 20 percent lignoceryl alcohol (C_{24}), 60 percent lignoceric acid (C_{24}), and 20 percent ferulic acid.



3 methoxy, 4 hydroxy cinnamic acid

Ferulic acid

The fraction insoluble in hexane was darker in color and contained about 25 percent of a fatty acid mixture, 24 percent of a phlobaphene, 26 percent of an ether soluble acid fraction, 5 percent of unsaponifiables, and glycerol.

In another paper, Kurth (1950) reported more fully and referred to an earlier report by Warth, "The Chemistry and Technology of Waxes" (Reinhold Publishing Company 1947, p. 148), on the presence of wax in the corky layers of Douglas-fir bark. Although no experimental data are presented, Warth mentions the presence of free mellissic acid (C_{30}), an ester thereof, and an unsaturated alcohol. This acid is a constituent of beeswax and carnauba wax. Kurth repeats the results given in the preceding paper (Kurth and Kiefer 1950) but with greater experimental detail. "The composition of the bark wax is different from that obtained from the lignin residue produced in the hydrolysis of Douglas-fir sawmill residues," referring to his own report in 1947 but not to the reports by Clark and coworkers (1947, 1948).

The significance of the finding of ferulic acid, probably free and combined in a wax, was emphasized. The relationship to coniferyl alcohol and possible lignin structure is significant.

Mellissic acid was not found. The presence of a phytosterol is confirmed (about 0.3 percent of the wax).

Although the presence of "lignoceric acid" is confirmed, "it has been recognized for a long time that natural lignoceric acid is a mixture of near homologues that cannot be separated by crystallization methods or fractional distillation of the esters." Oleic acid may be present (probably from glycerides in the inner bark).

Along about this time, the operators of the alcohol plant at Springfield, obviously not able to compete in the postwar industrial alcohol field, tried to make wax from the lignin residue from hydrolysis. The residue was extracted with hot benzene, yielding a dark, unrefined wax.

An article appeared on the subject (Anonymous 1950):

> ...After many months of development the Oregon Wood Chemical Company of Springfield, Oregon, began commercial production of wax from Douglas-fir bark--by means of hot benzene as an extracting agent. The benzene is then separated from the dissolved wax by steam distillation, and the resulting wax is harder than beeswax but not so hard as carnauba. Already many uses have been found for the wax, including polishes, ski wax, ointments, lubricants, soaps, art and sculpture work, preservatives, and a score of similar applications.

The effort was abortive. Although several hundred pounds of crude wax were produced, the plant could not be operated for wax satisfactorily, a minor product in comparison to the alcohol for which the plant was designed.

However, in 1952, negotiations were reported for a revival of the wax project from bark (Anonymous 1952b, p. 244). M. W. Kellog Co. was reported to be exploring the possibilities of extracting wax, dihydroquercetin, and tannin from Douglas-fir bark by the Kurth process. The option agreement granted by the State of Oregon was to cover an 8-month period of investigation, to be followed by an 18-month pilot-plant stage, and then an exclusive production contract for 5 years. In 1954, an announcement of a new agreement with Kellog Co. for an 18-month pilot-plant study appeared in "Notes," No. 10, January issue, by the Oregon Forest Products Laboratory.

> Initial commercial production is expected to be at the rate of 3,000,000 pounds a year. This would require 75,000 tons of bark (dry basis) annually. This production would be less than 10% of the 46,000,000 pound domestic use of high-quality wax for use in polishes, carbon paper, and lead pencils.

Kellog Co. also believed that they would get into tannins and dihydroquercetin.

This development was abortive and the option was never executed. Later developments, of course, have lessened use of natural waxes in many fields. Replacement of carbon paper by other methods of copying decreased the use of carnauba wax. Petroleum waxes and many synthetic modifications of them have competed successfully with the natural waxes, principally carnauba and beeswax. Consumption of the natural waxes in automobile, furniture, and floor polishes remains high, but it is an open question whether wax from Douglas-fir bark could compete. Present requirements for emulsifiable waxes add to the difficulty.

Kurth (1951, 1953a) reviewed the work by his pupils and himself. These articles pointed out the potential commercial value of tannin, wax, dihydroquercetin and quercetin. In earlier papers, he reviewed broadly the chemical composition of barks (1947b, 1949b).

Kurth's patent (1950) covered the general process of extracting wax from the residue of wood hydrolysis, and another patent (1953) covered selective solvent extraction of barks to recover tannin, waxes, phlobaphenes, etc. Recovery of dihydroquercetin was also reported.

Recovery of dihydroquercetin from Douglas-fir wood and its role in pulping had been previously reported by Pew (1948).

Kurth obtained a further patent (1954) on improving Douglas-fir bark wax. Wax was bleached with a mineral acid and then treated with a base-metal oxide. It was claimed that the wax was improved in color, hardness, and melting point.

The early 1950's marked some rather important progress in the general field of the chemistry of Douglas-fir bark. Especially was this true of developments having to do with cork, tannin, fiber, and phenolic acid fractions.

Kurth (1948, 1949a) published two summaries of his and coworkers' progress in 1948-49. These articles reviewed work that dealt mostly with application of conventional methods of wood analysis. It was becoming quite evident that such methods gave very little information about the composition of bark.

The general chemical nature of the various types of extractives was slowly being unraveled.

Kurth and Kiefer (1950) had shown the nature of the wax accompanying the cork fraction and distributed in small amounts in the other physical fractions.

CHAPTER VIII

CORK

Now, attention was given to the cork fraction.

Hergert and Kurth published an important paper in 1952. The authors prepared a cork fraction remarkably free from the other physical fractions. They proceeded to extract the various fractions, seriatim, with hexane, benzene, ether, alcohol, and hot water, and record the quantities obtained by each extraction. From several cork fractions they obtained free wax contents (sum of hexane and benzene extracts) varying from 5.6 percent to 10.35 percent. The ether extract of the cork, consisting mostly of dihydroquercetin, ran from 5.5 percent to 23.35, with most figures above 15 percent.

The free wax was examined. The hexane soluble fraction gave similar results to those earlier reported by Kurth (1950). The 1952 paper gave analysis of the saponified wax as:

	Percent
Lignoceric acid	49.3
Lignoceryl alcohol	27.5
Ferulic acid	9.8
Phytosterol	0.6
Undetermined acids and phenols	11.7

In the benzene-soluble fraction, upon saponification, were found lignoceryl alcohol, lignoceric acid, and hydroxy-palmitic acid, unsaturated hydroxy acids (not characterized) and "phlobaphene-like material." Glycerin was positively identified.

The ether extract from the wax-free cork (from mature trees) was about 92 percent dihydroquercetin. Most of the tanning effect of the extract from the cork was found to be due to dihydroquercetin.

Cork that had been exhaustively extracted as above was examined further. It was found that treatment with alcoholic KOH, or dioxane-HCl, yielded materials similar to the benzene-soluble, hexane-insoluble wax. The exhaustively extracted cork in 100-g. portions was refluxed with 2.0 liters of 1.2 N alcoholic KOH, in 500 cc. portions, for 8 hours, and the hydrolyzate examined. The following were found and determined:

	Percent
Cork residue	15.82
11-hydroxy lauric acid (C-12)	11.70
Hydroxy-palmitic acid (C-16)	2.44
Unsaturated hydroxy acids	10.46
Unidentified unsaturated acids	9.49
Glycerol and decomposed sugar	5.52
Phenolic acids	42.28

Particular attention is called to the large yield of phenolic acids. After comparing properties of the preparation from cork hydrolysis with those of the phlobaphene from the benzene-soluble wax, and with a similar preparation extracted from the fiber fraction (to be described later), the authors concluded that these materials were "similar in nature. They possess properties differing from the lignin in either hardwoods or softwoods."

It was indicated strongly that part of the hydroxy-acid content was present as an estolide-type linkage. Further examination yielded a product characterized as a phenolic-acid, hydroxy-acid ester.

The authors concluded that extractive free cork was composed essentially of two fractions: 82-85 percent soluble in alkali or dioxane-HCl, and about 15 percent a thin-walled, carbohydrate, cellular membrane.

The authors tried only a brief orienting experiment using dioxane-HCl as the reagent, to separate the bonding material from the cork structure. From the extractive free cork, the reagent extracted 82.46 percent of the weight. Following the usual technique for a lignin preparation, they obtained a dark-brown, amorphous precipitate, insoluble in hot water, dilute mineral acids, and neutral organic solvents, but soluble in warm 5 percent NaOH.

The material soluble in NaOH was reprecipitated with dilute HCl. Part of the precipitate was soluble in ethanol, indicating that the extract was a mixture of materials.

It seems to me that this technique deserves further attention, especially in view of the demonstrated "polyestolide" structures. A possibility exists of isolation and proof of structure of these substances. This is especially significant in view of the later publication by Kurth and Smith (1954) on the chemical nature of the lignin of Douglas-fir bark, in which the differences in the nature of alkaline extracts from the various sections of the bark are demonstrated. This article will be discussed later.

In Hergert and Kurth's (1952) work, the phenolic acids were characterized as quite different from ordinary lignin found in wood. The concept of mixed esterification of hydroxy acids and phenolic acids was really born. Related references, especially with respect to techniques applied to the study of the wax and cork fractions, are Hergert (1958), Hergert and Kurth (1953), and Burgon (1964). It will be well to include here two fairly recent references on the chemistry of cork, especially that from *Quercus suber* : Guillemonat (1960) and Guillemonat and Traynard (1963).

CHAPTER IX

ALKALI EXTRACTS

Previous reference has been made to the use of alkali in preparation of bark extracts for various purposes; e.g., patents to Heritage (1956b), Herrick and Bock (Canadian, 1959b; U.S., 1962; U.S., 1965; and U.S. 1966), Williams and Baxter (1960), and Howland (1954), and an article by Adams, Messer, and Howland (1951).

In the late fifties and sixties, much work was performed in attempts to realize commercially successful processes for recovery of useful fractions, based primarily on alkaline hydrolysis and extraction. Many of the patents issued are voluminous and complex. They must be studied in the original for detail.

Zenczak (1957) carried out work along similar lines. Bark (e.g., Douglas-fir) was treated with alcoholic KOH or NaOH, and the residue separated. After evaporation of the alcohol, the various materials in the alkaline solution were separated by various precipitations and extractions. Canadian patent 582,018 by Zenczak (1959) covers the same ground as the above. Zenczak and Burgon (Canadian, 1960) and Zenczak (1960) are also similar to the foregoing; procedure is the same as in Zenczak (1957) with some additions. For example, the crude mass left after evaporation of alcohol is extracted with a hydrocarbon solvent to remove the unsaponifiables. After filtration the remaining solids are dissolved in an aqueous solution of sulfuric acid, the solution cooled and filtered to remove the insoluble acidic components; these are extracted with benzene and the wax acids recovered from the benzene solution. The crude wax acids are extracted with hexane to recover crystalline lignoceric acid.

The two patents by Burgon and Zenczak (1959, a and b) are slight modifications of the preceding three. A Canadian patent by the same team, in 1960, deals with a method for obtaining lignoceryl alcohol and lignoceric acid. These procedures all depended upon processes for separation of potentially useful fractions of unknown chemical composition.

The work on the wax and cork fractions, as well as further work--especially by Kurth and Smith (1954) on the chemistry of the "lignin" of Douglas-fir bark (to be discussed later)--showed clearly that alkaline extracts were complex mixtures. The term "phenolic acids" instead of lignin began to be a more meaningful designation about this time. There was rising interest in various potential outlets for the substances extracted by alkali, in spite of their complexity and generally unknown chemical makeup. Kurth (1953a) had called attention to the potential uses of the tannin, waxes, etc., in drilling muds and ore concentration.

Weyerhaeuser Co., in addition to the work already discussed under "Physical Fractionation" and the production of their line of Silvacons, had embarked on a program aimed at the development of chemical products. The underlying motivation of this program and rationale behind the procedures developed may be best illustrated by quoting from the patent obtained by Heritage and Dowd in 1959:

> In view of the tendency to debark all logs utilized in sawmills and the necessity for removal of bark in plywood and pulp mills prior to peeling or chipping, there is created a byproduct in the form of the removed bark available in substantial quantities at all types of log processing plants.

The patentees reviewed previous work on aqueous and nonaqueous solvents, with particular reference to Kurth's patent of 1953:

> This patented process utilizes expensive and hazardous solvents such as aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, halogenated aliphatic hydrocarbon solvents, ethers and alcohols which require particular methods of handling and are difficult of recovery.
>
> It has now been found that the extractable chemicals of tree barks may be recovered and useful products obtained in an economic, nonhazardous and efficacious manner by an extraction procedure which comprises exhaustively extracting the bark material with an aqueous alkaline reagent which yields a lignocellulose residue and an aqueous solution followed by fractionation of the solution extract by simple acidification. If it is desired to recover the dihydroquercetin from the bark, a water extraction . . . should precede the caustic extraction because dihydroquercetin tends to be destroyed under hot alkaline

> conditions. Either previously unextracted bark or bark which has been submitted to an aqueous extraction or extraction by other selective solvent may therefore be employed as a starting material in this process.
>
> The process of this invention results in the production of three useful products which are: a high density particulate lignocellulose material which is useful as a component for moldable resin compounds, a mixture of high fatty acid waxes and acid phenolics, . . . and the phenolic components of which may be employed as adhesive laminates for paper, and in the preparation of drilling muds for oil wells. . . .

In the case of Douglas-fir bark, ground to pass an 8-mesh screen but retained by an 80-mesh screen, bark, water, and alkali ratios and ranges are given, along with prescribed temperature around 212° F. for various times, depending upon whether batch or continuous extraction was to be used. It is observed that the longer treatment times yield more wax, and it is assumed that this arises from the alkaline treatment cleaving complex molecules to produce smaller molecules having waxlike properties.

Various alkaline reagents were used and yields given. Also, the use of various acids in the precipitating phase was described and results given. "It is necessary to develop an acid potential in the range of pH1.5 to pH5.5." There are 10 claims, the substance of which is embodied in the first claim:

> The process of extracting chemical products from the bark of trees which comprises treating comminuted bark with an aqueous solution of an alkaline reacting substance selected from the group consisting of sodium hydroxide and potassium hydroxide, using from 10-20 percent of the alkaline reacting substance, based upon the dry weight of the bark, at a consistency of the bark of 10-25 percent and a temperature of about 100° C. for a period of from 15-180 minutes, separating the phases to yield a solid residue and an extraction solution, treating the said extraction solution with an acid reacting substance in sufficient quantity to produce a pH of from 1.5 to 5.5 whereby to yield a precipitate comprising phenolic substances and wax-like substances, and separating the precipitate from the solution.

A second Weyerhaeuser Co. patent, improving upon the above, was obtained in 1966 by Brink, Dowd, and Root. Extraction procedure, claimed for most western conifers and a few deciduous species, follows that outlined in the preceding patent. The extract obtained contains

> ...a highly complex mixture of materials, which it is desired to isolate by the presently described process. In general, it includes the following classes of materials, which are either present as such in the original bark, or are derived therefrom by hydrolysis or other chemical reaction during the alkaline extraction.

> Waxy components
>
> - Salts of fatty acids
> - Salts of hydroxy fatty acids
> - Salts of phenolic fatty acid esters
> - Neutral esters of fatty acids
> - Long chain alcohols
>
> Nonwaxy components
>
> - Salts of monomeric and polymeric phenolic substances
> - Salts of monomeric and polymeric phenolic acid substances
>
> It is the concern of the present invention, therefore, to achieve an effective separation of these two groups of materials.

The separation was effected by extracting the alkaline bark extract with alcohols or mixtures of alcohols with 4-12 carbon atoms, which dissolve the waxy components even though they are present as alkaline salts. Careful control of pH of the alkaline extract was required; preferably, pH 8-12, most preferably, pH 9.5-10.5.

The patentees claimed successful use of a large range of alcohols but preferred a mixture of amyl alcohols sold under the trade name of "Pentasol." The alcohol solution was preferably acidified to a pH of less than 4, washed to remove inorganic salts and steam distilled to recover the wax. The aqueous washings from the alcohol-wax solution were said to contain monomeric and polymeric phenolic acid materials useful in "various industrial applications." They could be obtained either by evaporation or they were precipitated at pH4 or less.

The processes described in the above two patents were operated in a pilot-plant phase at Longview, Wash.

The processes outlined above in Weyerhaeuser Co. patents were further studied and modified with a view to better separation of the crude alkaline extract. A voluminous and inclusive patent issued June 7, 1966, to Dowd and others summarizes the extensive work. This patent introduces a concept of separation of the phenolic acid fraction into

> ...fusible and infusible phenolics by use of combinations of pH control and selective solvent extractions in the liquid or liquid phase containing suspended solids.
>
> The alkaline extract of the barks of trees contains a complex mixture of organic chemicals classified into four general types. The wax fraction is comprised primarily of fatty acids, hydroxy fatty acids, and neutrals such as long chain alcohols and phytosterols. The fusible phenolic fraction contains low molecular weight polyphenolic acids and fatty acid esters of phenolic or polyphenolic acids and is characterized by being substantially completely fusible below the temperature of 160° C. The infusible phenolic fraction includes the higher molecular weight polyphenolic acids and is characterized by a decomposition temperature of about 275° to 300° C. The acids soluble phenolic fraction contains tannin and tannin-like materials and a small amount of carbohydrates.

There are 10 flowsheets illustrating the procedures.

Procedures of hydrolysis and extraction are similar to previous patents by the same group. "The alkaline extract is acidified . . . to convert soluble alkaline salts of the wax, fusible phenolics and insoluble phenolics to the insoluble free acid form. (pH 3 to 4)." Procedural precautions are outlined to prevent foaming and clumping of the precipitated materials. The acidified extract may be extracted with a variety of amyl alcohols, with mention of use of methyl-isobutyl ketone being made for the first time. The solvent phase contains the wax and "fusible phenolics" fractions. The aqueous phase contains the "infusible phenolics" and acid-soluble phenolics and inorganics. Various alternative procedures are noted for separating the fractions, and uses for the fractions are described.

To my knowledge, the techniques described in this rather involved patent did not become commercialized. A continuation of the above patent was issued in 1967 to Roberts, Gregory, and Morris. "This application is a continuation of Ser. No. 236,142 filed November 7, 1962, and now abandoned."

Although the date of filing is the same as for Dowd and others (1966), the serial number is different and evidently refers to an abandoned application which is not available. This patent deals with the use of the alkaline extract of Douglas-fir, hemlock, or other barks in improving the strength properties of liner board and corrugating medium, used extensively in packaging. Obviously, if the process described were widely adopted, a large tonnage of bark extract would be required. The general procedures for preparation of the alkaline extract follow those of the preceding Weyerhaeuser Co. patents, with the proviso that the extracts may be treated for removal of the wax fraction, since "it has been found that the wax-free fraction provides higher concora values than the untreated mixture."

The solids content of the alkaline extract is employed in concentrations of from 5 to 25 percent, preferably 15 percent, for impregnation of the formed, partially dried sheets of paper. "It will be understood that the feed rate of the solution to the paper, to achieve a desired degree of pickup, varies with the web speed, characteristics of the paper sheet being formed, solids content of the solution, and other factors." Significant increases in concora and flat crush values were recorded.

In spite of the claims of this patent, it is clear that either lower costs of competing materials or unanticipated technical difficulties in actual operation on paper machines prevented commercialization. It is not being used at present.

Aside from Douglas-fir bark, the two most used barks for alkaline extracts have been redwood and western hemlock.

The Pacific Lumber Company started intensive work on utilization of redwood bark at Scotia, Calif., in the 1940's. A major product for some years was "sodium palconate" as a drilling mud component. The process is described by Kottwitz and Forman (1948). This is a full engineering report on the process as developed by the Institute of Paper Chemistry on a grant from Pacific Lumber Co. According to recent personal information, the process has been discontinued.

A second important paper in this general field reports, in part, the extensive work by the Olympic Research Division of Rayonier Corp. at Shelton, Wash., on utilization of western hemlock bark (Hergert and others 1965). The reported work deals primarily with the line of "Rayflo" products, principally used in drilling muds. These products have had significant marketing success. The article includes results of much intensive chemical work on hemlock bark and a good bibliography.

It is not encouraging to be compelled to record that little of commercial significance survives from the apparently large and extensive expenditures of engineering and chemical talent in the general field of alkaline extraction of Douglas-fir bark, with the exception of limited invasion of the drilling mud field.

Wax and the wax components from cork clearly are useful materials that have not been able to create a profitable market. Perhaps such a market might appear if the wax were a part of a multiproducts system.

It has been observed that most effort has been expended in attempts to obtain reasonably uniform and predictable fractions of the phenolic acids without adequate knowledge of the true chemical nature of these substances or their modes of combination in the raw material.

CHAPTER X

FIBER

One important component of the bark, the fiber fraction, is left as a residue from extraction with alkali. These fibers, as described in the section on anatomy, are differentiated early in bark formation and are distributed throughout the bark, mostly in the older parenchymatous tissue. I have not been able to find an accurate record of the percentages of fiber according to age of tree and position in the trunk. However, Kiefer and Kurth (1953) give the following (values based on air-dry weight of materials): 110- to 260-year-old trees, 36.5 percent fiber; 80- to 95-year-old trees, 47.8 percent fiber.

These figures represent the physically separated fiber fraction. It may be assumed that a general average lies around 40 percent, with the older trees running lower, the younger ones higher and, probably, the fiber content increasing up the trunk.

Kiefer and Kurth report about 13.5 percent of total extractives in the fiber (hexane, benzene, ether, hot water, alcohol). They report a further loss of 31.35 percent upon extraction of the "extractive free fibers" with 1 percent NaOH for 1 hour at boiling temperature. Thus, extracting all these extraneous materials, 44.85 percent, would give a net yield of "purified fiber" of about 22 percent.

Weyerhaeuser's Silvacon Bulletin 10-A (Appendix) gives the following solubilities for the physical fiber fraction:

	Percent
Water	7
Ether	8
2-percent caustic	35
	50

The agreement, considering the difference in procedures, is reasonable, in that 44 to 50 percent of the crude physically separated fiber consists of materials other than the fiber itself.

At the time of the publication by Kiefer and Kurth (1953), there was still much confusion with regard to the "lignin" of Douglas-fir bark. Application of the usual method of lignin determination from pulp and paper chemistry measured as lignin a large proportion of the bark components that turned out to be only remotely related to the usual type of wood lignin.

The paper by Hergert and Kurth (1952), dealing with the cork fraction, refers to the Ph. D. thesis by Kiefer, upon which the above cited publication by Kiefer and Kurth was based.

Both Hergert and Kiefer found that the alkaline extract from cork and fiber gave substances with lower methoxyl contents, higher carboxyl and phenolic hydroxyl contents, than lignin proper. Quoting Hergert,

> On the basis of the ultraviolet spectra, physical properties and methoxyl content, the phlobaphene from the wax and the phenolic acid from the bast fibers and cork are similar in nature. These materials possess different properties than the lignin in either hardwoods or softwoods.

Kiefer and Kurth separated a fiber fraction practically free from other physical fractions by grinding, screening, and flotation procedures. The fiber sank in water whereas most of the other fractions floated.

However, the stiff, short fibers (1 to 1.5 mm. long by about 50 microns in diameter) were still surrounded by "a wall or matrix of reddish-brown lignified material which, under microscopic examination, appears to be removed by dilute alkali solutions. This lignified matrix is responsible for the relatively high lignin content of the fibers." They were still using "lignin" to designate the materials that later were called "phenolic acids."

The authors then proceeded to demonstrate radical differences between this matrix and the lignin extracted from the fibers that had been exhaustively extracted with solvents and with dilute NaOH.

> The fraction of "lignin" removed by 1 percent sodium hydroxide represented 49 percent of what appeared as Klason lignin, based on the whole extractive free fibers. This easily removed "lignin" was found by infrared and chemical analysis to resemble a high molecular weight phenolic acid rather than what is generally designated as lignin. A functional group analysis by methylation revealed that this phenolic acid contained: methoxyl 4.3 percent, carboxyl 4.9-5.3 percent, phenolic hydroxyl 8.3 percent, and alcoholic hydroxyl 4.2 percent. On this basis, one building unit of minimum molecular weight 850-918 would contain one carboxyl, one methoxyl, two alcoholic hydroxyl and four phenolic groups.

Using an assumed molecular weight of 850 and the above data on functional groups, the authors derived an empirical formula for the substance (or substances) of $C_{36}H_{35}O_{13}$.

"Oxidation of the phenolic acid from the bast fibers yielded 1.63 percent vanillin. Evidently, the phenolic acid does not resemble lignin in respect to the presence of a vanillin nucleus." The small yield of vanillin may have been from a small percentage of ferulic acid.

"The low methoxyl content of the bark fiber phenolic acid is comparable to the methoxyl content of the phlobaphene--2.77 percent methoxyl." Similarities in infrared spectra were also shown.

The true lignin extracted from the fiber by dioxane-HCl, after the fiber was extracted with solvents and caustic, amounted to 11.8 percent (based on the ovendry weight of the extracted fibers), or about 24 percent of the total "Klason lignin."

> Dioxane lignin was found to possess a greater similarity to softwood native lignin than to the phenolic acid of the fibers. Its functional groups were identified as follows: methoxyl 14.3 percent, alcoholic hydroxyl 4.4 percent, phenolic hydroxyl 3.2 percent, carboxyl 2.5 percent. Infrared absorption showed the presence of a carbonyl in the dioxane-HCl lignin.
>
> The "lignin" in the bast fibers is not a homogeneous material and further investigation into its chemistry should be performed on purified homogeneous fractions.

(This was done later, as will appear in the chapter on phenolic acids.)

Determination was made of the carbohydrate composition of the fiber. The alkali extraction removed a fraction amounting to: 1.89 percent pentosans, 2.62 percent uronic acid anhydride, and 5.49 percent hexosans.

The "holocellulose" fraction contained 77.8 percent alpha cellulose, 1.6 percent beta cellulose, and 20.6 percent gamma cellulose.

These papers, Hergert and Kurth (1952) and Kiefer and Kurth (1953), gave the working basis for much further work on the phenolic acids, now distinctly separated in thought from conventional lignin.

Further work on the chemistry of the fiber was reported by Lenz and Kurth in 1963. The authors used several "hydrotropic solvents" (e.g., sodium xylene-sulfonate) and compared fiber yields, phenolic acid recovery, and properties of the phenolic acids with the yields from extraction with sodium hydroxide (1 percent at 100° C.). The raw material was Weyerhaeuser's Silvacons 490 and 515.

The results are not very startling: Cooking at a low temperature (120° C. for 35 minutes) with sodium xylene sulfonate gave a phenolic acid yield with a little higher methoxyl content than any of the others or sodium hydroxide. This preparation also had the highest phenolic hydroxyl content and the lowest carboxyl content of any of the phenolic acids.

The authors conclude from their data that "the carboxyl group is an inherent part of the phenolic acid molecule and is not formed by oxidation in alkaline solution during the process of extraction." Hergert and others (1965), dealing with hemlock bark, later came to the belief that "the carboxyl group is an artifact due to the oxidative action of air and alkali on some of the pyrane rings in the phenolic polymers during isolation."

Again, an apparent molecular weight for the phenolic acids, based on methylation studies, was found to be around 1600 to 1840.

Infrared absorption spectra indicated presence of a =C=O group in the phenolic acids. This may be quite significant.

Although Howard (1923) had thought that the fiber in Douglas-fir bark might become a useful pulping material, nothing has apparently transpired to confirm his prediction.

But, principally as a result of the attempts to establish a chemical derivative industry based on alkaline extraction, the fiber residue from alkaline extraction has begun to assume some industrial promise.

As shown by Kiefer and Kurth (1953), the fiber is essentially a ligno-cellulosic complex, encrusted with a "phenolic acid" mixture which can be removed by treatment with alkali. It has also become apparent that the lignin in fiber is probably a true lignin, similar in constitution to that in wood itself.

Weyerhaeuser Co. operated a pilot plant in Longview, Wash., for some years, beginning about 1960, aiming at the various alkaline extracts and their uses.

The fiber produced was of much interest, primarily because of the physical nature of the product, tough, strong, very much different from normal wood fiber.

The principal elements of the processes developed for further refinement of the fiber are disclosed in a patent of 1966 issued to Gregory, Root, and Gygi. The shortcomings of the mechanically separated fiber fraction, particularly for fillers or reinforcing agents in resin compositions, are described. "The final product (by grinding and screening) is most difficult to control with the result that it exhibits varying degrees of purity." In attempts to produce a mechanically separated fiber of high purity, the yield is "so small as to be commercially impractical."

The encrusting bodies in the mechanically separated fiber are variable in quantity and often inhibit or prevent the cure of resins to which they are added, often preventing effective bonding of the resin to the fiber with reduction in the strength of the molded resinous product.

The process reported was designed to effect removal of most of the encrusting materials and produce a more uniform fiber. The crude fiber was extracted with alkali in single or multiple stages, batches or continuous, under conditions that could be varied according to the degree of quality required. A wide range of conditions is described; temperatures, for example, from 140°-212° F. These treatments, plus washing, were described as reducing the alkali-soluble content of the fibers from about 30 percent to about 5 percent. Remaining parenchyma or cork was rendered friable by drying in a rotary drier, the moisture content being reduced to less than 15 percent. The dried fiber was rod-milled and screened in successive operations, abrading the friable components from the fiber. It is stated that yields of 70-90 percent of the crude fiber content of the bark are recovered. The product is valuable as an ingredient of various resins.

Two subsequent Weyerhaeuser Co. patents deal with preparation of various molding compositions incorporating the improved fiber. The first, issued to Kreibich and others (1967) described the procedure for fiber preparation for use in the various phenol-formaldehyde resins, with suggested modifications for urea--or melamine-formaldehyde resins. Adaptations are described to one- and two-stage formulations and modifications to obtain various properties as described. Improvements in strength properties, surface, mold release, decreased "flash problems," and resin savings are claimed over other well-known fillers and extenders.

The product was extended to the polyester resins by the patent issued to Gregory and others (1968). This patent discloses adaptation of the chemically refined fiber to polyester-based resins, the advantages over such fibers as sisal and glass fiber, and numerous operating advantages. The claim is made that the new compositions are also important in adapting the polyester resins to automatic molding procedures.

In 1962, Gregory, D. F. Root, and R. O. Bathiany, all of Weyerhaeuser Co., presented an important paper dealing with the entire field of application of the fiber to the resin and plastics field. This paper was presented at the Forest Products Research Society 1962 national meeting in Spokane but was never published.[10]

There is an excellent bibliography, with most references concerning bark made to the Bulletin No. 191 of the Bibliographic Series (Roth and others 1960), referred to previously in this report, and also to the bibliography by Marian and Wissing in 1957. Only the summary of the report can be given here:

> Douglas-fir bark fiber, isolated chemically from the bark (e.g., by caustic extraction) has wide applicability as a plastics reinforcing filler. The inherently desirable strength, toughness, particle size, shape, and low resin absorption characteristics of the naturally occurring fiber are enhanced by chemical removal of nonfibrous bark substances. The fiber is chemically "clean" and contains no substances which will cause mold, stain or cure inhibition even at high levels of filling.
>
> Phenolic molding compounds in the medium impact class can be made with the extracted fiber. Cost savings are possible both in the form of raw materials and manufacturing costs. Unlike commercial medium impact molding compounds filled with cotton or paper flock, the bark filled compounds can be handled and molded in automatic high speed equipment.
>
> Used as a reinforcing filler in polyester premixes, the extracted bark fiber offers advantages over the conventional sisal filler in specific gravity, ease of flash cleaning, stronger knit lines and less warpages in the molded parts, and adaptability to transfer molding. Extracted bark fiber polyester premixes can be automatically preformed, handled, and molded in high speed automatic transfer molding equipment. Material costs are lower than for phenolics and impact strength is comparable to that for the higher impact grades. Overall, properties are acceptable for many of the uses now served by phenolic molding compounds.
>
> Applicability of extracted Douglas-fir bark fiber as a plastic filler extends to thermoplastics and other thermosetting resin compounds.

The product described has been marketed for several years from a pilot plant in Longview. Properties, applications and prices are currently described in brochures issued by Weyerhaeuser Co. The fiber is designated "WEF."

It may be of significance that the alkali extract from fiber purification could be marketed for drilling mud, for example.

Several papers have been presented by Weyerhaeuser people, dealing with the advantages and prospects of the fiber in the plastics field (Anonymous 1966).

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[10] A copy was very kindly furnished me and, doubtless, copies would be made available to others by Weyerhaeuser Co.

Hugh Hendrickson, of Weyerhaeuser Co., discussed the subject at a meeting of the Eastern Canadian Section of FPRS, March 11, 1966, at Montreal. In addition to description of applications to the automobile and furniture industries, he pointed out that the future of bark fiber in the thermoplastic field was very promising. The paper is not available.

An article by Soule and Hendrickson (1966) goes into the advantages of "WEF" over other fillers, especially in improving properties and operations. Attention is called to improved paintability of products, especially polypropylenes.

Gehr (1962) covered the history and technology of a reinforcing fiber from Douglas-fir bark to that date, with no reference to the thermoplastic uses developed later.

Evidence is here that a bark product can make and has made some successful inroads into an industry as complex and complicated as the plastic industry. It was not done, however, by mere production of a bulk product in the hope that somebody would use it.

It was necessary to learn intimately the nature of the industry and its problems. It was essential that the technology of fiber use be explored and proven before presenting it to the industry. Then, the closest followups and working relations with potential customers had to be built and maintained.

All these matters are far removed from the commercial efforts in selling wood products in general, but indispensable to successful efforts in penetrating markets already being served by competing materials.

This apparently successful venture, although contributing but little currently to the broad problem of bark utilization, shows clearly some of the factors required if a large chemical industry is ever to be based on Douglas-fir bark.

CHAPTER XI

TANNIN

Numerous previous references have been made to the importance of the "tannin" content of Douglas-fir bark, especially in the preparation of drilling muds. They generally refer to crude extracts processed for particular purposes and not prepared specifically for use in the leather industry.

The history of the use of native vegetable tannins in the leather industry of the United States in recent years is not encouraging with respect to the expansion of the now limited use. Much of this is due to fundamental changes in the demand for leather and requirements as to leather properties.

The inroads of substitute materials into fields formerly requiring large tonnages of heavy leather are particularly important. For example, the use of heavy leathers for harness has decreased greatly. Luggage, except for high-priced luxury items, has given way to plastics combined with various reinforcing materials, molded shapes, and many other combinations.

A recent communication from Dr. J. Naghski, Chief, Hides and Leather Laboratory, Eastern Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Philadelphia, contains some illuminating statements:

> In the U.S. the tanning of leather has been a static enterprise. . . . Sole leather production has been declining steadily. The latest statistics indicate that only 18 percent of shoes have leather soles. In a shrinking industry it is difficult to convince the trade that it is to their advantage to invest in more modern concepts. I, therefore, cannot be very optimistic about any expansion in the use of vegetable tannins.
>
> The world situation on vegetable tannins seems to be one of give and take. Production is more than adequate to meet demands. Actually, wattle plantations in South Africa are being closed out to prevent overproduction.
>
> The U.S. imports practically all of the tannins used, mostly quebracho and wattle.
>
> At one time our Laboratory was interested in Douglas-fir bark extractions because of their content of dihydroquercetin. [This subject will be covered later.]

The reasons, in a general way, for our almost complete dependence upon tannins of foreign origin are mostly economic, partly technical, and partly subjective.

In much older days, our leathers were mostly heavy and made from the tannins of eastern hemlock bark, chestnut oak bark, and chestnut. As time went on, quebracho from Argentina and Paraguay was available cheaply and effectively. An article by Jerome S. Rogers in 1947 gives a good summary. At that time, Mr. Rogers occupied the post now filled by Dr. Naghski. This country had just emerged from World War II during which the tannin supply was a critical problem:

> Twenty years ago this country imported less than half (44 percent) of the total tannins (118,000 tons) used in making leather. Today, more than 70 percent of our tannin comes from foreign sources.
>
> Of the domestic tannins that we produced 20 years ago, about 60 percent came from the wood of the chestnut tree and the remainder came principally from the barks of oak and hemlock and the leaves of sumac. Today the picture has materially changed, and it is safe to say that more than 90 percent of our domestic tannin comes from chestnut wood.

The chestnut tannin industry expired in 1956 as a large commercial industry. A few small tanneries survive using the small supplies of available domestic chestnut and oak. The eastern hemlock tannin industry is also practically dead.

During the war, importation of quebracho was seriously curtailed by submarine activity. Much interest prevailed in developing domestic sources for suitable tannins. For example, much work was done on the bark of western hemlock.

This subject had already been covered well by Smoot and Frey (1937), but there were no results in the establishment of an industry.

During the war, a process for making tannin extract from western hemlock bark was developed by the Western Regional Laboratory of the U. S. Department of Agriculture at Albany, Calif. (Potter and others 1944). It was never commercialized. In 1950, MacLean and Gardner published on the same subject.

In spite of the early references to the tannin content of Douglas-fir bark (Benson, 1915, 1917; Howard, 1923), little attention was given to this material as a source for tannin until Kurth and coworkers began their work at Oregon State University. Hemlock for pulping was barked at the mills and piles of bark were available. As mentioned before, barking of Douglas-fir for lumber and veneer production began to grow after the war, and this pile of raw material began to become available.

It should be noted that a small tannery at Dallas, Oreg., has used Douglas-fir bark in leather manufacture for well over a century and continues to do so. It has preferred second-growth bark, for reasons that will appear later.

But, manufacturers of logging and hunting boots, for example, have informed me that they now obtain practically all their supplies of heavy leather from Europe and Australia. American leathers are, in general, tanned with blends of imported tannins or chemicals; e. g., chromium salts and "syntans," with some vegetable retanning to obtain subjective properties such as color, feel, etc., that have little relationship to wearing qualities.

Part of these developments is due to the virtual abandonment of the old vat or pit tanning processes, which were slow and costly. These were replaced by rapid, continuous methods that depend largely on quick penetration of hides by the tanning materials. Quebracho tannin fills these needs.

In spite of the virtually complete loss of the domestic leather industry by native tanning materials, some inroads have been made in other industries using tannins or similar materials, Reference has been made to drilling muds, heavy users of quebracho, but now using various lignin derivatives, hemlock bark extracts, and some Douglas-fir extracts. Attempts have been made to introduce domestic tannin products into the ceramics industry, the cement industry, into ore flotation processes, and others. Technically, all these offer possibilities. Economically, products will have to be satisfactory competitors with foreign tannins, usually produced quite cheaply in comparison with American costs. There are also possibilities for use of modified tannins as carriers for biodegradable pesticides that warrant investigation. Attempts are recorded, also, that looked toward production of ion exchange resins and the like for use in water purification.

If satisfactory materials could be produced from Douglas-fir bark--probably as part of a multiproduct industry--a business might well follow. Again, it will require very close technical cooperation between research and the industries to be served.

In the meantime, we shall review the work on the chemistry of Douglas-fir bark tannin.

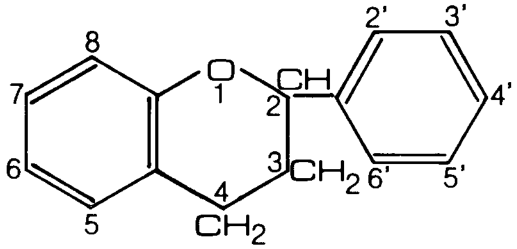
A good, brief discussion of tannins, especially from wood and bark, is given in "The Chemistry of Wood" (Browning 1963):

> The substances responsible for the formation of leather are known as the vegetable tannins. This is a very general term and includes materials of varied chemical composition. [For example, dihydroquercetin reacts with collagen to give a sort of leather, but the compound could not be classified as a tannin.]
>
> The vegetable tannins are comprised of substances with a high proportion of free phenolic hydroxyl groups of varying degrees of condensation or polymerization. Usually, only materials of relatively high molecular weight are considered true tannins, but some monomeric materials are fixed by hide powder.
>
> Several classification systems have been proposed for the tannins, some of them quite elaborate. As *the exact nature of most tannins is unknown*, only the simpler systems seem justified. [Italic ours.] Freudenberg has divided the tannins into the hydrolyzable class and the condensed tannins, or phlobaphene class. The former contain ester and/or glycosidic linkages, and on hydrolysis, yield acids, sugars, and/or alcohols. Gallic acid, ellagic acid and glucose are common hydrolysis products.
>
> The condensed tannins, on treatment with acid, are polymerized further, rather than being hydrolyzed into simpler substances . . . [the so-called phlobaphenes].
>
> Freudenberg suggested nearly 30 years ago that the condensed tannins are built up of catechin units, and that the tannins from the different sources differ chiefly in the hydroxylation pattern. Within the last few years, several investigators have recognized the common occurrence of leucoanthocyanin-like materials along with the condensed tannins, and have postulated that the tannins are built up, at least in part, of flavan--3, 4, diol units. This is supported by the common occurrence of leucoanthocyanin with tannins and by the discovery of complex leucoanthocyanins in common tannin preparations. . . . It seems likely that the condensed tannins are formed in the plant by the condensation and/or polymerization of hydroxyflavanes, both leucoanthocyanins and catechins and perhaps other materials. Since the monomers may differ in the degree of hydroxylation in the aromatic rings, as well as in the pyrane ring, the *formation of rather complex molecules is possible*. [Italic ours.]
>
> Color reactions have been used to detect the presence of tannins in plant tissues, but in some cases the materials are not considered to be tannins by the tanner. At present, the general term, polyphenols, is often used to designate this general class of materials; this seems to be a desirable usage. The tannins are often accompanied by similar materials, known as phlobaphenes, which are more highly condensed and are not water-soluble.

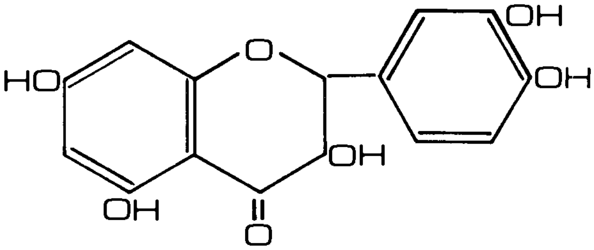
It is not within the limitations of this report to go deeply into the fundamental chemistry of the so-called condensed tannins, based generally on polymeric derivatives of the flavan--3, 4 diols, their extremely diverse phenolic derivatives, the varying states of oxidation of the pyrane ring, and the extremely large number of condensation products possible.

The chemistry of these materials has been very well brought together in "The Chemistry of Flavonoid Compounds" (Geissman 1962, chs. 17, 19). A fairly large library would be required to contain all that has been written concerning condensed tannins and their relatives. Naturally, in a field so long and heavily worked, there are great variations in nomenclature.

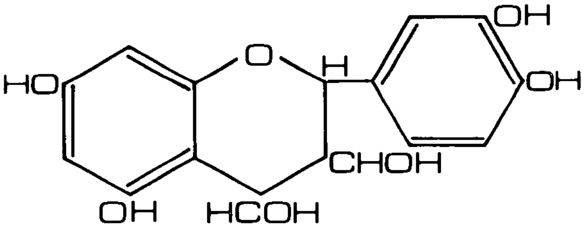
A few structural formulae are included here in order to help maintain orientation through the ensuing brief discussion.



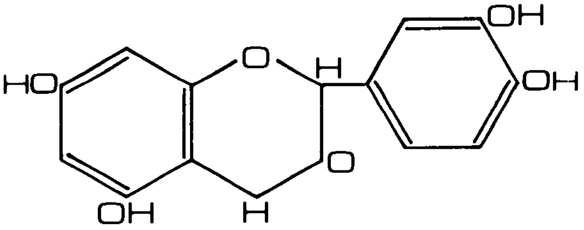
Flavan



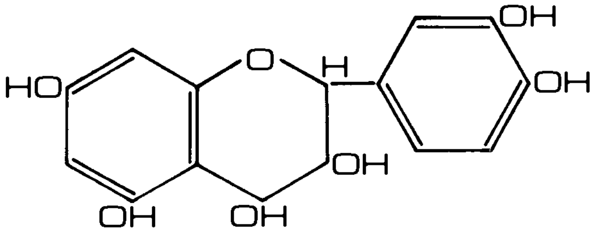
Dihydroquercetin
(a 3 flavanol-4-one)



(a 3,4, flavandiol)



(a catechin)



(a leucocyanidin)

Beginning in 1948, a series of publications by Kurth and his students dealt partly with tannin. The first article (Kurth, Kiefer, and Hubbard 1948) calls attention to the variation in tannin content of Douglas-fir bark with respect to age of tree and position on the trunk. Using the official methods of analysis for tannin of the American Leather Chemists Association, they found a variation from about 8 percent to 18 percent:

The bottom logs showed:

At age:	
50-80 years	9.8 percent
80-110 "	8.1 "
110-250 "	8.5 "

The top logs showed:

At age:	
50-80 years	18.3 percent
80-110 "	10.5 "
110-250 "	7.6 "

Although nothing was said about size of top logs, it may be assumed that they were cut to an 8-inch-diameter limit. The striking thing here is the large tannin content in the bark around young wood.

The tannin was leached from shredded bark with water at 140°-180° F. The liquor contained considerable amounts of dihydroquercetin and nontannins.

Phenolic substances soluble in acetone varied from 12.6 percent in the bark from the top logs of old trees to 17.0 percent in the bark from the bottom of young trees. The yield of wax extracted with a petroleum solvent ranged from 3.5 percent (young wood) to 6.0 percent (old wood).

From nonhydrolyzed bark the wax content goes up upon hydrolysis of the cork, as previously noted.

Kurth and his coauthors tried hard to interest the leather industry in Douglas-fir bark tannin, as exemplified by Hubbard and Kurth (1949). Attention was called to the fact that tannin from Douglas-fir bark has been used in leather manufacture by the Muir and McDonald Co., Dallas, Oreg., since 1863.

Summary:

> Douglas-fir bark contains from 7.6 percent to 18.3 percent tannins. . . . Floating of logs in mill ponds will cause some loss in tannin yield because of its solubility in cold water. The bark tannin belongs to the phlobatannin class. . . . It contains aliphatic and phenolic hydroxyl groups in the ratio of 1:3. A small amount of methoxyl is also present. The low yield of veratric acid, obtained upon oxidation of the fully methylated tannin [dimethylsulfate methylation] indicates that the catechol group is probably used as a link in polymerization. Extracted with the tannin is a considerable amount of dihydroquercetin. The U. V. absorption spectra of phlobaphene, and the tannin are somewhat similar to that of dihydroquercetin.

Several articles, addressed to the industry, were published, as exemplified by Kurth, Hubbard, and Gekeler (1949). There is little in this publication not previously covered. Engineering data on tannin extraction and use in tanning are given.

The article by Kurth and Chan (1953) goes more deeply into the engineering aspects of tannin extraction from Douglas-fir bark. Four methods were demonstrated.

> *Method 1.* The ground bark is first extracted with benzene or a chlorinated aliphatic hydrocarbon to remove the waxes. The dihydroquercetin is then recovered from the wax-free bark by extraction with a lower alkyl ether. Finally, the tannin is extracted with hot water from the bark residue.
>
> *Method 2.* The ground bark is extracted with an appropriate solvent to remove the waxes. The bark residue is then extracted counter-currently with hot water to remove tannin and dihydroquercetin. Subsequent separation of dihydroquercetin from tannin is effected by means of a lower alkyl ether such as diethyl ether or diisopropyl ether. For this step the tan liquor is evaporated to a small volume or to a dry powder. As the tannin is less soluble in diisopropyl ether than in diethyl ether, the former solvent will give relatively pure dihydroquercetin. A longer extraction period, however, is required because of the lower degree of solubility of dihydroquercetin in diisopropyl than in diethyl ether.
>
> *Method 3.* The ground bark is extracted countercurrently with hot water to remove tannin and dihydroquercetin. The residue is then extracted with an appropriate solvent to remove the waxes.
>
> *Method 4.* The ground bark is extracted with a constant boiling mixture of alcohol-benzene. With this solvent, the waxes, dihydroquercetin, tannin and phlobaphene are largely removed from the bark in one operation. After removing the alcohol-benzene mixture from the extract, the waxes are extracted with hot benzene and the dihydroquercetin with ether. The tannins and phlobaphene, which remain, are then separated by dissolving the tannin in hot water.

Fresh, unstored bark from young trees (16-24 inches in diameter) gave the following yields per ton:

146-200 lbs.	of tannin
130-204 lbs.	of wax
80-152 lbs.	of dihydroquercetin

> Two industrial laboratories have reported that Douglas fir bark tannin compares favorably with quebracho tannin for controlling the consistency of oil-well drilling muds.
>
> The Bureau of Mines' Laboratory at Tuscaloosa, Alabama, was interested in finding a material that would be beneficial for the concentration of low grade iron ores. Their tests on Douglas fir bark tannin extracts indicate that it is as efficient as quebracho tannin for this purpose.

Summary:

> The data indicate that about 80-85 percent of the tannin will be extracted from the bark in a countercurrent, batch extraction unit containing five leachers, when the water to bark ratio is sufficient to completely cover the bark. Because of the lower solubility of the dihydroquercetin and because it is present largely in the cork fraction of the bark, the efficiency of the dihydroquercetin extraction under the same conditions, will be only 55 to 65 percent. . . . The total solids content of the tan liquor from the bark was approximately 2 percent. (Five leachers, countercurrent, about 15 hours.) Removal of the wax from the bark with benzene extraction prior to tannin extraction with hot water gave the most efficient extraction of total solids, tannin, and dihydroquercetin.
>
> The reducing sugar content of the Douglas fir bark tannin extracts was 18.1 to 18.4 percent of the ovendry weight of the total solids.
>
> Purity of the tannin extracts varied with the condition of the bark prior to extraction. A purity of 55-60 percent tannin content apparently may be considered normal for tannin extracts from properly cured, sound Douglas fir bark.
>
> For maximum yield of tannin and purity of the tannin extract, the bark must be removed from the logs and dried soon after the trees are felled.

A publication by Kurth (1953a) is a sort of summary of the work in his laboratory on Douglas-fir bark. This paper includes much cost and engineering data, most of which is now obsolete.

I have found only one patent dealing directly with Douglas-fir tannin, that of Shutung Tu (1954). Redwood waste or Douglas-fir bark are extracted with alkaline water (pH extract 6.0 to 8.5) and the extract is acidified with sulfur dioxide to pH4 and then autoclaved below 150° C. The product is suitable for ordinary tanning, yielding leather of satisfactory color and a shrinkage temperature of 75° C.

I find no record of commercialization. It would appear that the product would be similar to some described under "Alkali Extracts."

Hergert (1960) published further work more closely related to the tannins. Much of the work reported in that paper is included in Geissman (1962, ch. 17). I strongly urge that workers in the field of tannin genesis study this paper in the original. It can be reviewed only briefly here; since a number of coniferous species are discussed, we must confine our review to Douglas-fir.

Hergert, using well-advanced, two-dimensional paper chromatography and ultraviolet and infrared spectra along with quite sophisticated but well-known organic techniques, made an important contribution to the general field of biosynthesis, especially of the condensed tannins.

> All of the coniferous species examined during this study were found to contain either catechins and monomeric leucocyanidins, the closely related gallocatechins and leucodelphinidins, or both. These compounds were present in highest concentration in the inner bark adjacent to the cambium and in the cork cambium. A decrease in amount of these compounds centrifugally from the cambium . . . was accompanied by an increase in polymeric polyphenols (tannins). . . . This observation alone strongly suggests that the polymeric bark tannins are formed from the catechins and leucocyanidins present in a given species. . . .
>
> Examination of the structure of leucocyanidin shows that it can exist in four pairs of enantiomorphs.

Hergert then discusses the significance of this fact in its probable effects on further condensations and the varying characteristics of the tannins from different species.

> Douglas fir: . . . The observation that dihydroquercetin is present in relatively large yields in the bark might suggest a relationship between this compound and the polymeric tannins. The stability of dihydroquercetin (as compared with catechin and leucocyanidin), the absence of carbonyl groups in Douglas fir tannin (as evidenced by the ultra-violet and infra-red spectra), and the distribution of dihydroquercetin (only present in outer bark) strongly suggest that the tannin polymer is not derived from dihydroquercetin.

Attention may be called to the higher state of oxidation of dihydroquercetin than catechin and leucocyanidin.

> Weinges (Weinges, K. - Annalen 615:203- (1958)) has recently isolated catechin and epicatechin from Douglas fir bark. In addition to these two compounds, paper chromatography shows the presence of monomeric leucocyanidins. They are present in large amounts adjacent to the cambium in the inner bark, but are practically absent (in the monomeric form) in the outer bark. . . .
>
> Pyrogallol derivatives . . . are not present in Douglas fir inner bark. . . . It is concluded that the tannins in Douglas fir bark are predominantly polymeric leucocyanidins.
>
> This paper has a good bibliography up to 1960.

A recent article from the Rayonier Laboratory at Shelton, Wash., goes further into the biogenesis of tannin in western hemlock (Sears 1970).

G. W. Holmes' Ph. D. thesis[11] makes some important contributions in this general field. The principal results of his work were published (Holmes and Kurth 1961). Certain observations by Holmes, reported in his thesis, are significant in this and allied fields; e.g., the phenolic acids.

---

[11] George W. Holmes. The chemical composition of the extractives from the newly formed inner bark of Douglas-fir. 1961. Ph. D. thesis on file at Oreg. State Univ., Corvallis.

Douglas-fir bark "phenolic acid" contains fewer methoxyl groups than lignin, and lignin proper has not been found to contain carboxyl groups. Due to the severe conditions of isolation (alkali) the existence of carboxyl groups before isolation may be doubted.

Wood lignin has not yielded phloroglucinol.

Phenolics do not give the Wiesner reaction (red color with phloroglucinol and HCl) characteristic of substances containing a free coniferyl aldehyde structure, a strong indication that the phenolics are off the route of lignin synthesis.

On page 22 of his thesis, Holmes described how, in an ethyl acetate extract from water solution, he obtained identical chromatograms from old, medium, and new bark showing "a weak carbonyl absorption band at 1,690 cm-1." (Dihydroquercetin gives 1,642 cm.-1 in the outer bark.)

In connection with the probability of the nonexistence of free carboxyls in the "phenolics" prior to alkali action, and the probable reactions of the products upon freeing by acidification, Holmes' observation of a "weak carbonyl" chromatogram *might* be significant.

Holmes found catechin in ether solubles from both inner and mature bark (see his thesis, p. 22-d).

Ether solubles extracted from the water solubles from the inner bark were mostly waxy or gummy (thesis, p. 33). There was a little brown oil whose IR gave a *strong carbonyl* absorption band.

I am reminded of my work on the phloem of slash pine, about 35 years ago. I found a trace of a substance, soluble in both water and ether, which was easily decomposed into a reducing sugar and a substance giving the color reactions of a resin acid. In Holmes' case, he might have been dealing with a glucoside of an hydroxy acid (or an ester) which, upon splitting, formed a lactone.

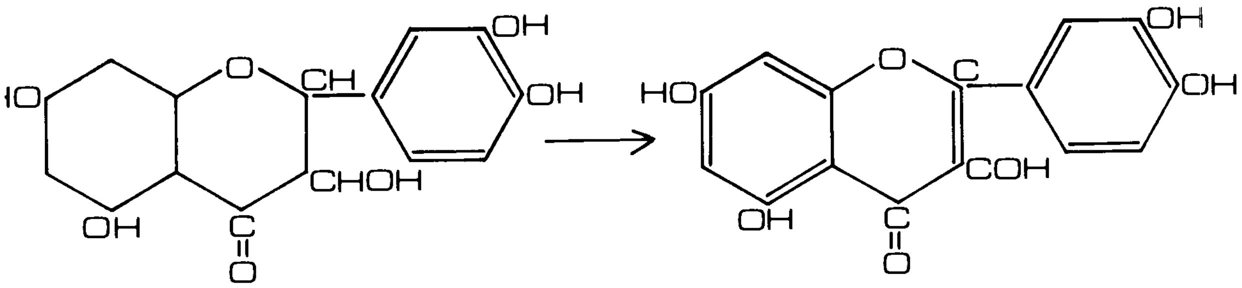
On pages 38-39, Holmes gave chromatographic evidence of quinic and shikimic acids, along with indications of six others (hydroaromatic compounds). This evidence is compatible with the general quinic-shikimic theory of biosynthesis.

On page 64, attention is called to the possibility of ester formation with the "phenolics," both on hydroxyl and carboxyl. This question of "free or combined" phenolics is still open.

Dässler and Wang wrote a paper on the general subject in 1963. They prepared an ethyl acetate extract of phloem, previously exhausted with chloroform. Treatment of the tannin with dilute mineral acid converted it to phlobaphenes, with splitting off of glucose. Enzymic fission gave dihydroquercetin and other fractions (evidence of presence of glucosides).

CHAPTER XII

DIHYDROQUERCETIN AND QUERCETIN



Dihydroquercetin
Taxifolin
(3,3',4',5,7
pentahydroxy flavanone)

Quercetin

(3,3',4',5,7
pentahydroxy flavone)

The production of "fine chemicals" from bark has long been a prime objective of much research with some notable results. It is natural that much attention should have been given to dihydroquercetin in Douglas-fir bark because of its relatively easy separation.

Its occurrence in the heartwood of Douglas-fir was first reported by Pew (1948) and its role in the pulping of Douglas-fir discussed the next year (Pew 1949).

Since then, the literature on the subject of dihydroquercetin--preparation, properties, and potential uses--is quite voluminous. Also, the derivative, quercetin, has attracted much attention.

Both compounds are widespread in the plant world and are close relatives of a number of other "bioflavonoids," such as hesperidin and naringin in citrus fruits. Rutin, which is a glycoside of quercetin, has had considerable use as a pharmaceutical, the activity being ascribed to the quercetin part of the molecule.

Rutin was first found in buckwheat, and its usefulness demonstrated in controlling capillary fragility. A cheaper source was found in a Chinese shrub, but this became unavailable to the Western World and a source was found in one of the Australian eucalypti, from which it is currently obtained. Strangely, the substance is widely used as a drug in Europe, but little used in the United States. About 2 years ago, on the recommendation of a committee of the U. S. Academy of Science, the Food and Drug Administration withdrew approval of the whole group of "bioflavonoids" as not having any demonstrable pharmacological use. A bibliography (see "Appendix"), supplied by Weyerhaeuser Co., is of interest in this matter. Although it was compiled only through 1954, it shows rather clearly that in some quarters quercetin is regarded otherwise.

A complete literature survey of the chemistry of quercetin was prepared in 1958 by A. S. Ryan, of Weyerhaeuser Co., when the company was interested in the possibility of volume production of the pure compound. This report covers 176 references in good detail and is included in the "Appendix" with the permission of Weyerhaeuser Co.

Weyerhaeuser Co. also has in its files a number of technical reports on uses of quercetin, as follows:

Technical report 05-0401-1 (1957). "Report on Properties, Reactions and Applications of Quercetin."

Technical report 05-0502-1 (1957). "Report on the Retarding of Oxidation of Lard and Tallow by Quercetin and Several Commercial Antioxidants."

Technical report 05-0502-2 (1957). "Report on the Retarding of Oxidation of Butter Fat by Quercetin and Several Commercial Antioxidants."

Technical report 05-0502-4 (1958). "Report on the Ultraviolet Light Transmission Properties of Quercetin."

Technical report 05-0502-6 (1958). "Report on the Retarding of Oxidation of Cottonseed and Safflower Oil by Quercetin and Several Commercial Antioxidants."

Technical report 05-0502-9 (1958). "Quercetin as an Antioxidant in Lard -- Alcott Test Method."

These reports can probably be obtained from Weyerhaeuser Co. upon appropriate request.

On the broad subject of antioxidants, Harvey Aft presented an excellent review in 1962. Another good review of the chemistry of dihydroquercetin is given in the chapter by Hergert in Geissman (1962, p. 575-579). In the same chapter, potential uses of wood and bark-derived flavonoids are discussed on pages 583-586.

The great interest in dihydroquercetin and quercetin prepared from it really was aroused by the considerable amounts found in Douglas-fir bark. Hergert, for example, states that "either whole Douglas-fir bark, which contains about 5 percent dihydroquercetin, or the cork fraction, which can readily be separated by screening and contains up to 22 percent dihydroquercetin, may be used." Quoting Kurth, in a reference to be cited, Hergert states that "approximately 150 million pounds of dihydroquercetin are potentially available each year in the residue bark from the lumber and pulp industries in the states of Oregon and Washington alone."

This statement, as of 1953, would need some updating to 1970, by virtue of the increasing percentage of younger timber being used. In the present state of the market, it is not of very great significance. A recent personal communication from A. S. Gregory of Weyerhaeuser Co. says the potential world market for quercetin probably does not currently exceed about 40,000 pounds.

It is also worthwhile to remark that little is known about dihydroquercetin or its probable precursors (perhaps as glycosides) in younger bark.

Hergert, in summarizing his chapter (Geissman 1962), states: "It is evident that marketing of flavonoids from bark or wood will require much additional research on more economic methods of recovery, and the development of additional suitable uses."

The earlier work on dihydroquercetin dealt largely with preparation and uses of the compound (Kurth and Chan 1951). The authors discussed the occurrence of DHQ and its conversion to quercetin with hot dilute mineral acids or bisulfite solutions. From specimens of old-growth bark (from California, New Mexico, Oregon) they obtained from

4 to 7.6 percent of DHQ, 6.5 to 10.2 percent of wax, and 7.3 to 13.6 percent of tannin. They discussed the methods of separating DHQ from aqueous extracts of Douglas-fir bark and of purifying the compound.

Effects of its use as an antioxidant in lard, butter oil, and cottonseed oil were given, indicating favorable results. Adequate stability was obtained with 0.03 percent DHQ, but in combination with citric acid in use, effective stability was obtained with 0.015 percent of DHQ. With lard, quercetin was slightly more effective than DHQ.

Hergert and Kurth (1952) described the recovery of DHQ from the cork fraction of Douglas-fir bark; this article is important in its conclusions with respect to the chemical composition of the cork.

Kurth and Chan (1953) also discussed methods of separation of DHQ from whole bark. They preferred extracting the whole bark with an appropriate solvent to remove the waxes and then extracting with hot water countercurrently to remove tannin and DHQ. Subsequently, DHQ was separated from tannin by extraction with diethyl--or diisopropyl ether. Or, alternatively, the bark was extracted countercurrently with hot water to remove tannin and DHQ. The residue was extracted with an appropriate solvent to remove the waxes. In these experiments they reported yields of 8 to 9.8 percent of DHQ.

Kurth (1953a) described conversion of DHQ to quercetin by use of bisulfites.

> Approximately 90 percent conversion to chemically pure quercetin is obtained by simple refluxing of DHQ in 5 to 20 percent aqueous solutions of sodium, potassium or ammonium bisulfite. Over 85 percent conversion is effected within concentrated solutions in one hour. Quercetin is insoluble in hot bisulfite solutions whereas DHQ and tannins are relatively soluble.

With hot calcium bisulfite liquor, Kurth found formation of a yellow, insoluble calcium complex of quercetin as a fine, impervious crust--an explanation in part of the difficulty of pulping Douglas-fir with calcium bisulfite.

Another article by Kurth (1953b) covers approximately the same ground as the preceding one.

Kurth, Hergert, and Ross (1955) treat in detail methods of purification and separation of 3-hydroxyflavanones by treatment with bases, basic salts of the alkali metals and ammonia at a pH of 6.0 to 7.5. Refluxing solutions of such salts causes racemization and/or conversion to the corresponding flavanol.

A patent (1956a) for conversion of DHQ to quercetin was issued to Kurth. Similar procedures are covered in a Canadian patent issued to Kurth (1956b). Another patent referring only to precipitation of DHQ was issued to Kurth (1956c).

Hergert and Goldschmid (1958) reported the presence of the 3'-β-glucosides of DHQ and quercetin in Douglas-fir needles, cambium, and sapwood. They suggested that taxifolin (DHQ) is synthesized in the needles, where it is present as the glucoside, and is then transported to the heartwood and outer bark where it is found as the aglycone. This is an excellent article for the biochemist interested in the field of biogenesis.

Aft (1961) goes further into the chemistry of DHQ, a reduction derivative, eriodictyol, and the related astilbin and sakuranetin. Properties, preparation, UV spectra, and IR spectra for the various acetate derivatives are reported.

The methods for separation of DHQ and conversion to quercetin were not very attractive as chemical engineering processes. Weyerhaeuser Research Division, therefore, aimed much research at a process more efficient and economical for large scale production. This work was summarized by Gregory and others (1957), going rather deeply into the general question of extraction of Douglas-fir bark with a series of solvents and the general nature of the extracts so obtained.

For quercetin, the authors sought a process for converting DHQ in aqueous solution that:

(a) Could be carried out in simple equipment.
(b) Used small amounts of low cost reagents.
(c) Operated on extracts of varying concentration and composition.
(d) Had a minimum effect on the other components of the extract (degradation or contamination).
(e) Was capable of completion in a short time.
(f) Gave good yields and high product purity.

They carried out much work, controlling the following variables:

1. Hydrogen ion concentration.
2. Type of alkali used.
3. Temperature of reaction.
4. Oxygen concentration and aeration rate.
5. Degree of agitation.
6. Use of catalysts.
7. Concentration of extract.
8. Composition of extract.

Out of it, they concluded that they could obtain yields of 65-80 percent of the DHQ as quercetin by oxidizing with air in substantially neutral solutions. A patent covering the process was issued to Roberts and Gregory in 1958. This patent discloses a method of extracting water solubles from bark (e.g., Douglas-fir), such as phenolics, dihydroquercetin, and various carbohydrates. The extraction is by water in a series of countercurrent extraction cells. The process was claimed to reduce the number of extraction stages required.

This patent was followed by others in 1959 and 1961 issued to A. S. Gregory. These patents go into detail as to physical properties, solubilities, etc., leading to the process discussed in the article by Gregory and others (1957). Considerable quantities of quercetin were produced by this method in a pilot plant in Longview, Wash., but a market for commercial amounts did not develop.

An improvement or amplification of the above patents appeared in 1964 in the patent issued to Esterer and Dowd of Weyerhaeuser Co.

This patent describes a process for treating the aqueous extract to remove DHQ, thereby improving the usefulness of the extract for well-drilling mud compositions. In effect, the aqueous extract was extracted with amyl acetate, removing DHQ. Methods are given for recovering the DHQ.

Along similar lines is a patent (Brink 1965) which discloses a method of separating DHQ, along with the phenolics and other aromatic materials, from carbohydrates and "soluble residuals." The aqueous extract is adjusted to pH 10-12.5 by use of oxides or hydroxides of the alkaline earths. The precipitate so obtained contains high concentrations of DHQ and other phenolics, a starting material for "isolation and separation of chroman derivatives from other aromatics."

Esterer's patent of 1965 carried the general idea a little further. "The present invention provides for the contacting of an aqueous extract containing chroman derivatives and other soluble materials with a cation-exchange resin at a relatively low temperature and eluting the chroman derivative retained on said resin with hot water at a temperature from 95° - 100° C." The sorption phase was carried out at 45° - 55° C.

Numerous examples of suitable resins are given. The principal "chroman derivative" from Douglas-fir bark is DHQ, accompanied under some conditions by catechin.

Reference is made in the above patent to U.S. Patent 2,681,907 to Simon H. Wonder in 1954, assigned to U.S. Atomic Energy Commission. The process of adsorption was similar, but the elution was carried out with organic solvents.

It is apparent that considerable technology is available for separation of dihydroquercetin and its transformation to quercetin. It is also clear that the chemistry and reactions of quercetin have generated a large literature. If a use requiring large volumes of quercetin or DHQ is ever developed, an excellent source is available in Douglas-fir bark.

CHAPTER XIII

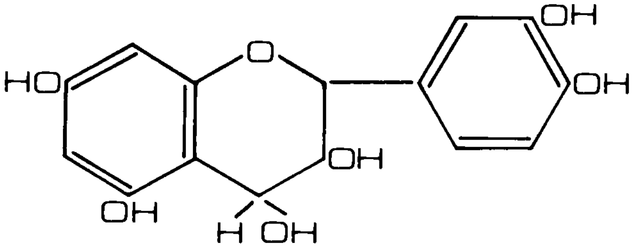
"PHENOLIC ACIDS"

The heading of this chapter appears in quotation marks because the term seems to have little, if any, specific reference.

Hergert (Geissman 1962, p. 573) makes the following statement under the heading "Phenolic Acids."

> Alkaline extraction of solvent-extracted bark yields a product termed "phenolic acid," so-named because it contains both phenolic and carboxyl groups. This polymeric polyphenolic fraction has been found in all coniferous and most hardwood species of bark examined to date. It comprises from 2 to 40 per cent by weight of the bark. *Structural elucidation is of importance in developing economic usage of the material.* [Italic ours.] The author's observation (Hergert, For. Prod. J., 1958, loc. cit.) that alkaline treatment of coniferous tannins or phlobaphenes leads to the formation of carboxyl groups in the polymer suggested that the phenolic acids were a degradation product of the fraction occurring *in situ*. Subsequent investigation has confirmed this and has shown that in many species of coniferous

bark, the so-called phenolic acids are actually polymeric leucocyanidins subsequently degraded by the action of alkali. . . . In short, the outer bark primarily consists of a lignocellulose impregnated with condensed tannins which were originally derived from flavan -3- and -3, 4 diols, but which now cannot be extracted with inert solvents.



Leucocyanidins

It is not possible in this report to cover the various theories of biogenesis and structures of the compounds involved. The worker interested in this field should review Geissman and the extensive bibliographies there. It will be well, also, to study the chapter by A. J. Birch (Geissman 1962) which brings out developments in the biosynthesis of the C_6 - C_3 - C_6 compounds. Further important developments have taken place since 1962. However, I find missing a logical explanation for the occurrence of the carboxyl groups in the phenolic acids.

From many previous references it is clear that the term "phenolic acids" is applied to a group of substances of generally unknown composition, found in all physical fractions of Douglas-fir bark.

Kurth and Kiefer (1950) had shown the presence of 20 percent of ferulic acid in the benzene-soluble wax. Hergert and Kurth (1952) showed, also, the presence of 9.8 percent ferulic acid in the hydrolyzed cork, accompanied by 11.7 percent uncharacterized "acids and phenols."

Further, Hergert and Kurth examined the cork fraction and showed that treatment of the extractive-free cork with hot alcoholic KOH gave a material characterized as "phenolic acids" up to over 40 percent of the base material. They showed the radical difference of this substance from lignin. They also showed that, in the cork, the hydroxy acids were probably esterified to the phenolic acid but also to each other in an estolide-type linkage.

The authors referred to Kiefer's thesis on the composition of the bast fibers of Douglas-fir bark. The results of Kiefer's work were published in 1953 (Kiefer and Kurth 1953).

The phenolic acid fraction was obtained from extractive-free fibers by heating with 1 percent NaOH solution at the temperature of a boiling water bath for 1 hour. The resulting dry, light brown, amorphous powder was "only slightly soluble in dioxane, alcohol, acetone, pyridine or ethyl acetate, although the moist precipitate when first isolated was completely dispersed in dioxane and acetone." The term "dispersed" is somewhat ambiguous, but the inference may be made that the freshly isolated material was undergoing change, resulting later in insolubility.

The product yielded no lignin color reaction and only 1.63 percent vanillin in contrast to much higher yields from true lignins.

The product was methylated both by diazomethane and dimethyl sulfate procedures and the following functional groups calculated:

	Percent	Number in molecule
Methoxyl	4.3	1.18
Carboxyl	5.3	1.00
Phenolic hydroxyl	8.3	4.14
Aliphatic hydroxyl	4.2	2.10

> On the assumption that the phenolic acid is monocarboxylic and contains 5.3 percent carboxyl groups, its minimum molecular weight is 850 and the molecule contains approximately one methoxyl, four phenolic groups and two aliphatic hydroxyl groups.
>
> Infrared absorption spectrum confirmed the presence of the carboxyl group, and showed similarity to the phlobaphene in the alcohol extract from the bast fibers.
>
> Both the phenolic acid and the phlobaphene spectra showed *little or no carbonyl* absorption. [Italic ours.]

In 1955, Chang, Mitchell, and Saeman[12] made a study, the purpose of which "was to apply the techniques of paper chromatography to the problem of separating the water-soluble constituents of Douglas-fir bark. Work on the identification of constituents was considered secondary in importance to the task of finding solvent systems that could resolve the mixtures into their constituents." Material was supplied by Weyerhaeuser Co.

The report of this study goes into considerable detail in many aspects of chromatographic analysis, but, with particular reference to the subject being discussed, a statement on page 13 is pertinent. The butanol extract (after ether) of the material showed "at least five phenolic components in the form of fairly concentrated spots." In ensuing pages methods are developed for further separation. A concluding sentence may be of interest: "The complexity of bark extracts is so great that a complete analysis is virtually impossible." Subsequent progress has changed this.

By the early fifties, it was generally accepted that the phenolic acids in Douglas-fir bark, as well as in other conifers, should be regarded as quite different from lignin in the wood. This notion came with difficulty.

For example, Brauns and Brauns (1960, p. 118) state: "Although this term (bark phenolic acids, as used by Kurth) instead of 'bark lignins' may be more appropriate for this type of material, it is not intended to denote that the bark phenolic acids are structurally unrelated to lignin."

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[12] Ying-Pe Chang, R. L. Mitchell, and J. F. Saeman. Chromatographic separation of water soluble extractives from Douglas-fir bark. Unpublished report, U.S. Forest Products Laboratory, Dec. 21, 1955.

The statement that the phenolic acids may originate from precursors the same as or similar to those of lignin can be made just as logically for literally thousands of compounds found in plants, all of the $C_6 - C_3$ basic formula, with the infinite number of configurations possible from various degrees of oxidation and types of condensation. As will appear, the properties of the phenolic acids are quite different from those of lignin, especially with regard to the presence of carboxyl groups.

The precursors of both lignin and phenolic acids and the pathway from sugars to their final forms are still the subject of much theorizing and will not be pursued in this report.

In 1954, James E. Smith submitted a Ph. D. thesis to Oregon State College.[13/] The results of his work were published that year (Kurth and Smith 1954).

Both papers give good summaries, with bibliographies, of the work to that date on Douglas-fir bark, with comparisons to similar work on redwood, white fir, and western hemlock.

The material used was from mature trees and was divided into inner bark and outer bark, the latter including the volumes outside of the cork cambium. The inner bark thus obtained amounted to 11.1 percent (ovendry weight) of the whole bark.

From these, six physical fractions were prepared. The inner bark was separated into bast fibers and fines (particles smaller than 100 mesh). The outer bark contained about 55 percent cork, 30 percent bast fibers, and 15 percent crushed phloem, and was separated into four fractions: cork, outer bark fines (particles smaller than 100 mesh and made up of small or broken bast fibers, crushed sieve cells, and phloem parenchyma), outer bark phloem, and crushed sieve cells and parenchyma.

The following tabulation shows the yield of phenolic acids from these fractions obtained by 1 percent sodium hydroxide extraction of bark components:

Bark component	25° C.	90° C.
	Percent	Percent
Inner bark bast fibers	2.9	8.1
Outer bark bast fibers	3.3	9.5
Inner bark fines	.1	21.6
Outer bark fines	12.0	58.8
Outer bark phloem sieve tubes and parenchyma	5.1	23.9
Cork	21.6	39.2

Methoxyl contents of these fractions decreased from 8.19 in the material from inner bark bast fibers to 4.21 in cork and 4.35 in outer bark fines.

Extensive chromatographic and absorption spectra results, given in the thesis proper, indicate considerable uniformity in the general composition of the fractions.

[13/] James E. Smith. The chemical nature of the "lignin" of the bark of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco). 1954. Ph. D. thesis on file at Oreg. State Univ., Corvallis.

These results strongly support previous statements that, for the most part, these substances are in some sort of combination in the bark, that is resolved by hot alkali. The method of combination in the cork has been discussed, but that in the other fractions remains to be resolved.

The large amounts found in the fines fractions are indicative of the possibilities in processing second-growth bark for fiber and phenolic acids.

The thesis, table 4, page 13, shows some interesting results that are not discussed in the published paper. In particular, it was found that 2 percent sodium sulfite at 90° C. extracted 6.53 percent of phenolic acids from inner bark bast fibers. This result seems to offer some suggestion of other than ester or estolide linkages.

The authors call attention to **carbonyl** absorption bands and similar results with preparations from other conifers. On page 103 of the thesis, Smith states: "It appears likely that [infrared] absorption in the region of 1688-1704 cm^{-1} is associated with the carboxyl group." This and subsequent observations should lead to investigation of lactone and other possible inner anhydride and intermolecular anhydride structures.

The summary of the published paper reads:

> Douglas-fir bark was separated into six physical fractions for an examination of its lignin-like materials. Extraction of the extractive-free bark fractions with hot 1 percent sodium hydroxide removed almost four times the amount of phenolic acid that was obtained when similar extractions were carried out at room temperature. This suggests that the removal of the phenolic acid from the bark is a saponification process as was found in an earlier study of Douglas-fir cork. In the cork, the phenolic acid exists naturally in the form of a phenolic acid-hydroxy acid ester.
>
> The phenolic acid contents of the Douglas-fir bark components were: cork 39.2 percent; outer bark fines 58.8 percent; inner bark fines 21.6 percent; outer bark bast fibers 9.5 percent; and outer bark phloem parenchyma 23.9 percent.
>
> All the phenolic acid fractions isolated from the outer bark components had methoxyl contents between 4.21 and 4.95 percent, while the inner bark phenolic acids contained 6.78-8.19 percent methoxyl. It appeared from chemical studies that the phenolic acids isolated from the various physical bark components were primarily definite chemical entities with small amounts of impurities. Differences observed may be mainly due to the extent of demethylation brought about by exposure, aging, and the action of the cork cambium in the process of tree growth. [I am strongly inclined to doubt the validity of this. Maybe mixtures of similar entities, but, as yet, quite undefined.]
>
> Freshly isolated bark phenolic acid preparations showed strong tendencies to dissolve in water. Like tannins, they could be precipitated from solution with sodium chloride. Other chemical tests indicated that the bark phenolic acid possessed phlobatannin properties. . . .[Treatment of tannin properties, dioxane lignin from bast fibers, and solvent systems should be consulted in the thesis.]

The formation of protocatechuic aldehyde and only small amounts of vanillin by alkaline nitrobenzene oxidation of bark phenolic acids indicated that a catechol nucleus may be an important building unit in the structure of these materials. Other low-methoxyl phenolic materials, such as phlobatannins and phlobaphenes, contain catechol nuclei which could also result in the formation of protocatechuic aldehyde. Further investigations concerned with the production of this aldehyde from low-methoxyl lignins and related materials should give informative results.

The alkaline oxidation with nitrobenzene actually gave a yield of 9 percent aldehydes, mostly protocatechuic with a little vanillin.

It is fairly clear that the products of the hydrolysis by hot alkali, when acidified for separation of the phenolic acids, are quite unstable and are reacting rapidly with each other. If the reactive hydroxyls and probably liberated carboxyls are present as Na-salts in the hydrolysis mixture, it would seem that differential methylation might produce some greater stability. It is even possible that hydroxyls could be methylated in the unhydrolyzed material, followed by methylation of carboxyls in the hydrolyzate.

In his thesis, page 91, Smith suggests, "This study showed that further examination of cork phenolic acid is necessary. Masking of the phenolic groups through methylation would prevent oxidation at the ortho-dihydroxy position . . . ."

Attention is called here to recent work by H. I. Bolker and coworkers (Bolker and Terashima 1966, 1967) at McGill University on a new technique for isolation of lignin from wood, the probable existence of lignin-carbohydrate covalent bonds, and the infrared absorption of isolated nonconjugated keto-groups in the phenyl propane side chain.

The reagents used are simple acetals of acetone (2,2,dimethoxypropane and 2,2, diethoxypropane) with HCl in dioxane. This technique could be of importance in the further study of the phenolic acids.

According to my correspondence with Dr. Bolker, he is just now (January 1970)

beginning to write papers for publication. The first will be a short note to appear in 'Science.'

The newer material is available only in the form of two theses, not available.

(1) C. H. Chew, 'The Solvolytic Extraction of Lignin from Wood.' Ph.D. thesis, McGill University, March 1968.
(2) H. S. Brenner, 'The Macromolecular Structure of Lignin.' M.S. thesis, McGill University, September 1969.

In 1957, Fahey, under Kurth, submitted a Ph. D. thesis[14] to Oregon State College and published results of the study in the same year (Fahey and Kurth 1957).

The thesis centers on the cork from white fir bark but includes considerable work on Douglas-fir bark for purposes of comparison. The methods of isolation of the phenolic acids were similar to those used previously for Douglas-fir. Methods are referred to as developed by Hergert in 1954, "Final file report on Project 5A4" at the Oregon Forest Products Laboratory. This report has not been found in the files at Corvallis.

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[14] M. D. Fahey. Organic chemistry of bark phenolic acids. 1957. Ph. D. thesis on file at Oreg. State Univ., Corvallis.

Fahey tried, with negative results, 52 solvent systems in attempts to obtain satisfactory chromatographic resolutions of the phenolic acids obtained by hydrolysis of the cork. In further attempts to get insight into the composition, he tried: ethanolysis, nitration and nitric acid oxidation, permanganate oxidation, mercuric oxide oxidation, cupric oxide oxidation, methylation, and nitrobenzene oxidation of the methylated products. He used intensive chromatographic methods throughout.

The following statements are from the "Discussion," pages 99-103, of his thesis:

> Chromatographic evidence in attempted resolution:
>
> The evidence favored the conclusion that the material was homogeneous or contained very small amounts of impurities. The conclusion was tentative since none of the solvents investigated were entirely satisfactory.
>
> Exploratory oxidations with nitric acid and permanganate were unsuccessful from the standpoint of degradation products. They did confirm that the phenolic acid was a highly condensed and highly active phenolic compound.
>
> The results from attempts to hydrolyze the phenolic acid in concentrated potassium hydroxide ruled out a structure of the chromone type, unless chromone groups were further linked by carbon to carbon bonds. . . .
>
> Alkaline fusion products obtained from both white fir and Douglas-fir were of the same composition . . . . The presence of phloroglucinol . . . differentiated phenolic acid and wood lignin.
>
> Alkaline nitrobenzene oxidation of the material from white fir yielded to qualitative analysis the presence of protocatechuic aldehyde, vanillin and p-hydroxy-benzaldehyde. [The last has not been shown in phenolic acids from Douglas-fir.]

Methylation studies with dimethyl sulfate gave a separation into large and small fractions, neither homogeneous.

> Methylated phenolic acid was oxidized with alkaline nitrobenzene, producing vanillin and vanilloyl formic acid.
>
> [A discussion of production of veratroyl formic acid by alkaline fusion of wood lignin and distinction from phenolic acids.]

Identified were carboxyl, phenolic hydroxyl, and aliphatic hydroxyl groups.

Among fusion products were: phloroglucinol, catechol and protocatechuic acid.

Oxidation with nitrobenzene or cupric oxide gave vanillin, 5-formyl-vanillic acid, 5-carboxyvanillin, p-hydroxybenzaldehyde, p-hydroxy-benzoic acid, protocatechualdehyde, vanillic acid, vanilloylformic acid, and several unidentified compounds.

The very large amount of work involved here and the paucity of positive results serve to emphasize the difficulties in determining the constitution of phenolic acids prepared by alkaline hydrolysis and acidification of the hydrolysate.

In the thesis by Holmes, some matters are discussed that did not appear in the publication (Holmes and Kurth 1961).

> An examination of the extractives from the newly formed inner bark of Douglas-fir revealed that the ether solubles contained predominately d-catechin and l-epicatechin.

Considerable reference is made to the paper by Hergert (1960).

> After ion-exchange separation, the water solubles were examined by paper chromatography. The following amino acids were shown to be present: glutamic acid, aspartic acid, serine, glycine, proline, alanine, threonine, valine, leucine, and isoleucine. Some evidence was obtained for the presence of tyrosine and phenylalanine. Sucrose, fructose, and glucose were present in varying amounts during the year but raffinose appeared to be present only during the growing season.
>
> In addition to six unidentified hydroaromatic substances, quinic and shikimic acids were present.

In the body of the thesis, there are some significant matters that were not published.

The ether solubles from new bark could not be separated into aldehydes, phenols and neutrals by classical methods [$NaHSO_3$, Na_2CO_3, NaOH].

On page 19 of the thesis, in an ethyl acetate extract from the water solution, he obtained identical chromatograms for old, medium, and new bark showing "a weak *carbonyl* absorption band at 1690 cm^{-1}."

Page 33 (thesis):

> Ether solubles extracted from water solubles from the inner bark yielded a little brown oil whose IR gave a strong *carbonyl* absorption band.

Page 64 (thesis):

> To the author's knowledge, no direct evidence has ever been published concerning the existence of carboxyl groups in the phenolic acids before isolation. Since the pyran ring in flavonoids is known to be very sensitive to alkaline and acid conditions,
> (Seshadri, T. R.
> 1959. Recent developments in the chemistry of flavonoids.
> Tetrahedron, 6, pp. 169-200)
> it would not seem unreasonable to assume that isolation cleaves the polymer at random pyran linkages, forming carboxyl groups.

Hydrotropic pulping of the fiber fraction was described by Lenz and Kurth (1963). The phenolic acids obtained in these procedures did not differ significantly in analysis from those obtained by alkaline extraction.

In 1963, Jim Wilson, a student of Kurth, presented an interesting and important thesis.[15] Although this work deals with a hemlock, it is important because of the range of experimental techniques used and the discussions of previous and related work involved. Using the fines as material, Wilson applied the following methods in attempting resolution of components:

Paper electrophoresis
Selective solvent fractionation
Absorption column chromatography
UV and IR spectra
Color reactions
Nonaqueous titrations
Molecular weight by vapor pressure osmometry.

No pure compounds were isolated and identified as such. The author concluded that the crude phenolic acid consisted of two principal fractions, approximately equal in percentage, that differed significantly in colors, solubilities, methoxyl content, and IR spectra. These acids were all obtained by the usual extraction with hot sodium hydroxide.

Referring to carboxyl absorption spectra, Wilson wrote: "The position of this peak would indicate that the carboxyl groups in these phenolic acids were aliphatic in nature. The spectra also indicate the presence of ether linkages in the phenolic acids." Wilson expressed the opinion that the basic monomer in his material was the same in all fractions.

An important article by Hergert and coworkers (Hergert and others 1965) dealt with extractives from western hemlock bark. This article deals with much of the work upon which the development of the "Rayflo" line of bark products by Rayonier, Inc. was based, but much information is contained on the methodology of work with phenolic acids (p. 487):

> The infrared spectrum, except for an absorption band at 1715 cm.$^{-1}$ due to a carboxyl group, was indistinguishable from that of the phlobaphene fraction. The carboxyl group is believed to be an artifact due to the oxidative action of air and alkali on some of the pyrane rings in the phenolic polymers during isolation. Treatment of catechin, leucocyanidin or hemlock tannin with dilute alkali results in the degradation of the pyrane ring and the formation of carboxyl groups. [Reference here to Hergert, "Unpublished work."]

If these remarks are valid they are important, but I do not believe they explain matters entirely.

Fujii and Kurth (1966) state:

> The major component of extractive-free conifer barks is the phenolic acid fraction soluble in dilute alkalies. This component is a mixture of related polyphenols differing in the extent of polymerization and types of molecular chemical linkages.

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[15] Jim Wilson. The isolation and the properties of the bark phenolic acids from mountain hemlock, *Tsuga mertensiana* (Bong.) Carr. 1963. Ph. D. thesis on file at Oreg. State Univ., Corvallis.

Alkaline hydrogenolysis of Douglas-fir bark phenolic acids fraction with Raney nickel in 6 percent sodium hydroxide solution at 150° to 200° C. gave a yield of 30 percent to 34 percent ethyl ether solubles. TLC (thin layer chromatography) indicated the presence of 12 compounds.[16]

Subsequent work on hydrogenolysis (confidential, at Weyerhaeuser Co. Research Center Laboratory) showed some promise. I strongly suggest that this might be pursued with advantage, with variation of catalysts and conditions.

Two papers should be of value in guiding future work, a thesis by Manners[17] and a paper by Manners and Aft.[18] Manners' thesis has been made available, but an abstract does not appear in Bibliographic Series No. 191, Supplement 1, from the Institute of Paper Chemistry (Roth and Weiner 1968). Neither is the paper by Manners and Aft reported.

Following is a summary of Manners' thesis:

> A detailed chromatographic examination of *Pseudotsuga menziesii* and three other *Pseudotsuga* species (*P. macrocarpa, P. japonica,* and *P. wilsoniana*) was made. The whole bark was sequentially extracted with hexane, benzene, ethyl ether, ethyl alcohol and water.
>
> [One wonders at the omission of acetone or ethyl acetate before alcohol.]
>
> Paper and thin layer chromatographic techniques were coupled with ultraviolet spectral procedures in the isolation and identification of individual compounds.
>
> Compounds identified and previously reported which were common to all species included: dihydroquercetin, quercetin, dihydroquercetin-3'-monoglucoside, l-epicatechin, d-catechin, vanillin, protocatechuic acid, coniferaldehyde, and leucoanthocyanins. Compounds discovered in the four species which have not been previously reported include: eriodictyol, vanillic acid, vanillyl alcohol, acetovanillone, and at least two esters of ferulic acid.

Subsequently, in 1968, the paper by Manners and Aft was presented. The original of this paper cannot be found, but a summary was supplied by Dr. Rowe.

The data included are the same as in Manners' thesis, with this addition: "From the hexane extract a mixture of fatty alcohol esters of ferulic acid was isolated, of which behenyl (C_{22}) ferulate is the principal component."

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[16] William E. Peterson. Hydrogenation and hydrogenolysis products from bark phenolic acids. 1964. M.S. thesis on file at Oreg. State Univ., Corvallis.

[17] G. D. Manners. Chemical composition of the bark extractives of four species of the genus *Pseudotsuga*. 1965. M.S. thesis on file at Oreg. State Univ., Corvallis.

[18] G. D. Manners and H. Aft. Phenolic bark extractives of four species of the genus *Pseudotsuga*. From the Sch. Forest., Oreg. State Univ., Corvallis (presented at the 155th Spring Meeting of American Chemical Society, 1968).

Although the results are clearly dependent only on chromatograms and spectra, they may furnish clues for subsequent work.

In their report on work on alkaline hydrogenolysis of Douglas-fir bark phenolic acids, Fujii and Kurth (1966) refer to the thesis by Peterson (see footnote 16).

This thesis is unavailable, but a brief abstract is given by Fujii and Kurth:

> Peterson attempted to obtain monomeric degradation products from Douglas-fir bark fines (Silvacon 490) by alkaline hydrogenolysis with Raney nickel catalyst at temperatures of 150-200° C. and with hydrogen pressure of 500 psig. He obtained ethyl ether soluble oils in yields of 30-34 percent. Aldehydes, acids and phenolic compounds containing the catechol and guaiacyl nuclei were present, in addition to p-hydroxybenzoic acid. Thin layer chromatography with silica-gel G indicated the presence of a total of 12 compounds.

The paper by Fujii and Kurth is the first of two dealing with ethanolysis of the Douglas-fir bark fines and substances found therein. Both papers carry valuable reviews of previous and related work, with adequate bibliographies.

The authors call attention to the extensive previous work using ethanolysis in the characterization of the monomers in wood lignin, producing the so-called Hibbert's ketones:

1-(4-hydroxy-3-methoxyphenyl)-1-propanone
1-(4-hydroxy-3-methoxyphenyl)-1, 2 propanedione (vanilloylacetyl)
1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone
1-(4-hydroxy-3-methoxyphenyl)-2-propanone (guaiacyl acetone)
Vanillin

In their work, the authors used paper chromatography and UV absorption to identify products. No Hibbert's ketones were observed in the substances from the bark.

They were able to identify the following: ethyl ferulate, ethyl protocatechuate, ethyl vanillate, protocatechuic acid, vanillic acid, and two unidentified compounds.

The original paper should be consulted for the methodology.

The second paper on alcoholysis products (Kurth, Aida, and Fujii 1968) is summarized (in part) as follows:

Identified ethanolysis products from dihydroquercetin were eriodictyol, quercetin and luteolin. When zinc dust was added to the ethanolysis mixture, the products were eriodictyol and phloroglucinol.

dl-catechin gave protocatechuic acid, 2, 4, 6 trihydroxyacetophenone and phloroglucinol, and in the presence of zinc dust, protocatechuic acid and phloroglucinol. Quercetin gave protocatechuic acid, 2, 4, 6 trihydroxybenzoic acid, and phloroglucinol.

Results are reported for mountain hemlock tannin.

Douglas-fir phlobaphene gave dihydroquercetin and protocatechuic acid. Extractive-free Douglas-fir bark fines gave cyanidin, peonidin, and two other unidentified anthocyanidins with methanolysis at room temperature. Other methanolysis products included ferulic acid, protocatechuic acid, and a large amount of dihydroquercetin.

The authors conclude that, in the reducing reactions, carbon to carbon bonds were broken. They suggest that the phlobatannin in Douglas-fir bark may be formed by:

(1) polymerization of dihydroquercetin,
(2) attachment of dihydroquercetin by either an ester or an ether linkage.

I have not attempted, in this review of phenolic acids, to cover the great numbers of publications in the general field dealing with similar fractions from other coniferous barks. This subject, important and complex, is worthy of a large volume.

One is tempted to speculate at length with regard to the application of other techniques that might be applied but this would be presumptuous, to say the least. But a few things seem fairly clear. The true chemical composition of the phenolic acids still eludes us, and the questions of biogenesis must be related to those fundamental matters regarding synthesis of the flavonoids and polymers thereof, still under discussion and research.

In general, it seems probable that the phenolic acids of Douglas-fir bark may be of different nature in the cork, fiber, and fines fractions. Certainly, the evidence for their modes of combination in the cork differs from that in the other fractions.

One thing is common to all: They must be obtained by treatment with alkali, a procedure that might indicate a number of things. But it seems to me it indicates clearly that the carboxyl groups of the underlying monomers are in some sort of combination. Some evidence, doubtful, of the presence of carbonyls was adduced by various workers. The suspicion arises that these two matters may indicate lactone structures or similar intramolecular condensations.

With the liberation of the carboxyls by acidification after hydroxide extraction, opportunities for condensations with phenolic hydroxyls, or aliphatic hydroxyls, or conjugated carbonyls become infinite.

From the phenolic acids themselves, by the various methods of cleavage and isolation attempted, there have been obtained only fragments in small yields, and the composition of the mass remains undetermined.

Many have observed that the key to utilization of this most important bark substance, or group of substances, lies in better knowledge of its structure. This is undoubtedly true, and no phase of bark utilization offers more promising rewards to research, built upon the excellent and voluminous work already accomplished. Those rewards will doubtless be accompanied by frustrations. Perhaps one line of attack might be to stabilize the phenolic hydroxyls before splitting the polymers in order to remove them from condensation. Possibly, similar techniques might remove the side-chain hydroxyls from activity.

Perhaps we have been confused by the ease of access to some of the flavonoids and have paid too little attention to the carboxyls. Attention may be called, for example, to the large class of substances known as "lignans." A fine review of the field was published in 1955 (Hearon and MacGregor 1955). A surprising number of lignans are lactones. Since this reference is now 16 years old, an up-to-date review is desirable.

Perhaps it may be well to suggest the possibility of the presence of substances analogous to truxillic acid, with condensations taking place between the C_3 side chains in various states of oxidation. Similarly, the possibility of substances like the chalcones might prove interesting. However the task is attacked, the way will be long, difficult and tedious. The techniques of chromatography and spectrography work best on pure compounds; with mixtures, they are good road maps. But isolation, identification, and proofs of structure cannot be thus accomplished. Someday, somebody will build a continuous program, financed and staffed with postgraduate chemists.

A quite recent publication in the field by Polein and Rapson (1969) may be very important. The authors have developed a method for UV and visible spectral determination of lignin in situ. Under this procedure, it is possible to study the chromophoric properties of lignin and other ligninlike polyphenolic components directly in groundwood pulp without damaging them by isolation procedures.

The authors report in detail results on not only compounds considered as part of the macromolecular lignin in wood but a large number of related C_6 C_3 compounds and polymers. I think these may exist free or combined in Douglas-fir bark.

CHAPTER XIV

ADHESIVE COMPOSITIONS

The phenolic characteristics of bark extracts and physical fractions have attracted considerable effort aimed at making adhesive compositions, designed mostly for use in plywood and particleboard manufacture. Twenty years ago, such efforts were of more interest than at present, largely because of the then higher relative costs of synthetic resin ingredients.

These efforts were quite often aimed at bark from more than one species, but the general principles involved are usually fairly broad. Also, the patents considered often deal with physical fractions or extracts that overlap matters discussed in other chapters. For purposes of unity under one subject, they will be cited in this chapter, disregarding duplication of previous references.

The following patents and articles have certain characteristics in common. Generally speaking, they deal in empirical ways with bark extracts or fractions of unknown composition that would be very difficult to prepare industrially in a standard manner possessing predictable and duplicable properties. These preparations are reacted with various types of the well-known aldehyde-phenolic resin components, usually with excess aldehyde to condense with unknown quantities of phenolic groups of unknown reactivity:

Van Beckum and Cook (1951 patent), plywood adhesive.
Heritage (1954 patent), thermosetting compound.
Ayers and Bradley (1957b patent), phenolic resin glue.
Herrick and Bock (1958 article), thermosetting plywood adhesives.
Steinberg and Gray (1958 patent), products from bark digested in ammonia.
Herrick and Bock (1958 U.S. patent; five Canadian patents, 1959a, c, d, e, f), alkaline bark extraction and product. Canadian patent 577,506 (1959b) introduces a variation worthy of note. The thermosetting resin composition comprises a sodium salt of a polymethylolphenol and a sodium substituted derivative of the bark of coniferous trees, such as Douglas-fir bark or western hemlock. The bark derivatives are prepared "by extracting the bark with ammonia and reacting the ammonia extract with sodium hydroxide."

Baxter, Schoening, and Preusser (1959 patent), phenol-aldehyde adhesive composition.
Hall, Leonard, and Nicholls (1960 article), formaldehyde-tannin in bark from *Pinus radiata*.
Herrick and Conca (1960 article), cold-setting adhesives.
Williams and Baxter (1960 patent), phenol-aldehyde thermosetting resin.
Preusser (1960 Canadian patent), phenol-aldehyde thermosetting resin.
Anderson, Breuer, and Nicholls (1961 article), bonding particleboards with bark extracts.
Herrick and Bock (1962 patent), adhesive comprising sodium substituted bark derivative and sodium salt of polymethylolphenol.

Plywood manufacture, the laminating industry, and particleboard manufacture have in recent years become much more sophisticated than in earlier years, and consequently, more demanding with respect to standards for adhesives that permit rapid and continuous gluing of products with increasingly rigid performance requirements.

Although, unquestionably, crude bark extracts properly compounded can be and have been shown to make acceptable goods on a small scale, there has been no great industrial use of any of them.

It does seem possible that phenolic mixtures might be produced from bark, that, compounded with other phenols to strict standards, might be quite useful in preparing adhesives of strictly controlled properties. But it seems to me that the crude extracts fall short of these requirements.

CHAPTER XV

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CHAPTER XVI

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CHAPTER XVII

APPENDIX

In the two "Bibliographic Series, No. 191" (Roth and others 1960) and "No. 191, Supplement 1" (Roth and Weiner 1968) by the Institute of Paper Chemistry, there are 163 references on use of bark as fuel. As would be expected, most of these have to do with the bark from pulpwoods, drying, comminution, methods of burning, either alone or in mixture with other fuels. Since most Douglas-fir bark is produced at sawmills and plywood mills, most of these references have only indirect relationship to the general problem.

These photomicrographs, figures 1-4 and 6-11 (page 98), by Bror L. Grondal were published in *West Coast Lumberman*, October 1942.

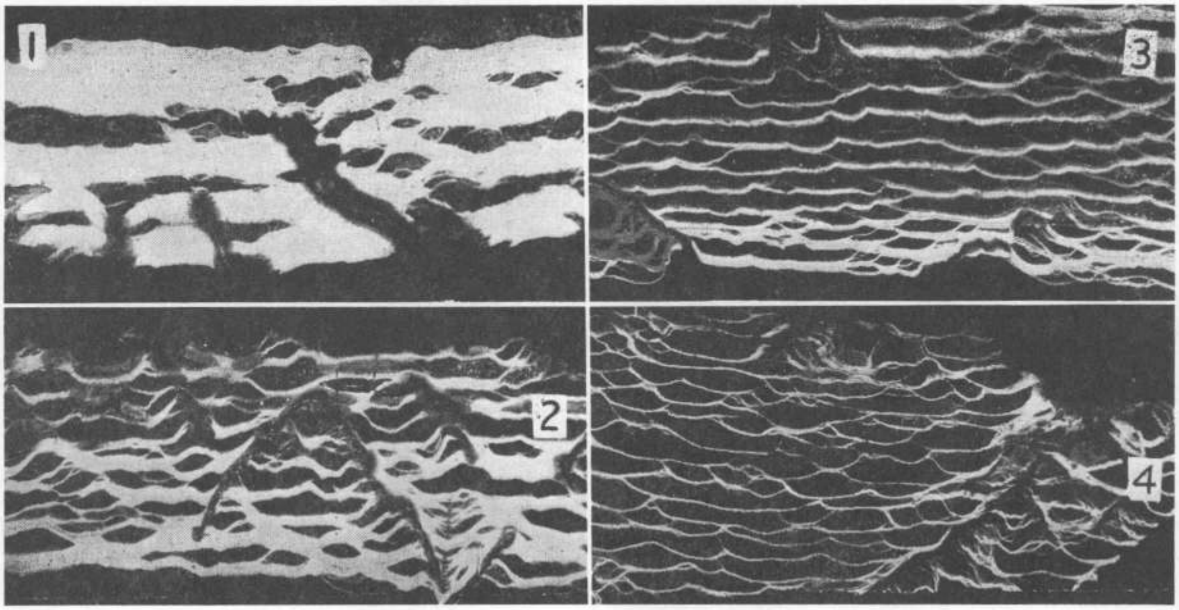


Figure 1, above, left. Grade 1 Douglas fir bark. Figure 2, below, left. Grade 2 bark. Figure 3, above, right. Grade 3 bark. Figure 4, below, right. Grade 4 bark. Full size. Bark on Douglas fir is sometimes a foot or more thick.

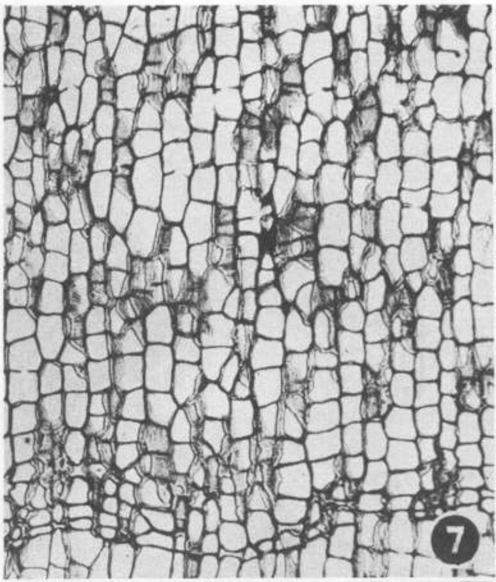


Figure 7—Cross-section of highest grade of Mediterranean cork, x 120.

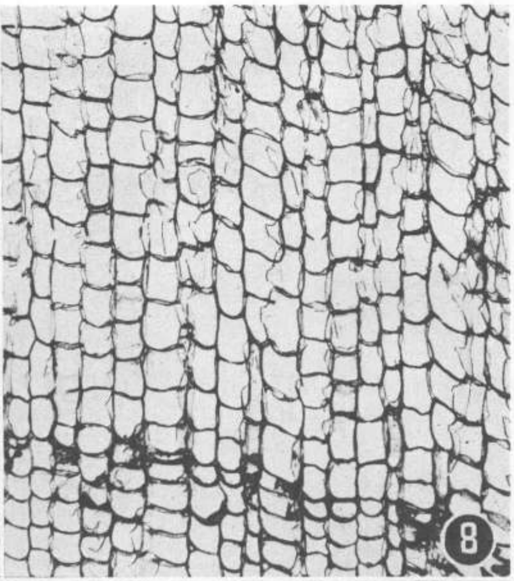


Figure 8—Cross-section of cork from No. 1 Douglas fir bark, x 120.

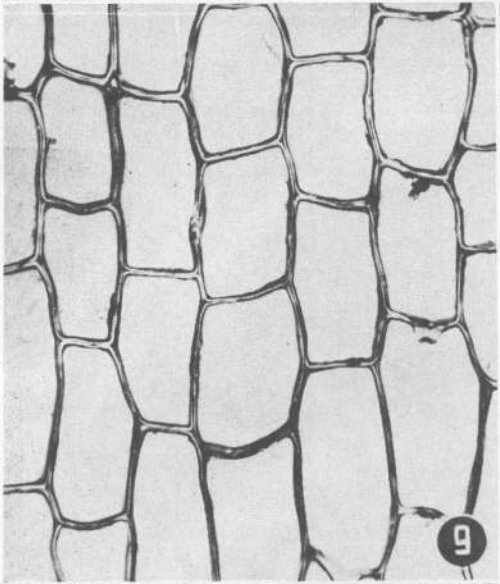


Figure 9—Highly magnified cross-section of Mediterranean cork, x 660. Note the uniform and sturdy cell walls.

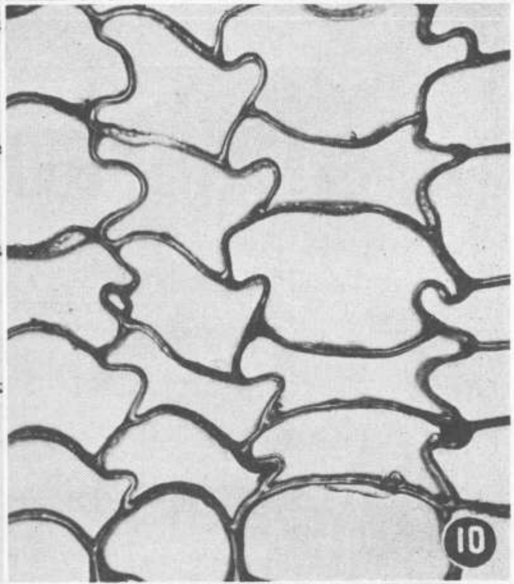


Figure 10—Highly magnified cross-section of Douglas fir cork, showing partial collapse of cells due to bark pressure, x 660. Treatments to expand the cells have been developed.

Figure 11 — Hard, inelastic schlerenchyma or "stone" cells are common in virgin Mediterranean cork, making it useless for many purposes, x 660. Such groups of stone cells are not commonly found in Douglas fir cork.

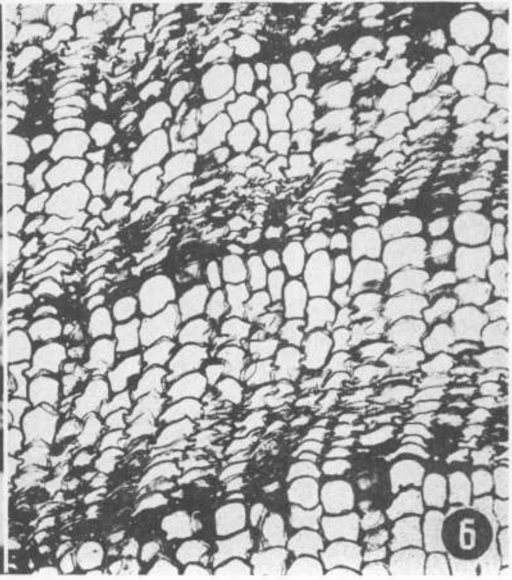


Figure 6—Cross-section of Douglas fir cork, x 120. Note the annual growth layers and compressed cells. From No. 2 bark. This section, as well as the sections in Figures 7 to 11, inclusive, was cut by Wm. I. West. Photomicrographs by Bror L. Grondal.

SANDY HILL
CORPORATION
HUDSON FALLS, NEW YORK 12839 · CABLE ADDRESS "IBWKS" · TEL. 518-747-3381

October 3, 1969
Our 111th Year

U. S. Department of Agriculture
Forest Service
Pacific Northwest Forest and
Range Experiment Station
P. O. Box 3141
Portland, Oregon 97208

Attention Mr. J. Alfred Hall
Consultant

Gentlemen:

This is to acknowledge receipt of your letter No. 4830, dated September 30, 1969, with reference to the Letts Burnet Machine.

Sandy Hill did build one production machine for the manufacture of burnets. This machine was built for Mr. Letts and was built to his design. The basic design had been worked out by Mr. Letts and we worked to his design with the exception of a few changes which we had suggested to facilitate manufacturing.

Only one production Burnet Machine was ever built. This machine was operated for a considerable period of time at Mr. Letts' plant in Northville, N. Y., and was later moved to Warrensburgh, N. Y., where it operated for quite some period. However, the Burnet operation at Warrensburgh was discontinued and the Burnet machine was sold. A few years before his death, I talked to Mr. Letts on the phone and attempted to find out from him the present location of the Burnet machine. He advised that he had sold it to a Forestry College in Vermont and that the machine was later shipped to the coal mine region of Pennsylvania. He advised that attempts were being made to compress coal dust into a cylindrical form, but he did not know how successful was the operation.

The patents on the machine were held by Mr. Letts and we have no knowledge of the status of the patents.

DESIGNERS AND BUILDERS OF PULP AND PAPER MACHINERY SINCE 1858

U. S. Department of Agriculture
Forest Service

10/3/69

Mr. Letts had spent many years and, undoubtedly, a considerable sum of money in the development of the Burnet machine. However, the Burnet machine, as designed and built, was not completely successful. It was felt that additional work was required to make the machine more successful and efficient. For some reason or other, Mr. Letts declined all suggestions that further engineering work be done on the machine and, since he owned the patent, no further development work was done.

From time to time, we have heard rumors that a machine similar to Mr. Letts' Burnet Machine was being manufactured, but we have never been able to verify these rumors.

In your letter you ask if we feel that the machine was adaptable to the manufacture of briquets from bark. One of the problems with the Letts Burnet Machine was its tendency to plug, and the material had to be put through a hammer mill before it was introduced to the Burnet Machine. It would appear that it would be quite difficult to work bark down to the fine particle size which would be required for the Burnet Machine. It would be questionable if the Letts Burnet Machine, as last designed, would be suitable for the manufacture of burnets from any type of bark.

At one time, we expected that the burnet machine would be a very successful piece of equipment since the basic design appeared to be correct. However, unfortunately, Mr. Letts did not see fit to pursue the matter further and the manufacture of the Letts Burnet Machine was discontinued.

We regret that we must give you such a negative report on the Letts Burnet Machine, but these are the facts.

If we can be of any further assistance to you at any time in any manner, please do not hesitate to contact us.

Very truly yours,

SANDY HILL CORPORATION
Redacted for privacy

B. D. Riordan
Sales Engineering Department

BDR:1

GOVERNMENT FOREST EXPERIMENT STATION
MINISTRY OF AGRICULTURE AND FORESTRY
MEGURO, TOKYO, JAPAN

October 18, 1969

c/o Director
Pacific Northwest Forest and Range Experiment Station
809 N. E. Sixth Avenue
Mail Address P. O. Box 3141
Portland, Oregon 97208
U. S. A.

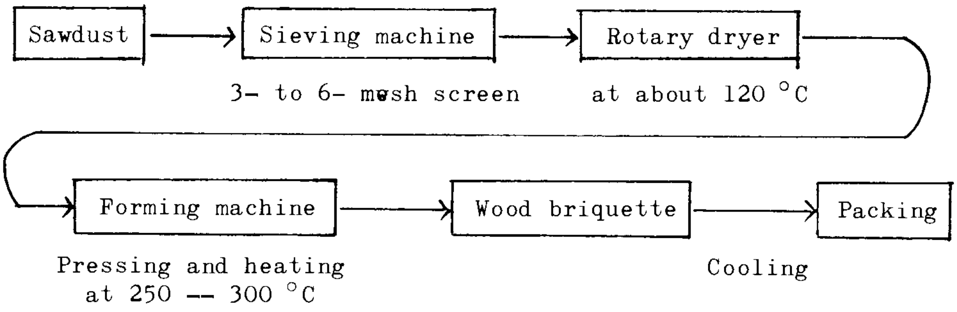
Dear Dr. J. Alfred Hall,

In reply to your letter of the 24th September, addressed to G. F. E. Station, it gives me pleasure to answer as follows.

In Japan wood briquettes are mainly made from sawdust. Moreover, shavings, chiping dust, bark, and small pieces of wood are crushed and mixed in a proper quantity to sawdust, and these are ordinarily used as auxilidary raw material. The mixing proportions of bark in briquette are ordinarily less than 30 % in weight. But briquettes made from bark alone are producing a little, because bark is generally difficult to crush and form briquette, and has much ash content. Therefore, users generally don't prefer bark briquette as domestic fuel.

Wood briquettes produced in Japan are ordinarily 5 to 7 cm in diameter. Those of 5 to 6 cm in diameter are used as a domestic bath fuel, while those of 7 cm in diameter are used as a stove fuel in winter.

The process of wood briquette production is as follows:



GOVERNMENT FOREST EXPERIMENT STATION
MINISTRY OF AGRICULTURE AND FORESTRY
MEGURO, TOKYO, JAPAN

October 18, 1969

In general, sawdust contains about 40 % moisture bulk specific gravity about 0.2 ton per m^3 in wet basis. An example of the particle size distribution of air-dried sawdust is as follows: 60 to 70 % pass through 10- to 50-mesh screen, 20 to 30 % pass through 50- to 100-mesh screen, and 10 % pass through over 100-mesh screen.

In this process, the sawdust is first passed through a sieve (3- to 4-mesh screen) to remove large pieces of wood, small stones, nails and other undesirable materials after dring less than 10 % moisture content with a rotary dryer. The dried sawdust is then pressed and heated by a forming machine which converts it into a dense product of about twice the density of starting wood materials, then the hot briquettes are cooled for one or two day, and they are packed with kraft papers and placed in the storage room. The wood briquette usually has a volumetric gravity of 1.20~1.25 and 4,700~4,800 Kcal/kg.

In Japan, the present production of wood briquettes amounts to about 500,000 tons per year. But the demend of Japanese domestic fuels is replacing from solid fuels to liquid and gas fuels or electricity, therefore the wood briquettes production may be decrease in the future.

Yours sincerely,

Redacted for privacy

Yasumasa Yonezawa
Chief,
Forest Products Chemistry Division,
Forest Experiment Station

(3 enclosures)

1. Qualities of Wood Briquettes in Japan
2. Wood Briquettes Machinery Makers
3. Catalogue of Wood-Waste Briquettor

GOVERNMENT FOREST EXPERIMENT STATION
MINISTRY OF AGRICULTURE AND FORESTRY
MEGURO. TOKYO, JAPAN

I. Qualities of Wood Briquettes in Japan

a) Sample No.	1	2	3	4
b) Raw material	Sawdust 80:bark 20	Sawdust 100	Sawdust 100	Sadust 100
c) Shape in cross section	Circular	Circular	Octagonal	Octagonal
d) Outer diameter, cm	7	7	5.5	5.5
e) Diameter of central hole, cm	0.7	1.2	1.0	0.8
f) Volumetric gravity	1.26	1.15	1.29	1.21
g) Compressive strength at cross section, kg/cm^2	412	415	210	382
h) Power requirement of motor for forming machine, Hp	50	50	20	25

2. Wood Briquettes Machinery Makers

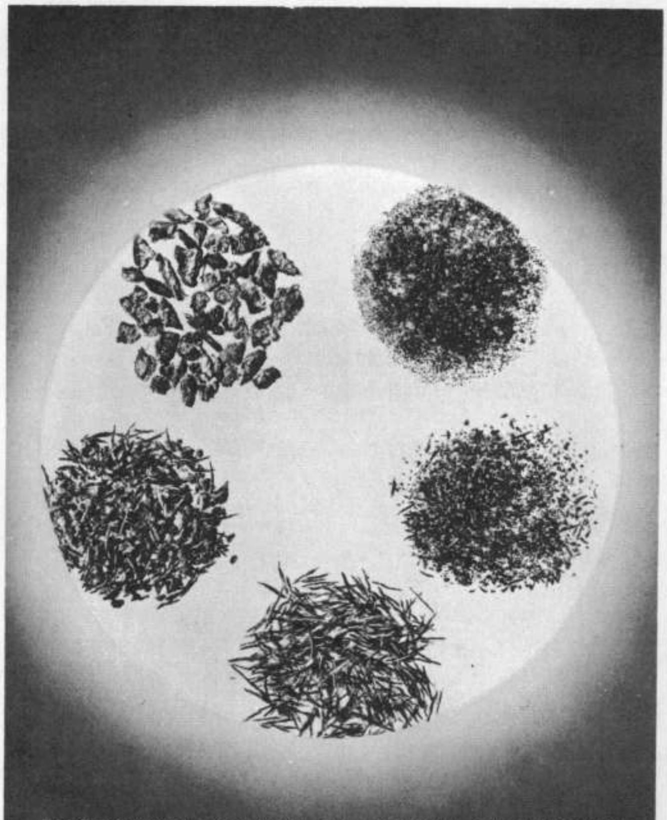
A) For producing wood briquette of 5.5 cm in diameter :

(1) Nihon Koseino Mokutan Kenkyusho Co.
8-6, Showamachi, Morihigashi, Higashi Maizuru, Kyoto Prefecture.

(2) Kobayashi Kikai Seisakusho Co.
21, Matsunagacho, Fukuyama, Hiroshima Prefecture.

B) For producing wood briquettes of 7 cm in diameter :

(1) Nisshin Co. Ltd.
29-14, Hirayashiki, Shimokuriyagawa, Morioka, Iwate Prefecture.



PHOTOMICROGRAPH OF TYPICAL SILVACONS

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Silvatek
PRODUCT

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applications in industrial products and processes for improved quality and reduced costs

SILVATEK PRODUCTS DIVISION

WEYERHAEUSER TIMBER COMPANY

TACOMA 1, WASHINGTON

SILVACON®

Its application to industrial products and processes

SILVACON is the trademark designating products derived from Douglas fir bark by a patented fractionation method. There are three basic components — pliable, spongy flakes, tough needle-like fibers and fine amorphous powders. Because of their varied properties, these components are frequently combined in tailor-made blends to improve product quality and reduce processing costs. They are available in refined and super-refined form as special Silvacons.

A natural plastic, Silvacon contains the plasticizers, cellulose and resins found in Douglas fir bark. Silvacon flows under heat *and* pressure without additives, yet will not flow under heat alone. It also bands on heated milling rolls by itself — a quality desirable in the processing of rubber, plastics and similar materials.

Silvacon may be used by simple physical addition due to its compatability with many materials commonly used by industrial processors. When desirable, however, it may first be chemically reacted with 10-30% by weight of caustic or other alkali in aqueous medium before process utilization. This treatment develops valuable chemical properties which are not evidenced by simple physical addition. Soluble alkali products are thus formed.

Silvacon's many qualities are being demonstrated in a broad diversity of uses today. Its low specific gravity is an important factor in reducing costs when it is used as an extender, filler or additive. Its physical and chemical properties, tabulated at right, are proving valuable in the fields of product development, industrial research . . . and in both product and process improvement.

The supply of Silvacon is both dependable and unlimited. Quality and uniformity are carefully controlled during the manufacturing process to assure consistent performance. A sales or technical service representative is available to assist in the application of Silvacon to any process.

EXAMPLES OF SILVACON USES

PRODUCT	383(7)
Color	BROWN
Particle Size: % on 28 mesh	77
% on 65 mesh	22
% on 200 mesh	1
Odor-Taste (1)	None
Non-Impacted Bulk Density, lb./cu. ft. (2)	19
Impacted Bulk Density, lb./cu. ft. (3)	22
Resistance to Compression, lb (4)	1550
Equilibrium Moisture Content, % at 15% R.H.	7
Equilibrium Moisture Content, % at 65% R.H.	11
Specific Gravity ***(ultimate)***	1.38
% Cellulose	22
% Lignin ***(Sulfuric Acid Method)***	60
% Wax	10.0
% Flavanol Type Compound	8.0
% Ash	0.9
% Solubility in Water	11
% Solubility in Ether	18
% Solubility in Caustic (2%)	65
pH of Aqueous Slurry	3.6
Heat Resistance: % Loss of Weight at 340°F. (5)	0.3
% Loss of Weight at 370°F.	1.4
% Loss of Weight at 400°F.	----(6

*The data presented in this bulletin are based upon laboratory and field results which to the best of our knowledge are reliable. However, due to variation in methods and conditions of use of these products, they cannot be guaranteed to perform exactly as described at all times. The numerical values listed herein are average figures taken from production and laboratory evaluation records.

Physical and Chemical Properties

CORK				FIBER					POWDER	
386	**387**	**144(7)**	**384(7)**	**412**	**425**	**515**	**510**	**509**	**472**	**490**
LIGHT BROWN	LIGHT BROWN	BUFF	BUFF	BROWN	BROWN	BROWN	RED BROWN	RED BROWN	DARK BROWN	RED BROWN
83(8)	**83**(9)	**35**	**53**	------	------	------	------	------	------	------
16	**16**	**45**	**45**	**48**	**3**	**1**	**4**	------	-	------
1	**1**	**20**	**2**	**51**	**60**	**52**	**88**	**70**	**51**	**4**
None	**None**	**None**	**None**	**None**	**None**	**None**	**None**	**None**	**None**	**None**
17	**18**	**12**	**11**	**20**	**25**	**25**	**31**	**32**	**19**	**16**
21	**22**	**16**	**15**	**25**	**40**	**42**	**41**	**44**	**28**	**25**
2500	**2350**	**2750**	**3000**	**850**	**10**	**10**	**None**	**None**	**750**	**850**
6	**6**	**8**	**8**	**7**	**7**	**7**	**5**	**5**	**8**	**8**
10	**10**	**12**	**12**	**12**	**12**	**12**	**9**	**9**	**12**	**13**
1.36	**1.36**	**1.32**	**1.32**	**1.42**	**1.42**	**1.42**	**1.47**	**1.47**	**1.44**	**1.44**
19	**20**	**15**	**14**	**47**	**47**	**47**	**64**	**64**	**29**	**25**
61	**61**	**62**	**63**	**45**	**45**	**45**	**35**	**35**	**59**	**65**
11.0	**10.0**	**13.0**	**13.0**	**5.0**	**5.0**	**5.0**	**0.7**	**0.7**	**7.5**	**5.5**
9.0	**9.0**	**10.0**	**10.0**	**3.0**	**3.0**	**3.0**	**0.3**	**0.3**	**4.5**	**4.5**
0.4	**0.4**	**0.2**	**0.2**	**0.8**	**0.8**	**0.8**	**0.3**	**0.3**	**1.4**	**2.0**
12	**12**	**13**	**13**	**7**	**7**	**7**	**5**	**5**	**13**	**16**
20	**19**	**23**	**23**	**8**	**8**	**8**	**1**	**1**	**12**	**10**
76	**76**	**80**	**85**	**35**	**35**	**35**	**25**	**25**	**69**	**78**
3.6	**3.7**	**3.7**	**3.7**	**3.7**	**3.7**	**3.6**	**3.9**	**3.9**	**3.5**	**3.7**
0.3	**0.2**	**0.3**	**0.2**	**0.2**	**0.3**	**0.4**	**0.2**	**0.2**	**0.5**	**1.0**
1.3	**1.3**	**1.2**	**1.2**	**0.9**	**1.0**	**1.2**	**0.6**	**0.8**	**2.0**	(6)
(6)	(6)	(6)	(6)	(6)	(6)	(6)	**2.7**	**3.6**	(6)	

(1) Evaluated by "Butter Test" for 48 hours at 40° F.

(2) 40 Grams under force of own weight in a 250 c.c. graduate.

(3) Maximum density attained by vibrating and compacting 40 gram samples.

(4) Pounds force to compress 1 lb. to 30 lb. per cu. ft. density in 6-inch diameter can.

(5) Incurred after one-half hour at indicated temperature.

(6) Ignited.

(7) This product also available in fine grind form.

(8) 100% Minus 8 mesh.

(9) 100% Minus 10 mesh.

ALSO CONSIDER SILVACEL INDUSTRIAL WOOD FIBERS

SILVACEL is manufactured from *sound wood* chips . . . in contrast to Silvacon, which is made from Douglas fir bark. Silvacel wood fibers are not altered in the defibrating process and retain all the characteristics of wood fiber as it exists in nature.

Silvacel's basic properties . . . fibrous structure, light weight and felting quality . . . make the product applicable to a number of industrial products and processes. These include such diverse uses as roofing felts, filter media, building papers, shell wads, battery separators and others.

Tailor-made Silvacels are available in a variety of particle sizes and physical and chemical characteristics. Their broad range of properties offers many opportunities in the field of research and product development.

Write us for special Silvacel literature and samples. Sales or technical service representatives will call on request.

SILVACON USES

TECHNICAL LITERATURE pertaining to most Silvacon uses is available. Sales and technical service representatives will gladly assist in specific applications of Silvacon to your industry. Supplies of Silvacon are located in key areas throughout the United States.

[illegible] Cost reduction through lower resin requirements without sacrifice of quality. Provides greater flow with less resin. Silvacons 412, 425, 472 and 515 are commonly used for such compounds.

[illegible] Gives an improved low-cost glue for plywood and other industries. Silvacons 472 and 490 are recommended.

[illegible] An agglomeration preventative for toxic ingredients of insecticides, for fertilizer, for ground quebracho, etc. — Silvacon 490.

[illegible] For easier, faster processing, higher loadings and lower costs in hard rubber products, mechanical goods, shoe soling, sponge rubber and floor tile, Silvacons 412, 425, 472 and 490 are used.

[illegible] Overcomes casting defects; promotes collapsibility, green compression and flowability — Silvacons 425 and 472.

[illegible] Reduces weight, gives low temperature flexibility and high abrasion and chemical resistance — Silvacons 386, 472, 490.

[illegible] Compatible with most thermoplastics; reduces costs with little change in physical properties. Silvacons 425, 472, 490.

[illegible] Lowers specific gravity, reduces costs and improves quality — Silvacons 412 and 425 are normally used.

[illegible] Extensively used in boxcar and industrial flooring. Also in accoustical plaster and tile of magnesite base — Nos. 387, 412.

CASTING RESIN REINFORCEMENT
Silvacons 412, 425

ACCOUSTICAL PRODUCTS
Silvacon 387

SEED CLEANING MEDIUM
Silvacon 412

CORK PRODUCTS
Nos. 144, 383, 384, 386, 387

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Weyerhaeuser Timber Company
Central Research Department
Longview, Washington

A REVIEW OF THE CHEMISTRY OF QUERCETIN

A. S. Ryan

The dyeing industry in America can be said to have started from the work of Edward Bancroft (1744-1821), a chemist, a spy for the Revolutionary Army and an early American historian. At sometime prior to 1771, he discovered that the extract of the inner bark of American black oak (Quercus tinctoria) would function as a yellow dye. This was called quercetron, or oak yellow, and it became one of the principal exports of the United States for over 100 years. In 1917, 8000 tons of this color were produced in this country.(8)

Quercitrin, the 3-rhamnoside of quercetin (I), is the coloring matter in quercetron extract. Although quercetin is now recognized as the most widespread of the plant pigments and is of current interest, along with other flavonoids, for its pharmaceutical and antioxidant applications, no review of its chemistry has been presented since the monumental work of Perkin and Everest (1) in 1918. In this review, an attempt has been made to collect the information made available during the last forty years.

I. Structure and Properties

The relation of quercetin (3, 3', 4', 5, 7 - pentahydroxy flavone) (I) to some other common flavonoid compounds is illustrated in Figure 1. It is rather remarkable that recognition of the flavonols (3-hydroxy flavones) as being different from other hydroxylated flavones (such as luteolin (III)) came very early in the chemistry of these substances. As will become evident in the following discussion, the 3-hydroxyl group has a profound effect on the chemical reactivity.

The solubility of quercetin is given in Table 1. This chemical, like most hydroxylated flavones, is insoluble in water and its solubility in most organic solvents is much lower than would be predicted from consideration of Ring A, with a phloroglucinol configuration, or Ring B, with a catechol configuration. The conjugated pyrone ring contributes considerable benzenoid character. Fischer-Hirschfelder models illustrate that Ring A and the pyrone ring are almost planar, leading to a high degree of hydrogen bonding in the crystal and thus a high melting point and low solubility.

That the hydroxyl groups in quercetin are acidic is evidenced by the high solubility in basic solvents. Although values for quercetin itself have not been reported, the 7-hydroxyl and 4'-hydroxyl groups in rutin (quercetin-3 rhamnoglucoside) have ionization constants of 4×10^{-8} and 2×10^{-9} respectively,(9) making them more acidic than catechol or resorcinol ($k = 4 \times 10^{-10}$). That these hydroxyl groups would be the most acidic is predicted from consideration of resonance structures of the various ions (Fig. 2) and of the chelation effects discussed below.

Three of the hydroxyl hydrogen atoms in quercetin are chelated, the 5-hydroxyl so strongly with the carbonyl group that quercetin resists chemical attack (esterification, etherification) at the 5 position. The 3-hydroxyl is also chelated with the carbonyl, although less strongly,(10) and following ionization of the 4' hydrogen, the 3' hydrogen would be expected to exhibit chelation. Such chelated systems are shown in Figure 2, XII.

When alcoholic solutions of quercetin are treated with sodium or potassium basic salts, the insoluble monosalt substituted at the three position is formed.(11,12) This occurs probably not because of any abnormal acidity of the 3-hydroxyl group,(13,14,15) but because of the unusual opportunity for the metal ion to chelate with the carbonyl oxygen. Because of the larger size of the metal ion, chelation would be more favorable than with hydrogen.

The ultraviolet spectra of quercetin and its derivatives have been utilized extensively as an analytical tool, both for structure interpretation and analysis.(4,14,57,66,153,154;172,176) Quercetin has strong absorption bands with maxima at 258 and 375 mu. The latter band is influenced most strongly by etherification of the phenolic hydroxyls, especially the 5 hydroxyl.(14) The infrared spectra of quercetin, its derivatives and other flavonoids, in conjunction with chemical properties, indicate that the carbonyl group in the flavones is different than the same group in the closely related flavanones and chalcones.(171)

II. Occurrence and Isolation

For the occurrence of quercetin and its derivatives in natural products, the reader is referred to the reviews in Beilstein,(5) Klein,(2) Griffith et al,(4) and Perkin and Everest.(1) Typical methods for isolation and identification of quercetin and other flavonoids have been described by Wender.(16) The 3-rhamnoside (quercetrin), the 3-rhamnoglucoside (rutin), the 3-galactoside (hyperoside), the 3-glucoside (isoquercetrin) and the 3-diglucoside occur fairly widely. Other glycosides that have been reported are the 3-arabinoside (avicularin),(17) the 7-glucoside,(18,19,20) and the 3' glucoside.(20) Certain methyl ethers of quercetin such as the 7-methyl (rhamnetin), 3',7-dimethyl (rhamnazin) and 3'-methyl (isorhamnetin) are also widely occurring, although not comparable to quercetin.

Quercetin is commercially available via the hydrolysis of rutin from buckwheat and by the air oxidation of 2,3-dihydroquercetin in the water extract of Douglas fir bark.(21,22) The laboratory methods for the oxidation of dihydroquercetin to quercetin have been summarized by Gregory, et al.(21) Of these, sodium bisulfite is favored because of high yields and purity.(23)

Total synthesis of quercetin was accomplished by St. von Kostanecki in 1904 by condensing 4,6-dimethyl phloroacetophenone with veratric aldehyde, cyclizing the resulting chalcone, introducing a hydroxyl at the 3 position via the oximo intermediate, followed by hydrolysis and demethylation. A more direct method was introduced by Robinson in

1926 involving the condensation of ω-methoxyphloroacetophenone with veratric anhydride, in the presence of potassium veratrate. The steps in both of these syntheses have been outlined previously.(6)

III. Reactions of the Hydroxyl Groups

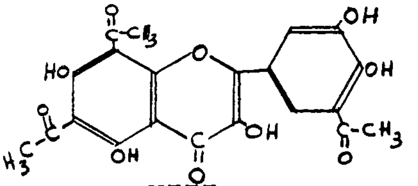
A. Esterification

The hydroxyl groups of quercetin are readily esterified with acid anhydrides or acid chlorides in the presence of base. Because of chelation with the carbonyl oxygen, the 5-hydroxyl reacts less readily and by suitable moderation of conditions can be left unattacked. A summary of the various esters of quercetin is given in Table 2.

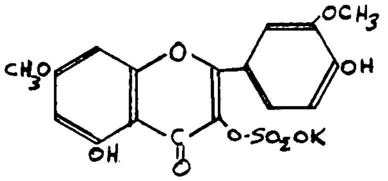
Quercetin pentaacetate is easily prepared and has long served as the standard for identification. Pure quercetin can be prepared by hydrolysis of the pentaacetate with acid in aqueous alcohol.(4) Higher yields are obtained if the pentaacetate rather than quercetin is used in methylation,(26) caustic cleavage(27) or in reduction.(28,2

Both the pentaacetate and the pentabenzoate have yielded ring substituted products via Fries rearrangement.(30)

The product from the latter was an oil, but triacetyl quercetin was a crystalline solid (m. 300°C.) with the probable structure XIII.



XIII



XIV

The $KHSO_4$ monoester of rhamnazin (XIV) was isolated from Polygonum hydropiper in 1953.(31) Such 3-substituted inorganic monoesters have since been found to be widely distributed in marsh plants.(32) Similar esters of sulfuric and phosphoric acids have been the subject of recent patents.(33,34) These esters are water soluble and are of interest in pharmaceutical applications.

B. Etherification

Of the thirty-one possible methyl ethers of quercetin, twenty-four have been described in the literature (Table 3). These furnish a good opportunity for study of the various hydroxyl groups insofar as they affect physical properties and reactivity.

Only two trimethyl ethers and five dimethyl ethers are unknown. Inspection of Table 3 indicates that more ethers have been obtained by total synthesis (usually via the Allan-Robinson route(25)) than by methylation of quercetin, and newer procedures for selective alkylation are needed.

Methyl ethers containing the 7-methoxyl and/or the 4' methoxyl group generally have the lowest melting point and ethers with the 3' methoxyl, the highest melting point. It is interesting that only three ethers are colorless; the pentamethyl, the 3,3', 4',5-tetramethyl and the 3',4',5,7-tetramethyl (e.g., a free hydroxyl at the 7 or 3 position). The latter of these has in many cases been obtained yellow and further investigation of this derivative appears warranted.

In the methylation of hydroxy flavones with dimethyl sulfate and alcoholic base, Simpson(42) has shown that the reaction rate order is 7-4'-3'-3 (ascending) while in anhydrous acetone with sodium bicarbonate the reverse rate order prevails. From the resonance forms VII-XI, either the 3'-or the 3-hydrogen in quercetin would be predicted as the least acidic and the corresponding anions from these, being strong conjugate bases, would be expected to react fastest with dimethyl sulfate in alkali.(43) The 5-hydroxyl hydrogen, as mentioned previously, is chelated too strongly to enter into reaction. The products obtained on methylating quercetin in alcoholic base tend to confirm the predicted order, although the 3, 3', 4'-trimethyl ether is the least substituted ether obtained by such a procedure.(44)

To selectively methylate the hydroxyl groups, it is necessary to resort to special techniques. Methylation in the presence of sodium acid borate, which complexes the 3',4' and 5 hydroxyl groups, yields the 3,7-dimethyl ether.(45,46,47)

Methylation of the 3, 3', 4', 7-tetraacetate with diazomethane or methyl iodide (41) yields the 5-methyl ether after hydrolysis. Similar treatment (methyl iodide) of the pentaacetate gives 7-methyl quercetin.(41) Extended treatment with methyl iodide and methanolic base has given, in addition to the pentamethyl ether, smaller amounts of 6-C-methyl-pentamethyl and 6-C-methyl-3, 3', 4', 7-tetramethyl quercetin.(49,107) These derivatives offer evidence of a high electron density at the C_6 position, one of the resonance forms involved in ionization of the 7-hydroxyl (VII). With diazomethane, the 3, 3', 4', 7-tetramethyl(50,51) and the pentamethyl ethers(51) are produced.

Complete demethylation with aqueous hydriodic acid has been a common step with quercetin methyl ethers. The 3-hydroxyl can be regenerated selectively from the pentamethyl ether by refluxing with dilute sulfuric acid(51,52) or with anhydrous aluminum chloride in boiling ether.(13) Decomposition of pentamethyl quercetin hydrochloride at 160°C., however, regenerates the 5-hydroxyl group.(13) The latter two examples can be interpreted as the regeneration of a more stable chelate system, with the aluminum complexing the 3-hydroxyl-carbonyl. Cleavage of the 3-methyl is in conformance with the general ease of removal of sugar ethers at this position, but the methyl group should be more resistant.

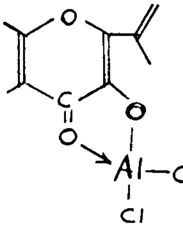
Etherification imparts hydrocarbon solubility to quercetin. Rhamnazin is sufficiently soluble in hot toluene to enable its separation from rhamnetin and quercetin.(53) The benzyl ethers of quercetin are of particular interest since they are more readily hydrolyzed.

Sugar ethers of quercetin, the glycosides (VI), represent by far the most widely occurring type of derivative, with the sugar groups attached most often at the 3 position. The properties and function of these compounds in plants have been described by McIlroy(7) and, for rutin, by Griffith, et al.(4) The relation of the position of the sugar to the color developed on dyeing, especially with aluminum and tin mordants, has been discussed by Perkin,(72) who found that free hydroxyl groups at the 3' and 4' position were main contributors to color, with a free 3-hydroxyl imparting only a slight yellow cast.

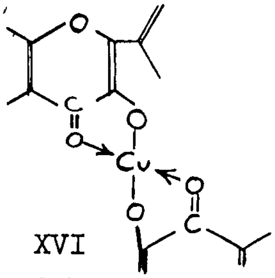
Selective hydrolysis of the rhamnose moiety from rutin and other rhamnoglucosides is affected by boiling formic acid in cyclohexanol.(166)

IV. Metal Complexes and Oxonium Salts

The 3-hydroxyl-carbonyl and 5-hydroxyl-carbonyl chelating ability of quercetin allows formation of complexes with many metal ions such as aluminum,(79,80,81) copper,(79,80,81,82,83,84) zirconium,(79,81,85,96) thorium,(86) antimony,(87) titanium,(80) cadmium,(80) uranium,(88) lead and many others. In most of these, structural evidence was obtained by light absorption techniques that indicated either a 1:1 metal-flavonol or a 1:2 metal-flavonol ratio (XV or XVI).

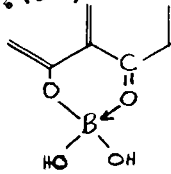


XV

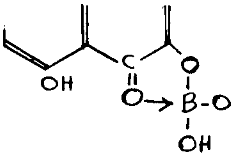


XVI

Solid boric acid-quercetin complexes prepared by precipitation from glacial acetic acid solution are thought to represent chelation as in XVII or XVIII.(51)



XVII

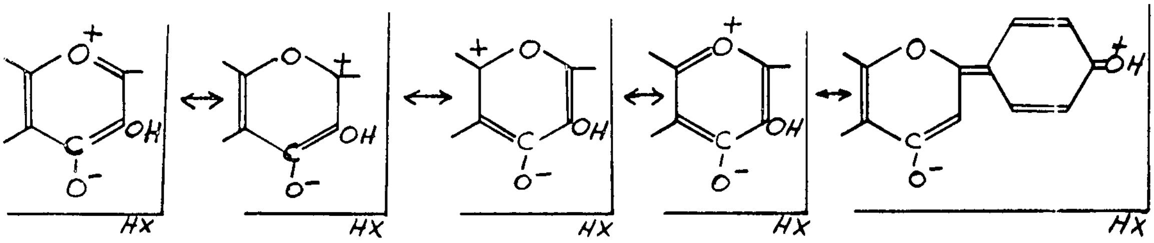


XVIII

In aqueous borate solutions, however, chelation is only with the 5-OH-carbonyl and with the 3', 4' hydroxyl groups,(46,89) probably because of sodium-carbonyl chelation at the C_3 position.

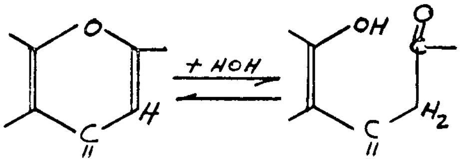
The intense colors produced by metal complexing have long been the basis for both qualitative and quantitative tests for quercetin and for the metal ions involved. The boric acid-organic acid color(91,92) has been used as a test for flavonols. Antimony trichloride(97,87) and pentachloride(93) behave similarly. In addition to those metals listed above, germanium,(94,102) niobium and tantalum,(95) iron,(100,98) ammonium molybdate and sodium tungstate,(99) and beryllium(101,81) have all been mentioned as forming colors with quercetin or other flavonols.

The complexes of metallic salts and quercetin appear to differ from the oxonium salts formed with mineral acids and quercetin only in the relative strength of the coordinate bonds to oxygen. The hydrobromide, hydrochloride, hydroiodide and sulfate, both of quercetin and of its ethers were prepared very early by Perkin and his coworkers.(1) These oxonium salts are orange to red colored solids that decompose on heating or by the addition of water and polar solvents. Their structure is still somewhat a matter of controversy(14,15) but probably consists of the following resonating forms.



XIX

The pyrone ring in quercetin, like the flavonols in general, is quite stable under acidic conditions (but unstable in base; Part VI). With the flavones, however, both closed and open ring systems appear to be in equilibrium (XX) and rotation of the A ring around the C_4 bond causes a mixture of isomers to be formed.(90,170)



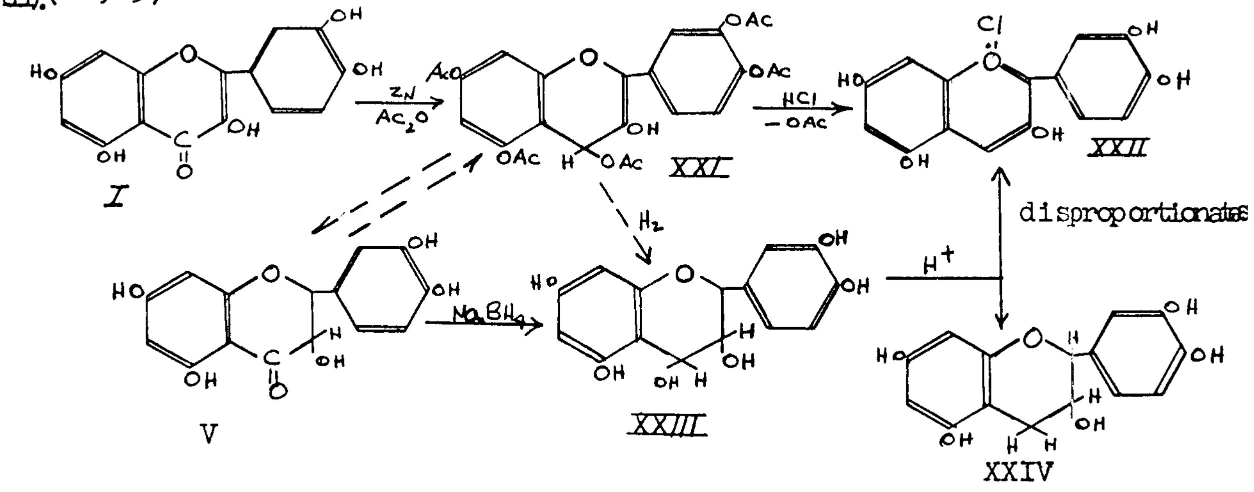
XX

Reduction

Because it is chelated from both sides and because it has an unusual opportunity to lose its identity via resonance, the carbonyl group in quercetin is refractive to most reagents. It does not react with bisulfites, hydroxylamine or phenylhydrazine(167) and it is reduced with difficulty, and only by a certain class of reagents.

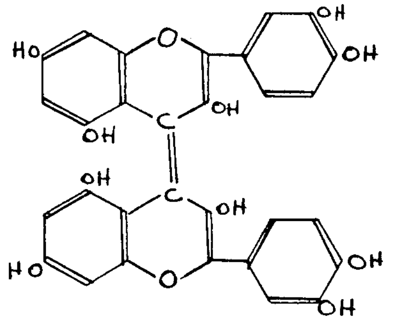
The published literature on the reduction of quercetin is summarized in Table 4. It will be noted that the successful methods for carbonyl reduction involve (a) acid conditions, which preserve the pyrone ring and (b) metals. Reduction of quercetin pentaacetate has been more consistently successful than reduction of quercetin itself, due to release of the C_5-carbonyl chelation.

The initial product of reduction is the pseudo base of the flavylium salt (XXI) which has not been obtained as a crystalline entity but as an amorphous, dark red product, converted by acid to cyanidin (XXII).(28,29)



Further reduction of (XXI), or of the tautomeric flavanone (V), yields the flavan-diol (XXIII),(30) a structure also proposed for the leuco-anthocyanidins (colorless precursors of the anthocyanidins) which also show the red color attributed to cyanidin on acid treatment, possibly by disproportionation.(103,104,105,106,108,109,173)

Complete reduction of quercetin to substances giving colors attributed to cyanidin was accomplished very early by Willstatter,(110) but since similar colors were given by metallic complexes(111,112,113,114,168) or by mixtures of various flavanone and chalcone derivatives(115,116) produced on reduction, the formation of cyanidin was not certain. Malkin and Nierenstein considered that the dimer XXV was the normal product.(117)



XXV

More recent experiments(28,29,118) tend to show that cyanidin is indeed formed on reduction, in some cases in considerable yield. A similar process has long been recognized as a possibility in the formation of the anthocyanidin colors in fall foliage where glycosides of quercetin and cyanidin often exist side by side.(165,170)

The failure of quercetin to undergo catalytic reduction with hydrogen has been found to be a general feature of flavones with 3', 4' or 4' hydroxyl groups,(119) indicating the importance of resonance forms such as VIII on stabilization of the molecule.(130)

The C_2 -C_3 double bond of quercetin can be selectively reduced to 2,3-dihydroquercetin by the use of massive amounts of sodium hydrosulfite.(120) Yields are improved if borax is present.(121)

By partial methylation and formation of selected tosyl esters followed by hydrogenation at room temperature with Raney nickel, phenolic hydroxyl groups can be removed. Compounds of the fisetin (3,3',4',7-hydroxy)(112) and kaempferol (3,4',5,7-hydroxy)(123) series have been made in this manner.

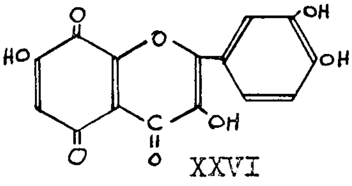
Polarographic reduction of quercetin and other flavonoids has demonstrated the aforementioned retarding action of the C_5-carbonyl chelation and the relatively weak C_3-carbonyl interaction.(130,131) Comparisons have been made of the relative ease of reduction (as measured by $E_{1/2}$) of quercetin, myricetin, morin, rutin, quercitrin, hesperidin and dihydroquercetin, using in some cases conditions applicable to the analysis of mixtures.(132,133,134,163)

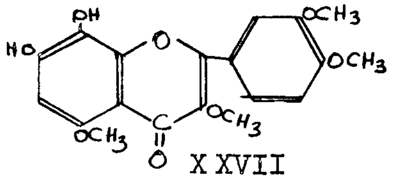
VI. Oxidation and Oxidative Cleavage

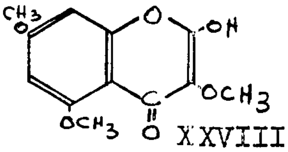
Oxidation reactions involving quercetin can be divided into two groups: (1) those where the pyrone ring remains intact and (2) those in which cleavage products are produced.

Since the pyrone ring is already at its highest state of oxidation, reactions of type (1) involve either phenolic Ring A or B. Acid conditions are conducive to this type since the 3-hydroxyl group causes pyrone ring stabilization in such media. By employing the methyl ethers, however, some phenolic ring oxidations can be effected in alkali. Rutin (VI) is more stable than quercetin in such alkaline solutions.(169)

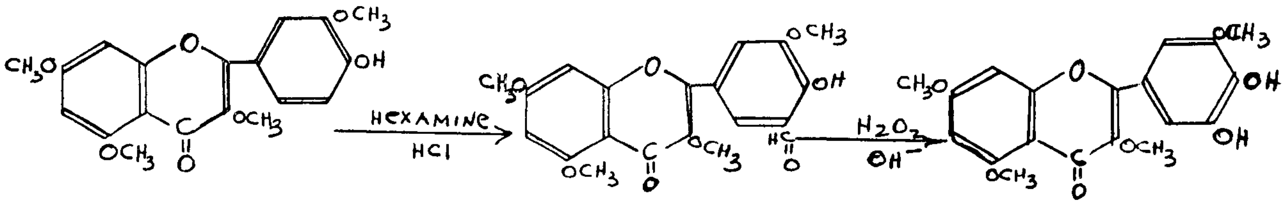
Chromic acid oxidation of quercetin to "quercetone" (XXVI)(135) and alkaline persulfate oxidation(136,67) to the 8-hydroxy (gossypetin) series (XXVII) are examples of type (1). Nitric acid oxidation of 8-ethoxy pentamethyl quercetin also yields gossypetin derivatives.(137) Complete destruction of Ring B to XXVIII occurred when the mononitro derivative of pentamethyl quercetin was treated with chromic acid.(30)


XXVI


XXVII


XXVIII

A more subtle method of oxidation of a phenolic ring involves introduction of a formyl group and subsequent oxidation via the Dakin reaction (XXIX-XXXI).(138)



XXIX

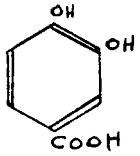
XXX

XXXI

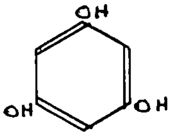
Oxidative cleavage of quercetin and its derivatives occurs readily and the technique has long been used to furnish structural evidence. The 3-hydroxyl group aids in ring fission in alkaline solutions in the presence of oxygen, as was noted very early by Perkin,(1) but in the absence of oxygen the pyrone ring is much more stable and hydroxy flavones and flavonols behave similarly.(3)

With strong oxidizing agents such as potassium permanganate and alkaline hydrogen peroxide, usually only the B ring fragments (e.g., protocatechuic acid, XXXII) can be isolated.(139,140,141) Phloroglucinol (XXXIII) has usually been detected by less conclusive color tests.(142) Molho showed that flavones with multiple hydroxyl groups on Rings A and B yielded only the B ring fragment with alkaline hydrogen peroxide.(143) Under these conditions, 3,3',4',-7-tetramethyl quercetin was oxidized with difficulty, yielding dimethyl protocatechuic acid. Fragments from Ring A were isolated from fisetin derivatives, however, indicating the greater stability of products with resorcinol as compared with the phloroglucinol configuration.

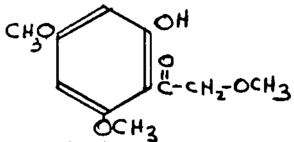
Where cleavage is carried out via fusion with alkali or by heating with solutions of strong bases, both Ring A and Ring B fragments are produced. Phloroglucinol production from quercetin by this method was achieved during the course of early structural studies. (124,144,145,146) Recent work has shown that quercetin pentamethyl ether and quercetin pentaacetate give higher yields of cleavage products than quercetin itself and up to quantitative yields of 2'-hydroxy-2,4',6'-trimethoxy acetophenone (XXXIV), veratric acid (XXXV), (147,148) phloroglucinol (XXXIII)(149) and protocatechuic acid (XXXII).(27) The use of non-porcelain apparatus was found to be essential to high yields in the latter degradation.



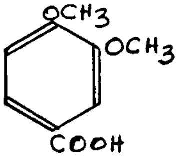
XXXII



XXXIII

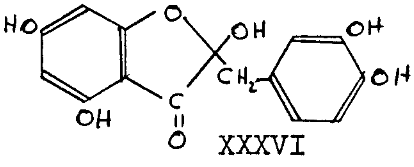


XXXIV



XXXV

Caustic treatment under nitrogen has yielded a product with the proposed structure XXXVI.(150)



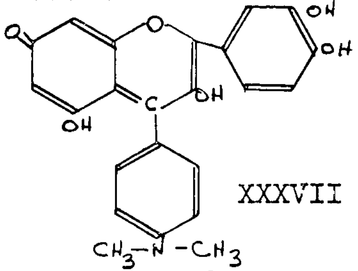
XXXVI

Some color tests for metal ions depend upon a combination of oxidation and metal complexing for color development. The red color with vanadate(151) and the violet color with cerium(152) are examples. Quercetin in dioxane which contains peroxides develops bright red colors on heating.

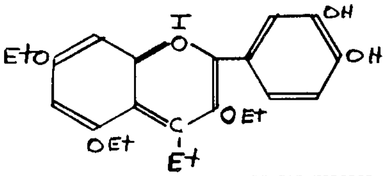
Aromatic Ring Substitutions and Miscellaneous Reactions

In the early years of this century, considerable effort was made by Watson and coworkers(30,141,155) to produce dyes from quercetin that were more light stable or gave other colors than the yellows and browns normally associated with this chemical. Most of the new derivatives (Table 5) resulting from his work were formed by direct attack of the aromatic nucleii. Earlier, Liebermann(156) had made the dibromine derivative, useful in the identification of small amounts of quercetin.(2)

Several of the quercetin dyes produced by Watson resulted from reactions of the carbonyl group, such as XXXVII, from dimethylaniline with phosphoryl chloride, and XXXVIII, from reacting ethyl magnesium iodide with the pentaethyl ether, followed by partial deethylation. The latter was the most effective dye found in his studies. Other compounds proposed as dyes and representing the coupling of flavonoids at the 5' ring position with diazotized aniline have been the subject of recent patents.(157,158,159)



XXXVII



XXXVIII

Condensation of quercetin or rutin with hexamethylene tetramine,(161) with urea in alkali,(162) or with urotropine(164) yields products of improved water solubility for pharmaceutical purposes.

MELTING POINT	316-318 (dec)
SOLUBILITY (g./100 g. OF SOLVENT), 25°C	
WATER	<0.0006
ETHANOL 95 %	2.5
CELLOSOLVE	19.1
SODIUM BICARBONATE (2 %)	0.5
SODIUM CARBONATE	0.6
SODIUM HYDROXIDE	7.4
ACETONE	8.3
ETHYL ACETATE	3.9
DIETHYL ETHER (WET)	0.26
DIOXANE	14.6
BENZENE	<0.0001
HEXANE	<0.0001
DICHLORETHYLENE	<0.0001
PYRIDINE	27.1
DIMETHYL FORMAMIDE	53.5

TABLE 1. PROPERTIES OF QUERCETIN

TABLE 2

Esters of Quercetin

Derivative	Melting Point,°C.	Preparation
Pentaacetate	196-197°	Hot acetic anhydride, with or without base (35)
Tetraacetate (3,3',4',7)	193-194°	Cold (25°C.) acetic anhydride and pyridine, short reaction time(11,36)
Triacetate (3,3',4'?)	167-169°	Potassium salt plus cold acetic anhydride (11)
Pentachloracetate	180°	Hot chloracetic anhydride and pyridine (30)
Pentamethoxyacetate	97-98°	Boiling methoxy acetic anhydride (37)
Pentabenzoate	239°	Hot benzoyl chloride and pyridine (38)
Pentamethane sulfonate	(a) 199-201° (b) 180° (2 forms)	Methane sulfonyl chloride and pyridine (39)
Tetramethane sulfonate	201-3°	Methane sulfonyl chloride and dilute sodium hydroxide (39)
Sulfate	(decomp. on heating)	Concentrated sulfuric acid in pyridine below 20°C. (33)
Phosphate	(decomp.;-isolate as salt)	$POCl_3$ in pyridine below 20°C., (34,40) or PCl_5 and sodium hydroxide in carbon tetrachloride suspension (160)

TABLE 3A

Methyl Ethers of Quercetin

Position	M.°C.	Color	Acetate M.°C.	Derivation(a)	Common Name	Reference
3	273-5	Yellow	182-4	S,H		54,55,52
3'	305-7	Yellow	203-5	S,H	Isorhamnetin	56,57,58,59,60
4'	260	Yellow	165 (203-4)	H		61,62
5	305-8	Yellow	196-8	S,H,E	"Azaleatin"	54,63,48,41
7	300	Yellow	186-8	H,E,S	Rhamnetin	64,65,45,41,66
3,3'	257-8	Yellow Plates	199-200	S		67
3,4'	232-3	-	-	S		68
3,7	241-2		163-5	S,E		47,45,46
3',7	215-16		154-5	S,H	Rhamnazin	69,53
4',7	229-30		-	H,S	Ombuin	70,71,55
3,3',4'	240-5	Pale Yellow	159-60	S,E		54,25,44
3,3',5	274-76		129-30	S		54
3,3',7	174-5		118-19	S		54,67
3,4',7	172-3	Yellow	176-7	H	"Ayanin"	68
3,5,7	282-4		-	S		56
3',4',5	292-4		146-8	S		54
3',4',7	190		195-6	S,H		54,72
3',5,7	208-10		206-8	S		54
3,3',4',7	159-60	Yellow	169-70	E		57,68,70,50,73
3,4',5,7	223-4	Yellow	147-8	E		47,68
3,3',5,7	202-3	Yellow	178-180	S		69,67
3,3',4',5	284-5	Colorless	174-5	H,S		72,74
3',4',5,7	193-6	Colorless (b)	160-3	H,E		63,70,32,51,52
3,3',4',5,7	150-1	Colorless	-	E		75,76,26,77,49

(a) S = Synthesis (total or by demethylation of higher ethers).
H = Hydrolysis of methylated quercetin glycosides.
E = Methylation of quercetin or its esters or ethers (arranged in order of references cited)

(b) Sometimes obtained yellow.

TABLE 3B

Mixed Ethers of Quercetin

Position	M.°C.	Acetate M.°C.	Derivation	Reference
3,3',4',7-ethyl	120-222		E	78
3,4',5,7- benzyl	166	176	E	41
3-Me,3'.4'-di.Et.	216-217	-	E	45
3,7 Me,3',4',5-tri.Et.	151-152	-	S,E	45
3,7 Me,3',4'-di.Et.	120-121	-	E	45
4',7 Me,3,3',5-tri.Et.	146-148		E	70
Pentaethyl	116-118	-	E	78
3 Me,3',4'-benzyl	153-155	-	S	47
3,3' Me,4'-benzyl	258-259	-	S	67
3,3',7 Me,4'-benzyl	151-152		E	67
3,3',5,7 Me,4'-benzyl	162-163	-	E	67
3,3',4',5 Me,7-benzyl	171-172	-	E	41,74
3,7 Me,3',4'-benzyl	122-123	-	E	47
7-benzyl	245-6		E	41

TABLE 4

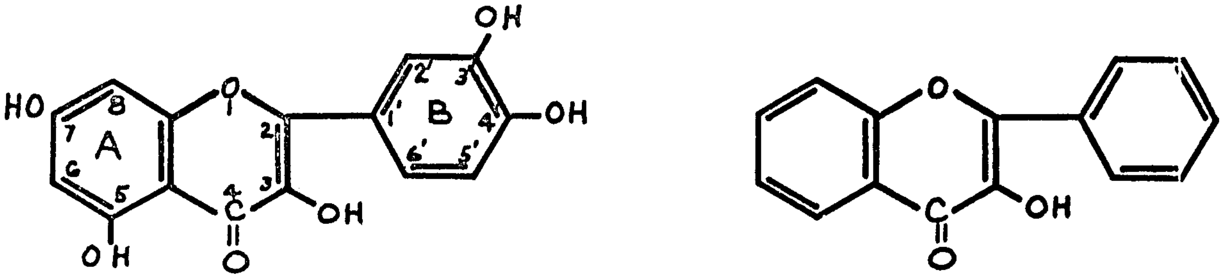
Reduction of Quercetin

Reagents	Products	Reference
Sodium amalgam in acid-alcohol	Blue-red colors attributed to cyanidin chloride	110
Sodium amalgam in hot alkali	Phloroglucinol and protocatechuic acid fragments	124
Sodium amalgam in alkali	Quercetin not reduced; pentamethyl quercetin gave "pseudobase of cyanidin"	114
Sodium amalgam (in acid)	A 3,4-flavan-diol,easily oxidized to quercetin	30
Sodium amalgam in methanol	Cyanidin	118
Zinc and magnesium in HCl-amyl alcohol	Colorless anthocyanidin pseudobase	2
Zinc and acetic anhydride	Amorphous diol acetates, convertible to cyanidin with acid	107
Lithium aluminum hydride	Quercetin pentaacetate gives cyanidin chloride in good yield	108 (see also 125 175)
Fermenting yeast	Not successful	126
Hydrogen, PtO_2 catalyst	Not successful	127
Hydrogen, Raney nickel or Cu-chromite	Not successful	128
Hydrogen, Pt. catalyst	With pentamethyl quercetin, an 11% yield of pentamethyl, d,l-epicatechin	129
Sodium hydrosulfite	2,3-dihydroquercetin and 3',4,4',6-tetrahydroxy, 2-benzyl, 3-coumaranone	120,121 127
Hydrogen, Raney nickel	With tosyl ester of methylated quercetin, corresponding de-oxy compounds are produced	122,123

TABLE 5

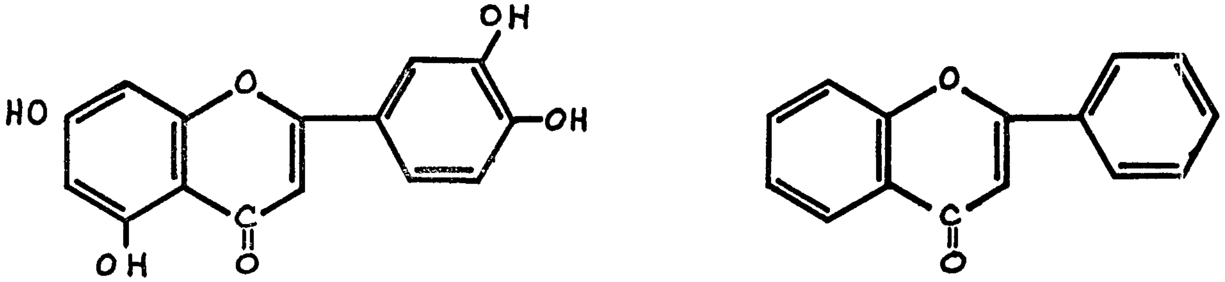
Aromatic Ring Substituted Quercetin Derivatives

Compound	Properties	Method of Preparation	Reference
6,8-dibrom.-	Yellow Needles M. 236-237°	Bromination ($2BR_2/1Q$) in acetic acid solution	156,2,1, 146,144
dibrom.-pentamethyl	M. 173-5°	Bromination of pentamethyl quercetin.	141
dibrom.-tetraethyl-	Yellow, M. 169-173° (Acetate, M. 172-5°)	Bromination of tetraethyl quercetin in cold sodium acetate solution.	141
6'nitro-pentamethyl	Yellow, M. 203-4°	Nitric acid nitration of quercetin.	141
6'nitro-dimethyl	-	$AlCl_3$ demethylation of the pentamethyl derivative.	30
6'-amino-pentamethyl	White, M. 200-2°	Reduction of 6'nitro derivative.	141
6'-amino-	Yellow,good dye; dec. >320°C.	HI demethylation of pentamethyl derivative.	141
tri-nitro-pentamethyl	Yellow, M. 190-205°	Nitration of pentamethyl quercetin.	141
triacetyl-	Yellow, M. 300°	Via Fries rearrangement of quercetin pentaacetate (160°C. with $AlCl_3$)	30
6' sulfonic acid	Yellow, dec. >140°C.	Concentrated H_2SO_4, steam bath.	30
6'-β-naphtholzao-pentamethyl	Crimson, dec. 222-225°	Reaction of β-naphthol with the 6' diazonium chloride derivative of quercetin.	141
6'-β-naphtholazo-dimethyl	M. 248° (not crystalline)	Demethylation ($AlCl_3$) of the pentamethyl derivative.	



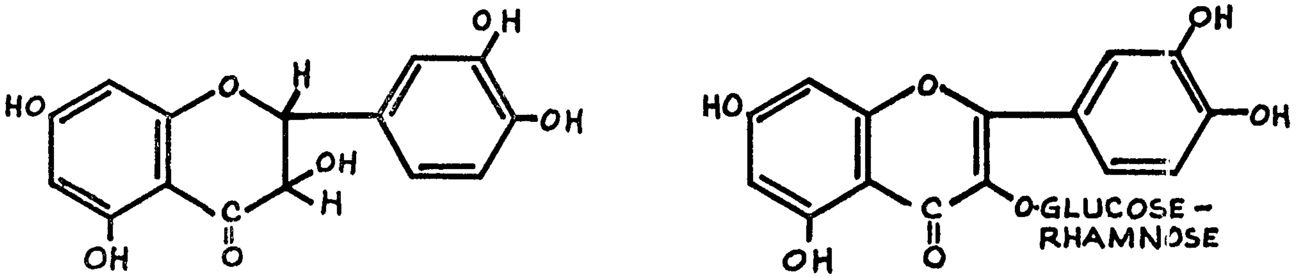
I QUERCETIN

II FLAVONOL



III LUTEOLIN

IV FLAVONE



V DIHYDROQUERCETN
(TAXIFOLIN)

VI RUTIN

FIGURE 1.-STRUCTURE OF TYPICAL FLAVANOID COMPOUNDS

J. D. HOLDER

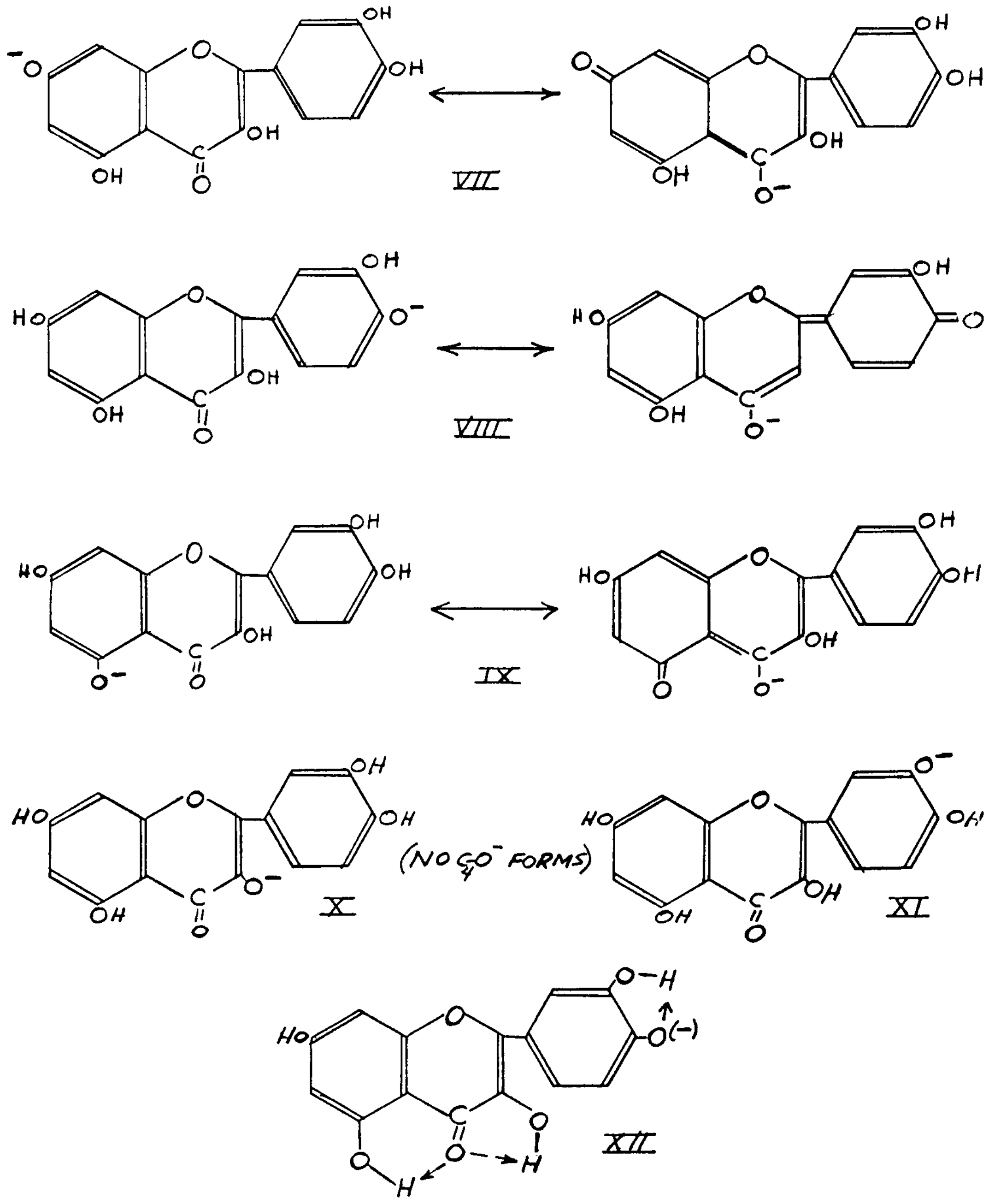


FIG. 2 Resonance Forms of Ions of Quercetin VII-XI
Chelated Systems in Quercetin - XII

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Pharmaceutical and Medical References for Quercetin

A. Capillary Fault

Quercetin has been reported to be superior to its glucorhamnoside rutin in correcting capillary fault and to be effective in cases not responding to rutin, (1, 2, 3). The maximum dosage of quercetin regarded for correction of capillary fault was about 1/7 that of rutin (3).

B. Capillary Fragility

Quercetin has been said to have activity in decreasing capillary fragility of blood vessels (4, 5).

C. Antibiotic

Quercetin has been found to inhibit the growth of Staphylococcus aureus (6). The formation of botulinus toxin is prevented by use of quercetin (7). An antagonistic effect is produced by quercetin on the antibiotic activity of crystalline Tomatine toward Candida albicans (8).

D. Sparing Action on Epinephrine

The oxidation of epinephrine is reported to be retarded by use of quercetin (9, 10).

E. Virus

Quercetin is said to have shown significant prophylactic activity against fixed rabies virus in mice (11).

F. Enzymes

Quercetin has been reported as an active inhibitor on histidine decarboxylose (12).

G. Histamine Shock

Quercetin has been found to give slight protection against histamine shock (2, 13, 14, 15).

H. Synergism with Ascorbic Acid

The synergistic effect has been shown in tests on laboratory animals receiving quercetin and sub-minimum amounts of ascorbic acid (2, 16).

I. Irradiation

Quercetin given simultaneously with ascorbic acid is reported to be as effective as rutin on reducing hemorrhagic diathesis and mortality (17, 21).

J. Frostbite

Some protection is said to be offered by quercetin when given orally immediately after freezing (18).

K. Experimental Cancer

Of the four compounds present in podophyllin accounting for most of the tumor damaging activity of that drug, quercetin was reported to be about 100 times more active than the other three when dissolved in sodium hydroxide solution (19).

L. Blood Pressure

Intravenous administration of quercetin in dogs and cats is said to cause a temporary fall in blood pressure (20).

M. Blood Clotting

Quercetin is said to have an antagonistic effect on the anticoagulative action of piperazine (3).

N. Stress Conditions

Quercetin is reported to essentially prevent the nasal excretion of a red pigment in Albino rats when maintained on vitamin B-deficient or water-restrictive diets at approximately 90 per cent relative humidity (22).

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