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EXTRACTIVES IN EASTERN HARDWOODS-A REVIEW.(U)
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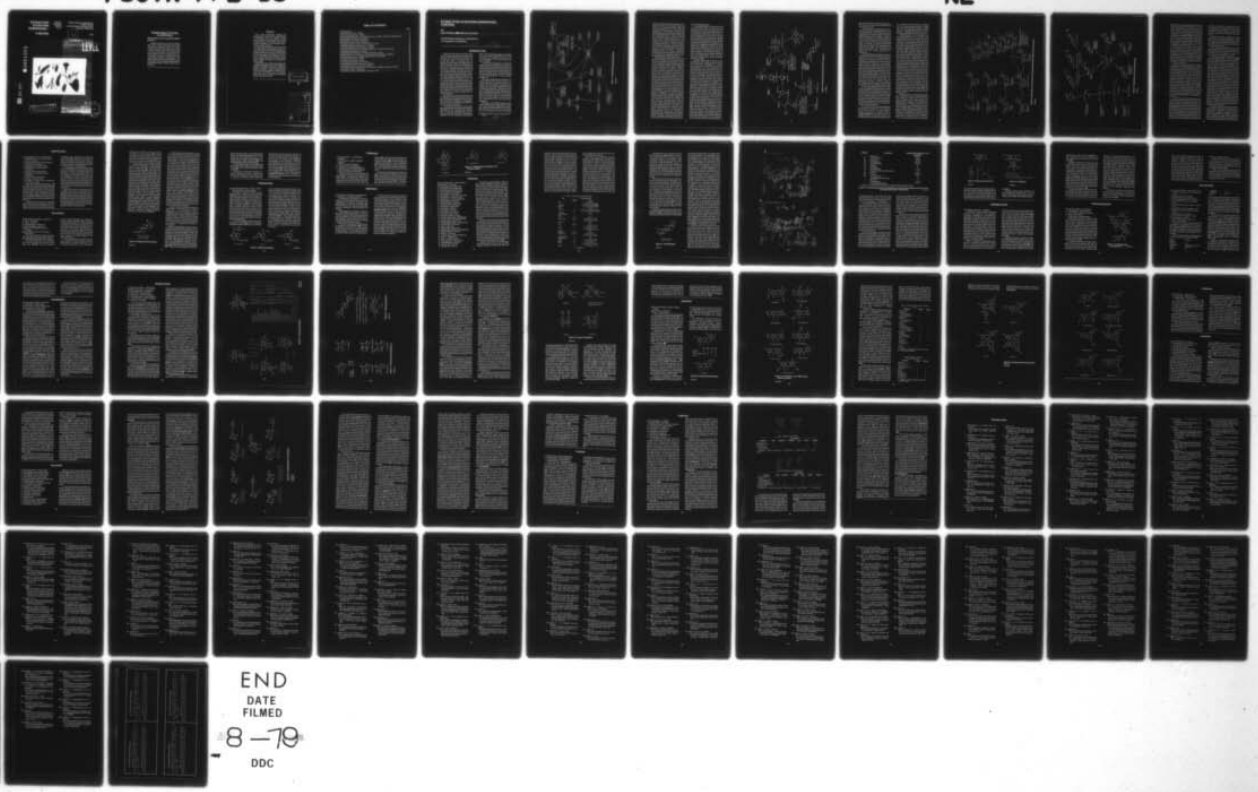

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EXTRACTIVES IN EASTERN HARDWOODS—

A REVIEW

GENERAL TECHNICAL REPORT FPL 18

FOREST PRODUCTS LABORATORY
FOREST SERVICE
U.S. DEPARTMENT OF AGRICULTURE
MADISON, WISCONSIN

1979

SIGNIFICANCE OF COVER ILLUSTRATION

(One example of how an extractive affected products)

Painted surfaces on the wood of slippery elm (*Ulmus rubra*) occasionally show yellow discoloration. Research at the U.S. Forest Products Laboratory has shown that this discoloration is due to a yellow extractive present in the outer heartwood. This extractive has been isolated in the form of brilliant canary yellow needles. Its structure is identified as a new napthalenoid cadalenic sesquiterpene. Left, surface painted gray showing bleedthrough of yellow stains; right, unfinished surface showing yellow streaks; center, crystals of yellow coloring matter.

ABSTRACT

SYNOPSIS

This report extensively reviews the chemistry of extractives from wood and bark of hardwoods from the eastern United States. While such extractives are not used to a great extent commercially, they may influence properties of the wood and performance of wood products.

For example, extractives can protect wood from decay, add color and odor to wood, accent grain pattern, and enhance strength properties. Extractives may also inhibit setting of concrete, glues, and finishes; cause problems in papermaking; contribute to corrosion of metals in contact with wood; present health hazards, and affect color stability of wood to light.

Hardwoods in this review are grouped and discussed alphabetically by their respective botanical families. Grouping botanically makes it possible to draw chemotaxonomic inferences related to genera. Literature searches cover 22 families and 174 species; species by family are listed at the beginning of each discussion section.

ABSTRACT

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EXTRACTIVES IN EASTERN HARDWOODS—A REVIEW

By

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U.S. Department of Agriculture

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INTRODUCTION

Extractives are natural products extraneous to a lignocellulose cell wall; they can be removed with inert solvents such as ether, benzene-alcohol, acetone, and cold water. Although cold water is considered inert, hot water will cause a slight, slow degradation of the lignocellulosic cell wall. Extractives may be within a cell wall, but are not chemically attached to it. Insoluble extraneous constituents will include crystalline inclusions such as calcium oxalate and silica, as well as starch granules and certain polymeric materials. The extractives in eastern hardwoods range from 0.1 to 3.5 percent ether extractives, 0.9 to 6.5 percent alcohol-benzene extractives, and 1.3 to 15.1 percent water extractives. Sequential extractions will result in lower values for alcohol-benzene and water extractives. Because of this extreme variability in extractives content, even within different pieces of wood from the same tree, analyses of the cell wall constituents of wood and bark are always carried out on extractive-free wood.

Extractives are from two general sources. The first source is the compounds involved in a tree's metabolic processes; the second is artifacts from further modification of metabolites by means other than metabolic processes of a tree or from external sources.

The extractives formed from a tree's metabolic processes can be divided into two general categories—primary and secondary metabolites. The primary metabolites are the bioorganic compounds that occur in essentially all organisms and that constitute the intermediates in the intermediary metabolic processes. Thus most primary metabolites can be interconverted in the organism into the other primary metabolites via the intermediary metabolic processes.

Typical primary metabolites include simple sugars, amino acids, simple fats, various carboxylic acids, and others. These will always be found among the extractives of living trees, although the amounts will vary depending on the time in the growth cycle, the nutritional state, the tissue, and the season. Reports of isolation of these metabolites are of little taxonomic significance.

Secondary metabolites are generally compounds more complex than the primary; taxonomic distribution is restricted and their formation within the organism is essentially irreversible. Thus secondary metabolites express individuality of a species in chemical terms. Figure 1 illustrates the general secondary pathways that bring about this type of extractives in eastern hardwoods. Glucose can be considered the primary product of photosynthesis and is the starting material for producing cell wall components and most secondary metabolites.

Although in the broadest sense, all secondary metabolites are taxonomically significant, certain secondary metabolites are apparently ubiquitous to hardwoods and in the context of this Review are not taxonomically

[1]Maintained in cooperation with the University of Wisconsin-Madison.

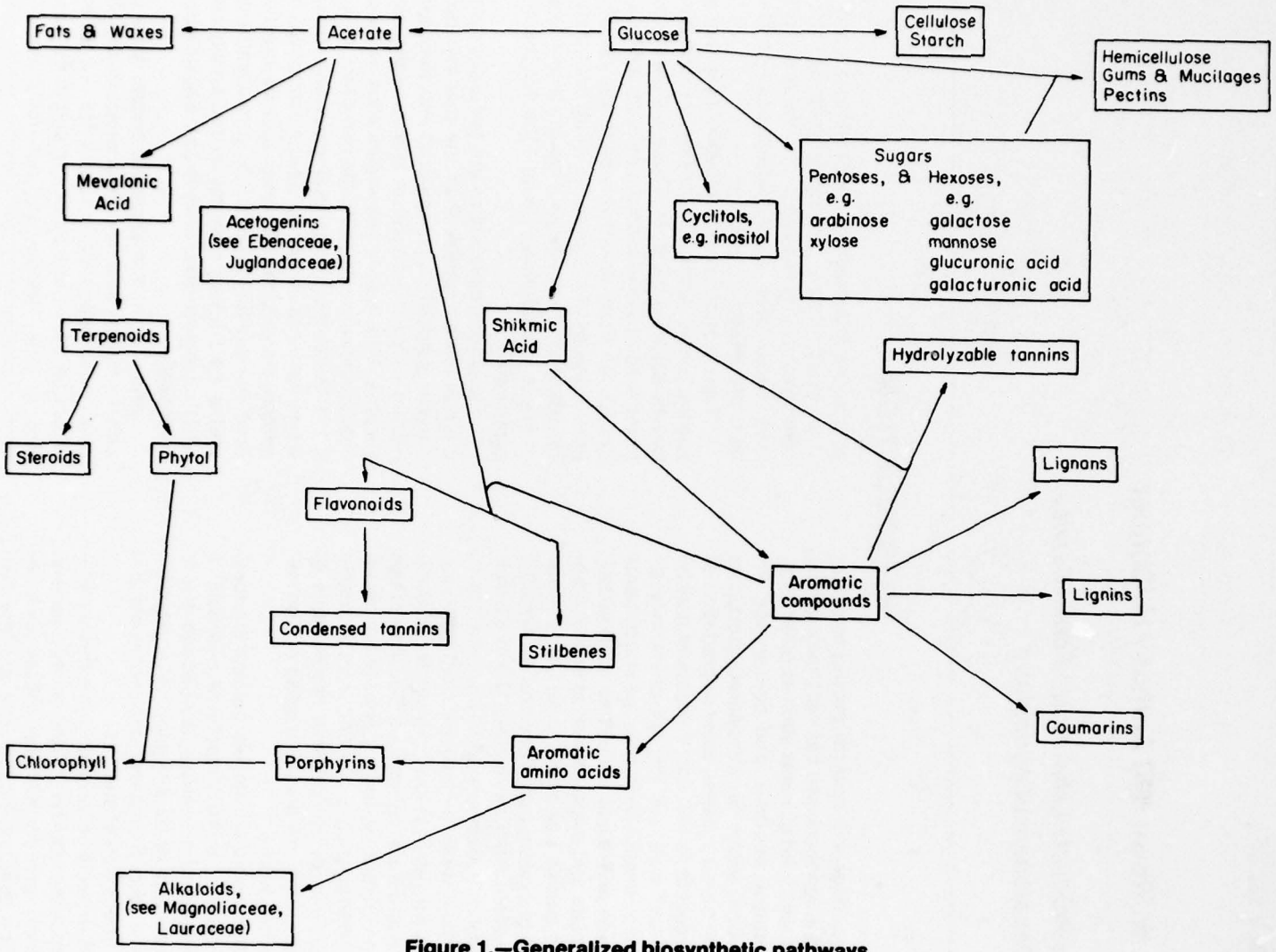

Figure 1.—Generalized biosynthetic pathways.

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significant. All hardwoods thus possess the enzymes necessary for producing these compounds. To a large extent these compounds are intermediates rather than final products of metabolism. In some species or tissues these intermediates accumulate in pools that are isolable in large quantities, whereas in others they are metabolized further as fast as they are formed, thus are isolated with difficulty, in only small amounts. Further, these pools of intermediates may be limited to specific tissues or by specific conditions; thus this accounts for their variability. Examples of secondary metabolites common to all hardwoods include starch, sitosterol, simple terpenoids, chlorophyll, phenylpropanoids, the common flavonoids, simple tannins, and probably compounds such as scopoletin (see Fagaceae) that are mentioned repeatedly throughout this Review.

Many secondary metabolites have a more restricted distribution than do the primary because not all biogenetic pathways are operative in all species or tissues and they may terminate at different stages. These metabolites may be characteristic of a family, a genus, a subgenus, a section, a subsection, a species, or even a chemical race within a species. They form a basis for chemotaxonomy because they reflect in part the enzyme systems that produced them, thus the genetic makeup of a tree. However, the expression of these enzymes may be controlled by environmental factors including season, nutritional state, the particular tissue being discussed, and if a tree is under attack by decay organisms that will elicit wound response reactions. Thus chemotaxonomic studies based on the relative amounts of various metabolites can be highly misleading if the sample is insufficient to warrant statistical treatment. Chemically these secondary metabolites will often be end products of metabolism, and will be more elaborate and complex than those common to all hard woods. These are among the most interest-provoking of the extractives of trees, examples of which are the alkaloids (Magnoliaceae and Lauraceae), complex flavonoids (Moraceae), complex monoterpenes (Bignoniaceae), sesquiterpenes (Magnoliaceae, Ulmaceae), acetogenins (Ebenaceae and Juglandaceae), phenol glycosides (Salicaceae), complex coumarins (Aceraceae), cyanogenic glycosides (Rosaceae), and other complex phenolics (Moraceae, Lauraceae, and Magnoliaceae).

The remaining types of extractive found in trees are artifacts. They can arise from many sources, none of which involves a tree's enzyme systems. Some may be metabolites of micro-organisms; apparently sound wood on careful investigation is often found to contain micro-organisms. Some extractives reported from tree barks may actually be lichen metabolites. But the most important artifacts are those formed by autoxidation and nonenzymatic free radical or acid-catalyzed condensations. These reactions are particularly common among the polyphenolic heartwood extractives. Thus the color in tannins is probably predominately an artifact. Similarly, the low decay resistance of central heartwood of many species results with time from polymerization of toxic phenolics caused, for example, by the acidity from anaerobic bacterial attack.

Aromatic compounds are formed biogenetically either from acetate via malonyl CoA to give the aromatic "acetogenins" or directly from glucose via the shikimic acid pathway. In some instances, *e.g.*, the flavonoids and stilbenes, different parts of the same molecule are derived via both pathways. Figure 2 shows in detail the biogenesis of simple aromatic compounds via the shikimic acid pathway and their conversion into lignin and the other common phenolic extractives obtained from eastern hardwoods—hydrolyzable and condensed tannins, flavonoids, coumarins, and lignans. The coumarins and their glycosides apparently are important in regulating the enzymes in a tree (**153**). Tannins are used in the leather industry for converting animal skins into a stable leather product by their ability to form multiple hydrogen bonds with proteins. Most water-soluble polyphenols in the molecular weight range 500 to 3,000 have this property. Thus tannins are capable of precipitating enzymes; and can detoxify microbial digestive enzymes as well as interfere with the activity of isolated plant organelles. They are markedly astringent and have been implicated in initiating esophageal cancer (**226**). The early literature on tannins must be treated with caution. Tannin was often considered as the amount of hot-water extract if this extract was capable of precipitating gelatin or being precipitated by heavy metals, alkaloids, or acidified formaldehyde. The percentage of tannin should be accompanied by the percent-

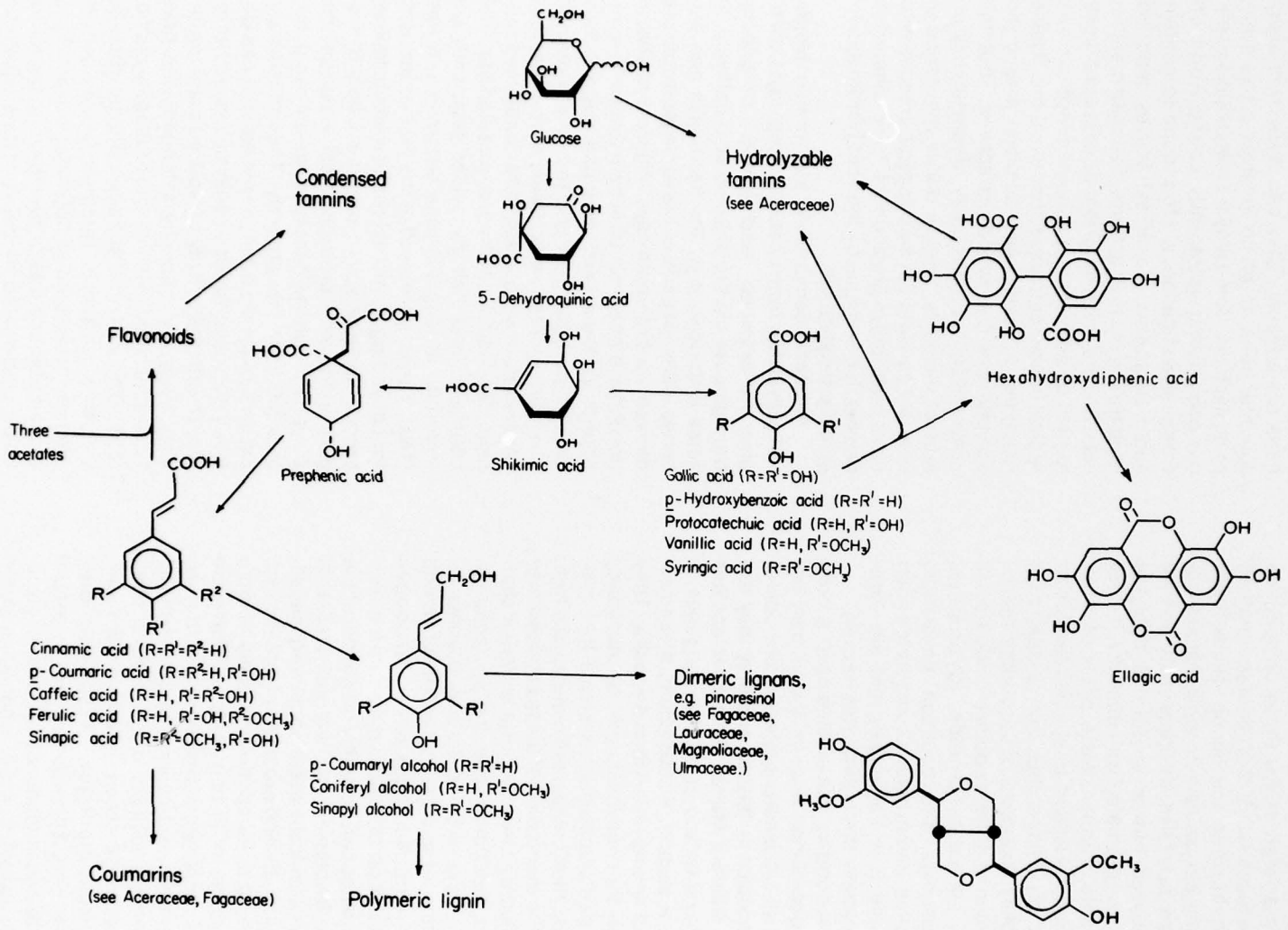

Figure 2.—Aromatic compounds derived from glucose.

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age purity of the tannin determined by the fraction of the hot-water extract absorbed by chromed hide powder.

Vegetable tannins may be divided structurally into two types: Hydrolyzable tannins and condensed tannins. Hydrolyzable tannins are characterized by having a polyhydric alcohol, predominately glucose, partially or wholly esterified with gallic acid, hexahydroxydiphenic acid, and their derivatives. Tannins with this type of structure can be readily hydrolyzed by acids or enzymes to give the carbohydrate moiety and the phenolic acid moieties such as gallic acid and ellagic acid (the dilactone of hexahydroxydiphenic acid). Therefore these tannins are also called gallotannins or ellagitannins.

Condensed tannins are flavonoid polymers that contain only phenolic moieties and give no significant amounts of low-molecular-weight compounds on hydrolysis. These tannins instead tend to polymerize further in acid solution to give insoluble, amorphous, colored phlobaphenes. Figure 3 outlines the general biogenetic interrelationships among the various types of flavonoids and the condensed tannins. The precise biosynthetic pathways have not been fully elucidated (**138**). The interrelationships are illustrated using the quercetin oxidation pattern that apparently is the most common although many other hydroxylation patterns are known (the Leguminosae and Moraceae). Quercetin, a common extractive from hardwoods, and related compounds was recently shown to have mutagenic activity (**35**).

O- and *C*-glycosylated flavonoids are also found in the eastern hardwoods as are a variety of methyl ethers and a few alkyl derivatives. The anthocyanins (the glycosylated derivatives of the anthocyanidins) contribute to the beautiful colors of autumn leaves of hardwoods (**140**). The leucoanthocyanidins also occur as glycosylated derivatives, the leucoanthocyanins. The leucoanthocyanins and leucoanthocyanidins are the colorless precursors of the anthocyanins and anthocyanidins.

The flavan-3,4-diol (leucoanthocyanidin) and flavan-3-ol precursors of the condensed tannins polymerize first into a wide variety of dimeric and trimeric proanthocyanidins (**19,138,139,354,372**) with diffrerent types of linkages between the flavonoid groups. The proanthocyanidins are predominately polymers of (+)-catechin and its 3-epimer (−)-epicatechin, as a result they yield cyanidin if treated with acid. Corresponding derivatives possessing a 3′,4′,5′-hydroxylation pattern [(+)-gallocatechin, (−)-epigallocatechin] yield the corresponding delphinidin on treatment with acid.

Proanthocyanidin A-2 is illustrated in the Hippocastanaceae and the catechin dimer (proanthocyanidin B-3) and trimer (proanthocyanidin C-2) in Figure 3. Further polymerization leads to higher oligomers of flavan-3,4-diol and flavan-3-ol principally responsible for the properties usually attributed to the true tannins. Eventually, polymerization leads to the high-molecular-weight phlobaphenes that are insoluble. Still higher molecular weight polymers, such as the red powder that drops out if laboratory corks are rolled to soften them, are probably the backbone on which suberin is laid in the formation of cork. Therefore, the cork fraction of bark consists of a three-dimensional network of insoluble polyflavonoids, together with polyestolide fats and waxes (suberin). Although largely insoluble in inert solvents, suberin can be dissolved by hot, dilute alkali to yield monomeric fatty and wax compounds, and a polyflavonoid "phenolic acid" that results from rearrangement of the flavonoid nucleus (**311**). Pure phenolic polymers are colorless, but the tannins found in nature are normally colored, presumably due to oxidation to extended, conjugated systems such as that shown in Figure 3 or to *o*-quinones. The condensed tannins and related polyflavonoids are extremely common extractives, especially in bark. Roux has written an excellent review of this subject (**299**) and Harborne has discussed the relationship between flavonoids and the evolution of the angiosperms (**131**).

Outlined in Figure 4 is the general biosynthetic relationships of the compounds derived from acetate (*i.e.*, acetyl CoA) via the intermediacy of mevalonic acid. These pathways are responsible for formation of the monoterpenes, sesquiterpenes, diterpenes, triterpenes, and steroids. Sterols (*i.e.*, phytosterols) are ubiquitous in the plant kingdom. The most common of these is sitosterol (24-ethylcholesterol) that always co-occurs with lesser amounts of its lower homologs, campesterol and cholesterol, and minor amounts of their saturated counterparts, stigmastanol, campestanol, and cholestanol. The co-occurrence of these six sterols sug-

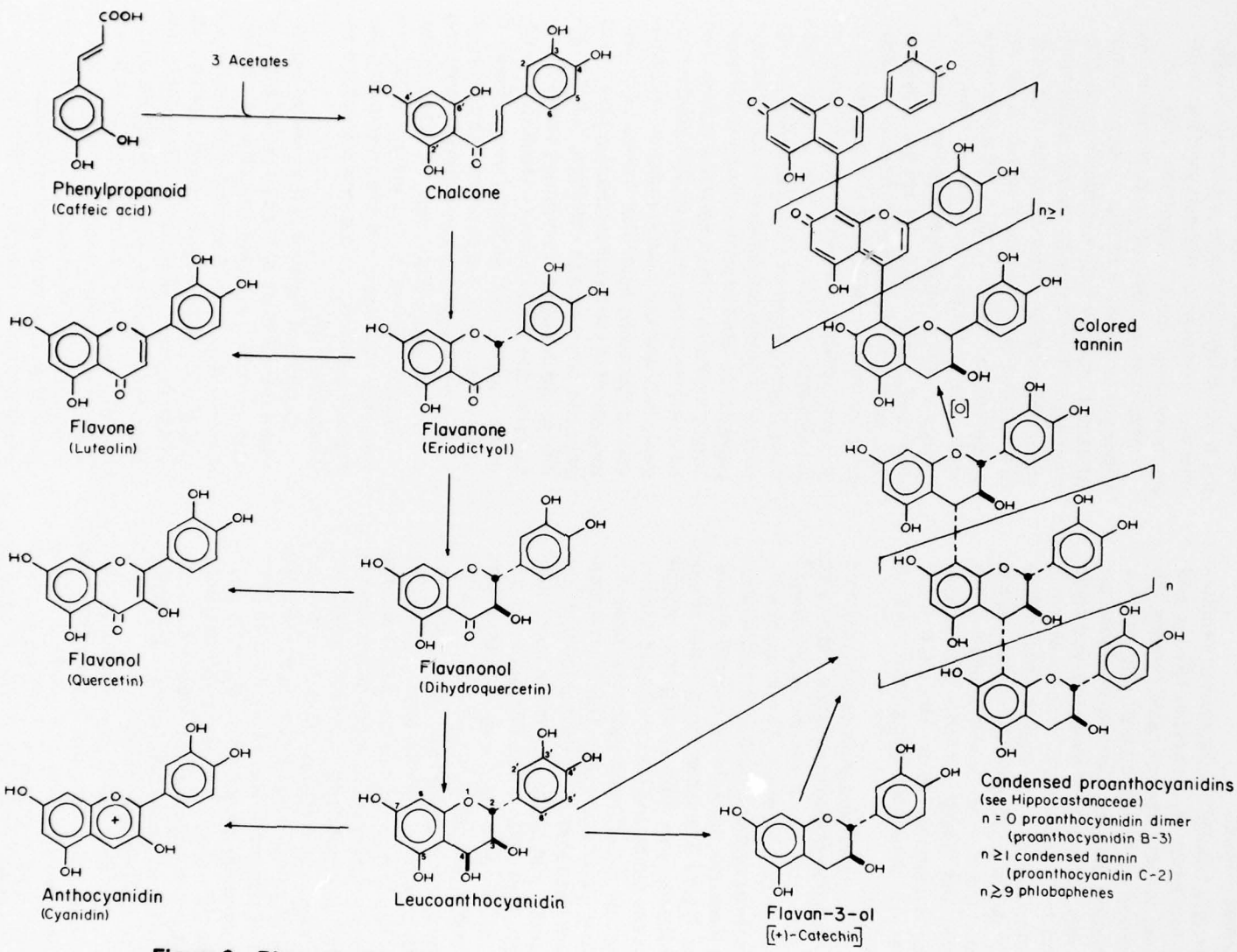

Figure 3.—Biosynthesis of flavonoids and condensed proanthocyanidins (condensed tannins).

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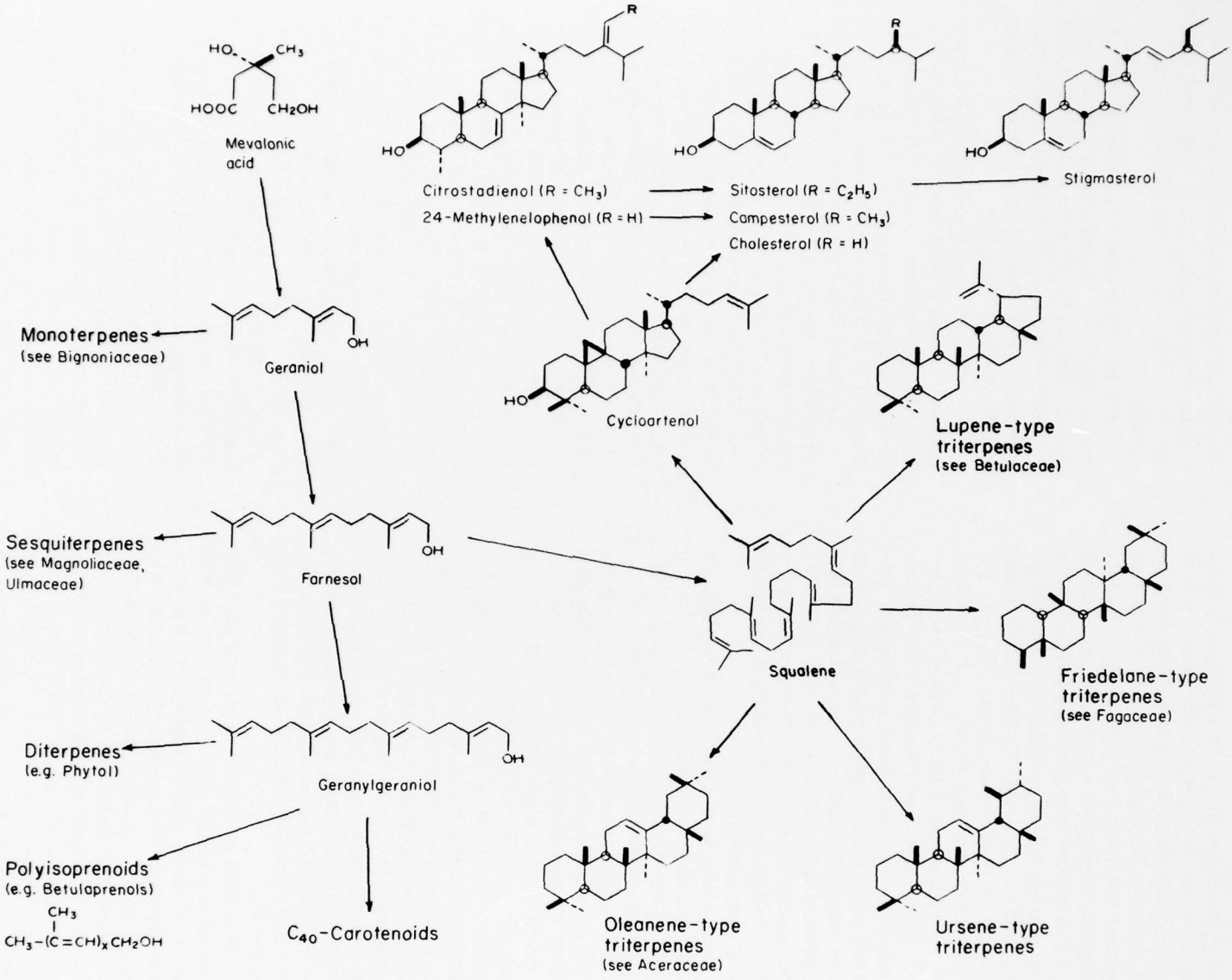

Figure 4.—Biosynthesis of steroids and terpenoids.

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gests that the hydrogenase enzyme that reduces the side-chain double bond is not completely stereospecific. In this Review, β-sitosterol is taken to represent the sitosterol-rich mixture of sitosterol and campesterol, whereas γ-sitosterol is the campesterol-rich mixture of sitosterol and campesterol (**355**). Various other sitosterols have been reported in early literature. α_1-Sitosterol has been shown identical to the triterpene citrostadienol (**18**) that is always accompanied by small amounts of its lower homolog, 24-methylenelophenol. The α_2- and α_3-sitosterols are now known to be mixtures rich in cycloartenol and its derivatives. Many other sterols are known that are intermediates between the initially formed cycloartenol and the last-formed sterol, stigmasterol, but in most cases these do not accumulate and are metabolized as rapidly as they are formed. Unlike the other sterols often found in the form of esters of fatty acids, stigmasterol usually is found predominately unesterified.

Wood and bark extractives from eastern hardwoods of the United States are not used to any great extent commercially. Extractives are nevertheless important in the utilization of eastern hardwoods because of their contributions to the properties of wood. The extractives can protect wood from decay, add color and odor to wood, accent grain pattern, and enhance strength properties. In contrast, they can contribute to corrosion of metals in contact with wood; inhibit setting of concrete, glues, and finishes; cause various problems during papermaking; present health hazards (*e.g.*, dermatitis, asthma, and cancer); and affect the color stability of wood to light. Seldomly can all of the color from wood or bark be removed by extraction because of polymerization of the extractives into insoluble deposits as discussed for the tannins.

Inner bark and sapwood generally are rich in simple monomers and nutrients such as fats, starch, sucrose, simple sugars, inositols, simple glycosides, free and esterified sterols, and phenylpropanoids and other simple phenolics. Heartwood and outer bark, by contrast tend to be deficient in nutrients, glycosides and metabolic intermediates, but are rich in compounds such as hydrolyzable and condensed tannins and many other phenolics, alkaloids, resins, essential oils, and specialized compounds of a wide variety of types. Heartwood and outer bark also tend to contain the various gums, kinos, and balsams that have evolved as part of the wound response mechanisms, as well as the compounds capable of protecting these metabolically inactive tissues against biological attack.

Apparently eastern hardwoods evolved earlier than did tropical angiosperms. Therefore it is not surprising that extractives of eastern hardwoods are generally less complex and less likely to contain compounds with significant physiological activity.

The most intriguing extractives are those compounds that can be used as chemotaxonomic markers and the compounds that can be correlated with some specific property of a wood such as decay resistance or color.

The species included in this Review are the eastern hardwoods listed in Little's Atlas (**207**) plus other representatives of the same genera that will be listed in a forthcoming volume of Little's Atlas that includes rare eastern hardwoods. A booklet that briefly describes the important trees of the eastern forest has been prepared (**234**). The hardwoods in this Review are grouped and discussed alphabetically by their respective botanical families. Grouping botanically makes it possible to draw chemotaxonomic inferences relating to genera. Literature searches cover 22 families and 174 species; species by family are listed at the beginning of each discussion section. The literature on the extractives of wood and bark has been thoroughly covered. The chemistry of specialized tissues such as leaves, seeds, flowers, and fruits can be quite different and is not mentioned except if of special interest or if very little information is available. Although there are many publications on the extractives of hardwoods of the eastern United States, most species have not been investigated and most of the species investigated have received only limited attention. In only a few have studies been extensive enough to provide understanding of the chemistry of the extractives.

Locating information on hardwood extractives in technical abstracts is difficult because this material is published in a wide variety of journals, all compounds isolated are not indexed, all species are not indexed by scientific name, changes have been made in botanical names or synonyms are used, and several common and systematic names for individual natu-

ral products are used. A recent three-volume work "Phytochemistry" (**222**) is a good general reference. Specialized information is available in the annual "Recent advances in phytochemistry," the proceedings of the annual symposium of the Phytochemical Society of North America. The "Lynn index" (**103**), of which eight volumes have now been published, contains brief coverage of plant components reported to 1954 and listed by species. Future volumes will index the chemical constituents. More up-to-date is the excellent series "Chemotaxonomie der Pflanzen" (**143**). The index includes both species and compounds. The four-volume series "Chemotaxonomy of flowering plants" (**118**) also contains useful information and is indexed by species and compounds. An excellent reference on structure and source of a natural product is the "Dictionary of organic compounds" (**288**), five-volumes plus up-dating supplements. Other useful references are "Konstitution and Vorkommen der organischen Pflanzenstoffe" (**177**), and the "Handbook of naturally occurring compounds" (**80**). Many specific types of natural products are reviewed in monographs: Alkaloids (**212,295,375,376**), terpenoids (**236**), organic acids (**41**), flavonoids (**116,133,210**), and steroids (**104**). One book concentrates on the chemistry of wood extractives (**148**). A recent report discusses the chemistry of the extractives of bark (**134**).

This Review will be limited to the chemistry of bark and wood. Most of the source material is derived from the authors' files. References to early results satisfactorily covered in secondary sources generally are not included. Data on amounts extractable with various solvents are also omitted because of great variability in values.

ACERACEAE

Acer barbatum Michx., Florida maple
A. leucoderme Small, chalk maple
A. negundo L., boxelder
A. nigrum Michx. f., black maple
A. pensylvanicum L., striped maple
A. rubrum L., red maple
A. saccharinum L., silver maple
A. saccharum Marsh., sugar maple
A. spicatum Lam., mountain maple

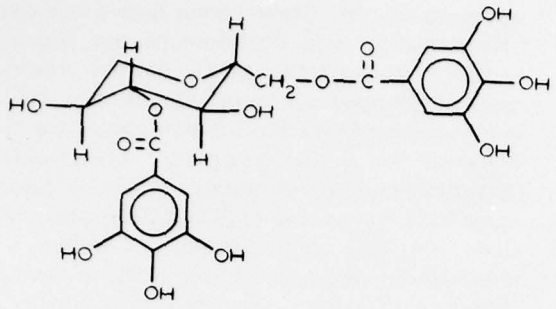
The literature on maples to 1961 has been ably summarized (**143**); a review in 1970 (**197**), added little.

The maples, especially black and sugar maples and to a lesser extent red and silver maples, are best known for maple sirup produced by boiling down the sap (**378**); this was an art taught to the early settlers by the Indians, who also used maple bark and the rotted wood as a dyestuff.

Maple sap consists primarily of sucrose and an arabinogalactan (**9**). Other constituents include quebrachitol (2-*O*-methylinositol) (**244,340**), phytokinins (**237**), two trisaccharides (**128**), glucose, fructose, allantoin, allantoic acid, vanillin, vanillic acid, syringaldehyde, coumarin, malic acid, coniferyl alcohol, coniferaldehyde, and guaiacol. Quebrachitol apparently is ubiquitous in the Aceraceae (**143**). In a study of the water-soluble polysaccharides of the sapwood, heartwood, and inner bark of sugar maple, the major component in each tissue was found to be glucomannan, 4-*O*-methylglucuronoxylan, and arabinogalactan, respectively (**8**).

Tannins apparently are not present in maple wood, although the barks reportedly contain relatively small amounts of them: Black maple, 1.9 percent; red maple, 6.9 percent; silver maple, 2.8 to 7.8 percent; sugar maple, 0.4 to 2.7 percent (**304**). An acertannin, isolated in 0.6 percent yield from mountain maple bark and assumed typical of the tannins from maples, was 3,6-di-*O*-galloyl-1,5-anhydrosorbitol (fig. 5). The general chemistry of boxelder and sugar maple barks has been investigated (**55**). Boxelder wood and bark contain essentially no tannin.

A chemical comparison of clear and mineral-stained sugar maple has been made (**196,198**). Peracetic acid and sodium chlorite will bleach mineral stain in sugar maple (**199**). Gallic acid and catechin are the main phenolics in the clear wood of both red and sugar maples (**343**). Significantly, these are both absent in



Acertannin (3,6-di-Q-galloyl-1,5-anhydrosorbitol)

Figure 5.—Tannin from mountain maple (*Acer spicatum*) bark.

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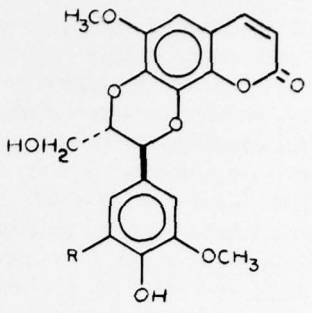

R = H
R = OH
R = OCH_3

Figure 6.—Antifungal fraxetin derivatives isolated from sugar maple (*Acer saccharum*) wood.

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discolored or decayed wood. The color cannot be completey extracted from this type of discolored wood. Presumably, the phenolics have been oxidatively polymerized. In a search of the precursors of this color, a closely related series of fraxetin derivatives (fig. 6) was isolated in 1 percent yield from mineral-stained sugar maple wood (**213**); they are absent in clear wood. These are antifungal and are apparently produced by the tree in response to stress.

Red maple wood and bark have been found to contain glucose, β-sitosterol, *D*-catechin, and a procyanidin consisting of leucocyanidin units linked 4-8 (**233,316**). However, the procyanidin from the wood was a dimer, whereas that from the bark was a trimer. The bark also contains pyrogallol and gallic acid. The bark of red and mountain maple (**187**) are used in folk medicine as an anthelmintic, tonic, and opthalmiatric. Maple-bark disease is a pulmonary hypersensitivity reaction to the fungus *Cryptostroma corticale*, it is marked by cough, and night sweats, and radiographic evidence of infiltration (**386**). Sugar maple wood and bark yielded β-sitosterol and a small amount of leucoanthocyanidins (**316**). Coniferaldehyde and sinapaldehyde are present in the wood (**36**). Silver maple bark contains β-sitosterol, gallic acid, and proanthocyanidins; boxelder wood and bark contain mannitol, glucose, galactose, and arabinose (**316**).

Among the most pharmaceutically interesting of the extractives in maple are the tumor-inhibiting saponins of boxelder leaves and stems (**191**). The aglycone of saponin P has been shown to be a mixture of *trans* (acerotin) and *cis* (acerocin) isomers of diesters of the new triterpene, acerogenic acid (fig. 7). The aglycone of saponin Q has been shown to be a similar ester of 24-hydroxyacerogenic acid. One of these aglycones may be the unknown triterpene carboxylic acid isolated along with β-sitosterol and sitosterol-*D*-glucoside from insect-infected boxelder wood (**183**).

Figure 7.—Aglycones of tumor-inhibiting saponins isolated from boxelder (*Acer negundo*).

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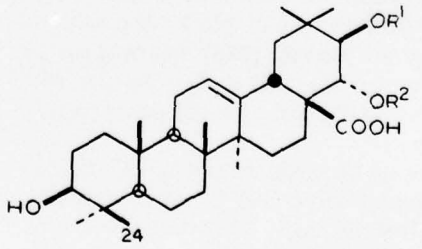


Acerogenic acid ($R^1 = R^2 = H$)

Acerotin (R^1 = Ac, $R^2 = -(C=O)\cdot(CH=CH)_2\cdot CH(CH_3)\cdot(C_2H_5)$)

Acerocin (R^1 = Ac, $R^2 = -(C=O)-CH=CH-CH=CH-CH(CH_3)\cdot(C_2H_5)$)

AQUIFOLIACEAE

Ilex ambigua (Michx.) Torr., Carolina holly
I. amelanchier M. A. Curt, juneberry holly
I. cassine L., dahoon
I. coriacea (Pursh) Chapm., large gallberry
I. decidua Walt., possumhaw
I. krugiana Loes., tawnyberry holly
I. laevigata (Pursh) A. Gray, smooth winterberry
I. longipes Chapm., Georgia holly
I. montana Torr. and Gray, mountain winterberry
I. myrtifolia Walt., myrtle dahoon
I. opaca Ait., American holly
I. verticillata (L.) A. Gray, common winterberry
I. vomitoria Ait., yaupon

Although the literature on hollies to 1963 has been ably summarized (**143**), essentially nothing is known about the extractives of eastern hollies. Neither the wood nor the bark apparently contains more than traces of tannins. That the wood is white, susceptible to decay, and permeable suggests that the extractives have no significant function for this genus. This genus is best known for the decorative Christmas holly.

In South America maté tea is prepared from the leaves of *Ilex paraguariensis*. A mild infusion is innocuous, but a stronger brew is an emetic and a diuretic. At one time it was given for diabetes, gout, smallpox, and to expel kidney stones (**226**). During the Civil War the leaves of American holly were a common substitute in the south for imported tea. The leaves of yaupon were used to prepare a tea for similar uses by the Indians in the Southeast.

An investigation of American holly leaves and fruit showed that the ethanol extract of the leaves, but not the fruit, was lethal to mice and hemolytic to human erythrocytes (**373**). The toxic substance in the ethanol extract could not be characterized. However, the extract was shown to contain a crude oleanolic acid saponin that was not toxic but was hemolytic to erythrocytes. Nonacosane was isolated from a nontoxic hexane extract of leaf material, and ursolic acid from the nontoxic ether extract of the ripe fruit.

Most recent reports in the literature on the chemistry of holly are on leaves and bark of Japanese hollies, which have been investigated extensively. Birdlime, the sticky ether extractables of the bark of Japanese holly used to ensnare small birds, is rich in pentacyclic triterpene esters, and the Chinese have found that triterpene saponins in the bark have antimalarial properties (**64**). The bark of American hollies probably contains similar materials.

BETULACEAE

Betula alleghaniensis Britton, yellow birch
B. lenta L., sweet birch
B. nigra L., river birch
B. papyrifera Marsh., paper birch
B. populifolia Marsh., gray birch
Carpinus caroliniana Walt., American hornbeam
Ostrya virginiana (Mill.) K. Koch, eastern hophornbeam

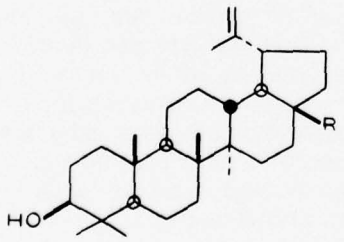
The extensive literature on the birches to 1961 has been summarized (**143**). A review in 1970 (**197**) added little additional information.

The most studied birch is, of course, sweet birch, the bark of which was a source of oil of sweet birch (**103,143**). The oil, an excellent source of methyl salicylate, was important in commerce before synthetic methyl salicylate became readily available. The methyl salicylate is formed from the 6-xylosidoglucoside of methyl salicylate if the bark is hydrolyzed with hot water. The American Indians obtained a birch tea, a red dye, and a decoction to treat bruises and cuts from birch bark. They chewed the inner bark, which is especially sweet and spicy in spring, and obtained sugar from the spring sap for food.

Tannins apparently are not present in birch wood. However, the barks contain relatively small amounts of tannins: Paper birch, 1.6 to 3.3 percent; yellow birch, 1.5 to 4.4 percent;

sweet birch, 3.5 percent; river birch, 5.6 percent; gray birch, 2 to 5 percent (**304**). Tannins are highest in barks of birches with dark-colored bark. The general chemistry of yellow and paper birch bark has been studied (**55**); a little more than 5 percent of formaldehyde-reactive tannin was present in the bark of each species.

A major characteristic of paper and gray birches is the white bark. A white powder, which has been reported to cause skin eruptions in mill workmen (**386**), can often be removed from the surface of these barks. The powder consists mostly of nontoxic pentacyclic lupane triterpenes, characteristic major components of birch barks (fig. 8). Paper birch bark contains 1.5 percent betulin (**317**). Other triterpenes present are betulinic acid, lupeol, oleanolic acid and acetyloleanolic acid as well as β-sitosterol and a procyanidin. The heartwood contains similar components, namely betulin, lupeol, β-sitosterol, and a very small amount of procyanidin (**317**). Sweet birch bark contains lupeol and betulin as major constituents with lupenone, oleanolic acid, β-sitosterol, methyl salicylate, and leucocyanidin; the heartwood contains lupeol, betulin, methyl acetylbetulinate, methyl salicylate, β-sitosterol, sitosterol-β-*D*-glucoside, and a small amount of a procyanidin (**316,317**). Yellow birch bark contains lupenone as the major constituent with betulin, lupeol and procyanidin. The heartwood contains betulin, lupeol, lupenone, methyl acetylbetulinate, β-sitosterol, sitosterol-β-*D*-glucoside and trace of procyanidin (**316,317**).



Betulin (R=CH_2OH)
Lupeol (R=CH_3)

Figure 8.—Triterpenes from birch barks.

M 146 165

These triterpenes in the wood may contribute to the yellowing of bleached birch pulp (**24**), and are certainly major components of the unsaponifiables. Thus one-third or more of the ether extract of paper birch (**44,45,67,231**) is unsaponifiables consisting of triterpenes, sterols, squalene, and related compounds. More than one-half of the ether extract is esters of fatty acids. Of these, 90 percent is triglycerides and 4 percent sterol esters. Linoleic acid is the predominant acid in the esters. Small amounts of free fatty acids and free triterpene acids such as betulinic and oleanolic acids are also present. Citrostadienol (**18**) was isolated from European silver birch wood (**25,205**) and is undoubtedly identical to the sterol indicated present in paper birch wood (**44**). The fatty acids in yellow birch wood are similar to those in paper birch (**67**). This pattern is probably typical of the nonpolar extractives of all birch wood, and is in agreement with the extensive research on European silver birch (**25,174,175,245,246**). Silver birch is often added to kraft cooks of softwoods; the adverse effect of the added birch on the yield and the composition of the tall oil has been of interest (**152**). The decrease in surface wettability of yellow birch on heating has been explained by autoxidation of the esters of linoleic acid esters (**145**). Acetone extraction of the surface prevented this decrease.

A group of neutral terpenoids isolated on saponification of the fatty esters of European silver birch is the betulaprenols (fig. 4) (**123,205**). They consist of long-chain aliphatic unsaturated terpene alcohols (polyprenols). Although they have not been reported in eastern American birches, their occurrence is probably widespread. Thus, a fraction isolated from paper birch wood (**44**) is probably betulaprenols. The chemistry of polyprenols has been reviewed (**144**).

Paper chromatography has been used to analyze the alcoholic extracts of the inner bark of paper birch and one of its hybrids, but only chlorophyll was identified (**66**). A pectic acid isolated in 4.5 percent yield from the inner bark has been shown to be 4-*O*-methylglucuronoxylan (**356**). Paper birch sap has been found to contain an arabinogalactan, *D*-glucose, *D*-fructose, sucrose, gentiobiose, melibiose, mannotricse, verbascotetraose, and two trisaccharides (**129**) as well as a complex polysaccharide (**360**). Catechin and glycosides of pyroca-

techol, coniferyl alcohol, and pyrogallol were found in the heartwood of paper birch. It is postulated that the reddish-brown stain in the heartwood is produced by fungal phenol oxidases acting on these compounds (**322**). The wood reportedly causes dermatitis (**314**).

The distribution of gum in yellow birch has been studied *via* scanning electron microscopy to elucidate how it affects properties of the wood (**185**).

The woods of American hornbeam and eastern hophornbeam contain no tannins, although the barks contain 3.7 to 4.8 percent and 4.1 percent, respectively (**304**). Essentially nothing else is known about the chemistry of the wood and the bark of these two species, although in the early literature, the chemistry of these genera is mentioned briefly (**103,143**). This suggests that the chemistry of these two species might be of interest because in recent years Japanese hophornbeam has been found to contain a series of homolignans with a biphenyl linkage (**388**). Similar diarylheptanoids have been reported in *Betula platyphylla* var. *japonica* (**346**) and six alders (Betulaceae) (**176,238,341,345,361**). The hornbeams are considered by some authorities to be members of the Corylaceae.

BIGNONIACEAE

Catalpa bignonioides Walt., southern catalpa
C. speciosa Warder, northern catalpa

Although the extractives chemistry of the Bignoniaceae to 1962 has been reviewed (**103,143**), almost nothing on the wood and the bark extractives of southern and northern catalpa has been reported in the last 20 years. Neither the wood nor the bark of northern catalpa contains tannins (**304**). The water extractives of northern catalpa are quite variable (**167**); cold-water extractives from the heartwood range from less than 2.7 percent in the summer to more than 7.5 percent in the spring. The wood and the root bark of southern catalpa accumulate remarkable amounts of stachyose (9.3 pct and 5.4 pct, respectively) as well as lesser amounts of sucrose, raffinose, and perhaps verbascose (**143**).

The most interesting extractive chemotaxonomically in the catalpas is the noriridoside, catalposide (catalpin) (**215**) (fig. 9). It has been found in different parts (especially the fruit) of several members of this genus; in 1888, it was found in southern catalpa bark (**143**). Because it is also reported in northern catalpa fruit, it presumably is also present in this bark. However, catalposide has not been reported in the wood from any eastern catalpas. Southern catalpa bark also has been reported to contain another heteroside called catalpinoside (heterocatalposide) (**143,287**). The most recent work on this genus has been studies on Japanese *Catalpa ovata* wood, which yielded β-sitosterol, cerotic acid, a series of simple phenolics and carbohydrates (**165**), a new phthalide (catalpalactone), and six prenylated naphthoquinones (**166,321**). These naphthoquinones are quite similar to the extractives characteristic of *Streptospermum, Tabebuia,* and other genera of the Bignoniaceae, and suggest that further studies on the extractives of northern and southern catalpa wood should be conducted.

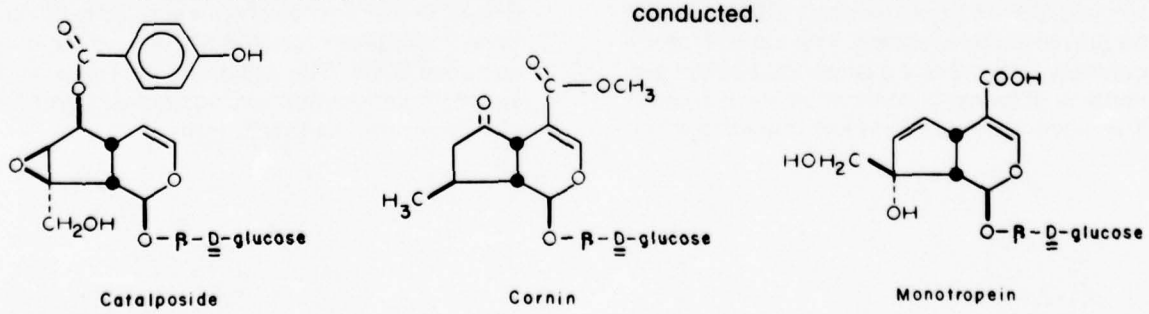


Figure 9.—Iridoid monoterpenes. M 146 166

CORNACEAE

Cornus alternifolia L. f., alternate-leaf dogwood
C. drummondii C. A. Meyer, roughleaf dogwood
C. florida L., flowering dogwood
C. racemosa Lam., gray dogwood
C. rugosa Lam., round-leaved dogwood
C. stolonifera Michx., red-osier dogwood
C. stricta Lam., stiffcornel dogwood

Present information on the chemistry of the dogwoods is predominately limited to the leaves (**143**). The proteins in red-osier dogwood have been studied (**164**), and the bark has been found to contain hyperin (quercetin-3-galactoside), fumaric acid, wax esters, and tannins (**232**). Flowering dogwood has been reported to contain no tannin in the wood but 3.3 percent in the bark (**304**). The bark contains the interesting iridoid (fig. 9), cornin (verbenalin) (**46**). A closely related compound, dihydrocornin in which the keto group has been reduced, has been isolated from the leaves and twigs (**171**).

The leaves of dogwood are an irritant but there are no reports of ill effects from the wood (**386**). A folk remedy for chills and fever was a potion of whiskey in which the inner bark of the flowering dogwood was steeped until all bitterness had been extracted (**226**). The Indians also used this bark as a tonic and a stimulant.

EBENACEAE

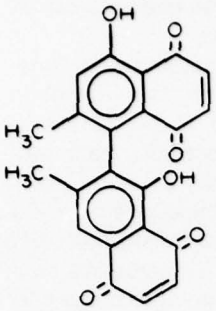
Diospyros texana Scheele, Texas persimmon
D. virginiana L., common persimmon

Of the eastern persimmons, only the extractives of the common persimmon have been investigated. A red pigment, isodiospyrin, has been isolated from the wood and bark (**102**). Another quinone, which may be a hydroxyl derivative of isodiospyrin, was also isolated from the bark.

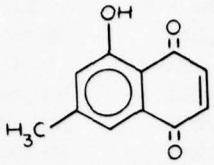
7-Methyljuglone was identified recently as the major termiticial component of wood of *Diospyros virginiana* (**52**). Isodiospyrin was also toxic to termites but to a lesser extent than 7-methyljuglone. Shinanolone and scopoletin (see Fagaceae) were also found in the wood but were not detrimental to termites.

The freshly cut sapwood can discolor from air oxidation of the extractives (**309**); this can be prevented by steaming. The early literature conflicts; either 0 or 8.5 is reported as the percentage of tannin in common persimmon bark. The wood, however, does not contain tannins.

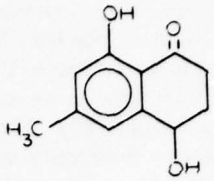
The paucity of information about persimmon contrasts sharply with the abundance of published material on the extractives of the many other *Diospyros* species, which include the African and the Asiatic ebonies. The literature to 1964 has been reviewed (**143**). A few of the significant publications on the extractives of other *Diospyros* species (**200-203, 230,342,347,365**) confirm the general pattern that the wood and the bark of this genus are characterized by pentacyclic triterpenes and naphthalene derivatives. Although these derivatives include napthols, naphthaldehydes and napthoic acids, the most predominant compounds are the naphthoquinones (fig. 10). Dimers with extended conjugation are common and even trimers have been reported. Foreign *Diospyros* species have been reported to cause severe allergies, presumably from the various quinones (**386**). The chemistry of Texas and common persimmon extractives apparently may be worthwhile to research.



Isodiospyrin



7 – Methyljuglone



Shinanolone

Figure 10.—Napthoquinone derivatives from *Diospyros* species.

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FAGACEAE

Fagus grandifolia Ehrh., American beech
Quercus alba L., white oak
Q. arkansana Sarg., Arkansas oak
Q. bicolor Willd., swamp white oak
Q. chapmanii Sarg., Chapman oak
Q. coccinea Muenchh., scarlet oak
Q. durandii Buckl., Durand oak
Q. ellipsoidalis E. J. Hill, northern pin oak
Q. falcata Michx., southern red oak
Q. georgiana M. A. Curtis, Georgia oak
Q. havardii Rydb., Havard oak
Q. ilicifolia Wangenh., bear oak
Q. imbricaria Michx., shingle oak
Q. incana Bartr., bluejack oak
Q. laceyi Small, Lacey oak
Q. laevis Walt., turkey oak
Q. laurifolia Michx., laurel oak
Q. lyrata Walt., overcup oak
Q. macrocarpa Michx., bur oak
Q. marilandica Muenchh., blackjack oak
Q. michauxii Nutt., swamp chestnut oak
Q. mohriana Buckl., Mohrs oak
Q. muehlenbergii Engelm., chinkapin oak
Q. myrtifolia Willd., myrtle oak
Q. nigra L., water oak
Q. nuttallii Palmer, Nuttall oak
Q. oglethorpensis Duncan, Oglethorpe oak
Q. palustris Muenchh., pin oak
Q. phellos L., willow oak
Q. prinoides Willd., dwarf chinkapin oak
Q. prinus L., chestnut oak
Q. rubra L., northern red oak
Q. shumardii Buckl., Shumard oak
Q. stellata Wangenh., post oak
Q. velutina Lam., black oak
Q. virginiana Mill., live oak

The literature on the Fagaceae to 1964 has been reviewed (**103,143**). However, almost all research on the extractives of beech has been on the European *Fagus sylvatica,* the sap of which is well known to cause dermatitis (**386**). Although the sapwood of American beech may contain up to 4 percent total extractives, the heartwood contains less than 2 percent (**167**). The wood does not contain tannins (**304**), whereas the bark contains only 2.4 percent (**143**). Extrapolating what is known about the rather ordinary extractives of other beeches as well as those of other members of this family plus the low level of extractives present suggests this would not be a rewarding species to examine. The bark is probably rich in the usual suberin components and pentacyclic triterpenes; the inner bark, in the usual simple sugars, fats, and steroids; and the heartwood probably contains a broad array of relatively simple phenolics.

The oaks not only include the largest group of species among the eastern hardwoods, but also constitute more than one-third of the total growing stock of eastern hardwoods. The oak bark formerly employed for internal and external pharmaceutical purposes was that of white oak. Because the bark contains tannins, it has been used as an astrigent and an antiseptic. A bark tea is used in Appalachia to treat burns and sore throat (**187**). Red oak bark has been used to treat dysentery, pulmonary and uterine hemorrhage, and intermittant fever (**226**).

Oaks are well known for the tannins isolated predominantly from the bark (**141,142**). Values for the tannin content of the oaks com-

piled from various sources are given in Table 1. Chestnut oak bark is known to be a satisfactory source of tannin. Blackjack, southern red, and black oak barks apparently have commercial potential (**22**). Although any tannin content above 8 percent suggests commercial potential, various other factors must be considered. The purity of the tannins, the stability of the solutions, the color of the resultant leather, and the reactivity with formaldehyde (for use in adhesives) affect commercial potential. The yield may be considerably increased if extraction is with aqueous sodium sulfite (**95**). This results in part from sulfonation, which increases solubility, and in part from the alkaline degradation of the high-molecular-weight polymeric flavonoids in cork to soluble so-called bark phenolic acids. The mechanism of this degradation has been elegantly elucidated (**311**). Oak is not now a commercial source of tannin in the United States. The last significant domestic production of tannin was from the American chestnut (also in Fagaceae), which has been almost exterminated by chestnut blight.

Oak barks contain *D*-catechin and *D*-gallocatechin, leucopelargonidin, leucocyanidin, leucodelphinidin, gallic acid, and various condensed tannins based on catechin-gallocatechin polymers. The structures of seven different dimers in European oak bark have been elucidated, as more recently has the structure of a catechin trimer (fig. 3) (**10**). Compounds such as these are probably common in all barks containing condensed tannins. In contrast to the condensed tannins that predominate in the bark, hydrolyzable tannins predominate in oak wood. The gallotannins and the ellagitannins isolated from European oak have been extensively studied, and many individual structures determined (**219**). The series of natural products most difficult to study among eastern hardwood extractives is the complex mixture of individual condensed tannins in the bark and the individual hydrolyzable tannins in the wood.

Table 1.—*Tannin content of oak wood and bark*

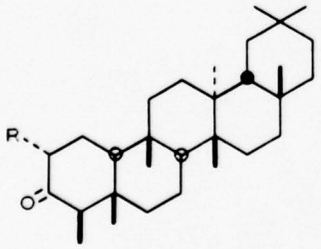
Oak	Percent tannin in	
	Wood[1]	Bark
Black	I	5.6, 8.4, 6-12, 9.2-9.3 (av) 58% pure (**22**)
Blackjack	I	7.7, 8.8-9.2 (av) 64% pure (**22**)
Bluejack	I	7.7, 6.7, (av) 56% pure (**298**)
Bur		4.6, 5.6
Chestnut	3.3	6.25, 7.2-11.1 (**143**), 10.8, 10-12, 8-14, 15.3-16.0 (av) 63% pure (**22**)
Chinkapin	5.2	4.8
Dwarf chinkapin		4.3-10.3
Laurel	I	
Live	6.9	4.0, 10.5
Northern red	1.8, 2.5	4.6, 5.5, 5.4-11.1, 10.9, 5.4-6.4 (av) 53% pure (**22**)
Overcup	0, I	6.5
Pin	0	4.3, 7.6
Post	2.9, 5.4	2.3, 3.1, 7.1-7.4 (av) 59% pure (**22**)
Scarlet	0	6.6, 6-8, 7.7, 7.1-10.6 (av) 58% pure (**22**)
Shingle	1.6	3.8
Shumard	0, 3, 1	4.3, 5.2
Southern red	0, 1.8, 2.0	6.4-8.7, 8.6, 10.0, 9.7-9.9 (av) 67% pure (**22**)
Swamp chestnut	3.1	9.1
Swamp white		14.2
Turkey	2.4	10.5 (av) 59% pure (**298**)
Water	1.0	4.3, 4.6, 7-8
White	2.7	2.3, 6, 6.3, 5.1-7.2, 7, 7.9, 6.1-6.6 (av) 57% pure (**22**)
Willow	0, I	7.3, 10.1

[1] I, Insignificant.

Commercially cork is derived primarily from the bark of the Mediterranean cork oak, *Q. suber*, if grown slowly on dry poor soils. The innumerable studies on this complex of highly polymerized flavonoids and estolide waxes have been reviewed (**69,195**). Cork is, of course, the original source of the pentacyclic triterpenes, friedelin and cerin (fig. 11), and oak barks have been found to contain more than 12 triterpenes with friedelane, glutinane, ursane, oleanane, lupane, and dammarane skeletons. Also common are various soluble waxy components, sterols, and esters such as lignoceryl ferulate.

Black oak inner bark (quercitron bark) contains the simple flavonoids, kaempferol, myricetin, and probably quercetin. An additional flavonoid found in this bark is quercitrin (quercetin 3-*O*-rhamnoside), which was extracted at one time for use as a yellow dye for wool and hair. Quercitrin is also present in willow oak bark. These flavonoids apparently are common minor constituents of oak bark and wood. The European drug Cortex Quercus is the astringent extract of oak inner bark. Oak bark also contains inositols such as quercitol, first found in cork oak. Quercitol is also present in bear, bur, pin, and willow oak barks (**285**). The inhibitory substances in oak bark used for growing orchids have been identified as gallic acid and tannins (**107**).

Northern red oak has been the most thoroughly investigated of the eastern oaks. The relationship between heartwood formation and phenolic extractives has been examined (**235**).



Friedelin (R = H)
Cerin (R = OH)

Figure 11.—Oak triterpenes.

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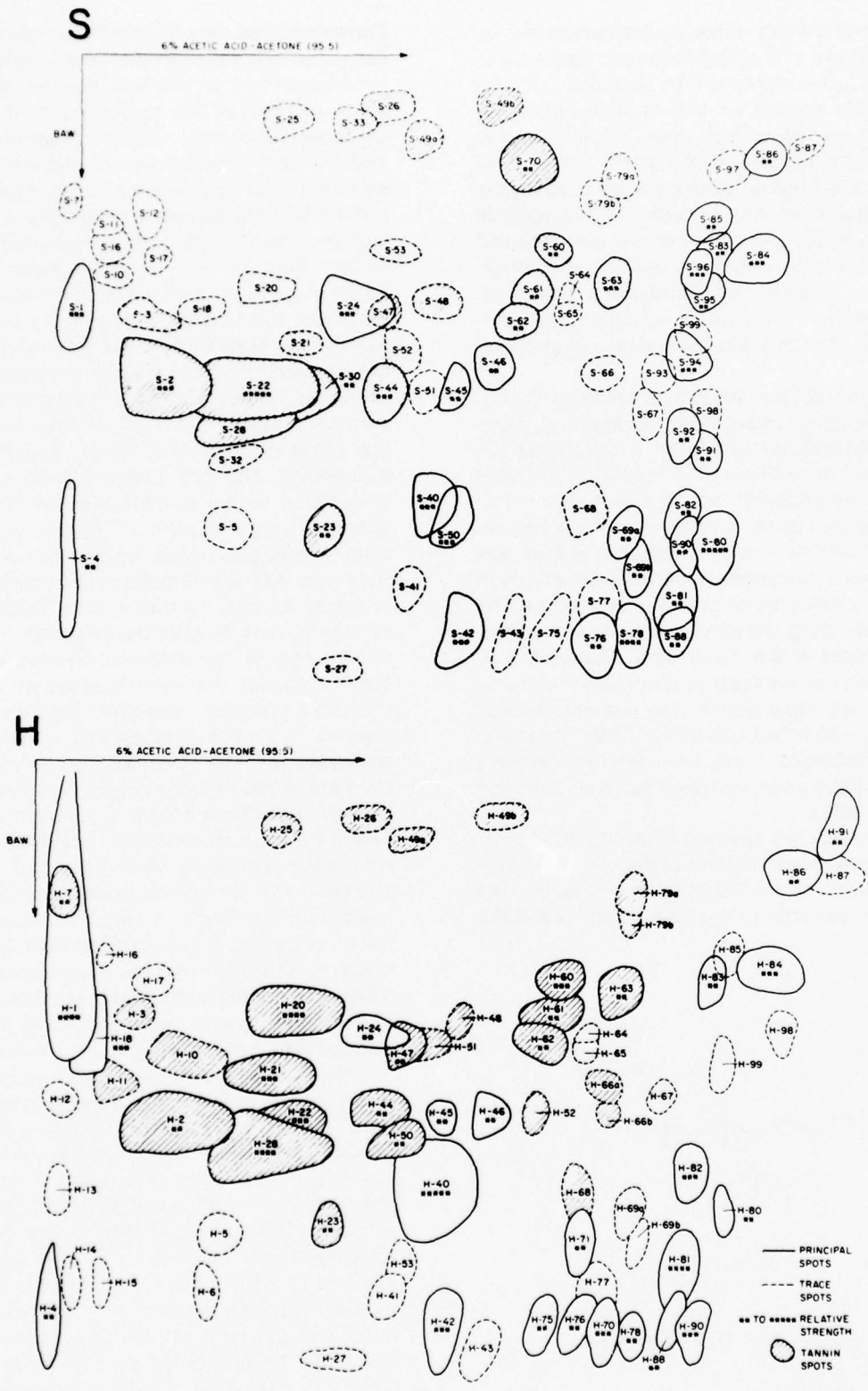
The extractives were shown to contribute to the dimensional stability of the wood (**320**). Figure 12 shows the result of a two-dimensional paper chromatogram of the sapwood and the heartwood acetone-water (95:5) extractives (**313**). The contrast between the components of the sapwood and the heartwood is particularly noteworthy. Hydrolyzable gallotannins such as hamamelitannin [5-galloyl-2-(galloylhydroxymethyl)-ribofuranose] and ellagitannins predominate, and are also the main components in the more polar acetone-water (1:1) and water extracts. In addition to the compounds listed, the sapwood contains leucoanthocyanins and possibly pinoresinol (fig. 2). *m*-Digallic acid apparently is present in both the heartwood and the sapwood, but surprisingly gallocatechin was absent. The most interesting components in addition to the tannins are the coumarin, scopoletin (fig. 13) and the lignans, syringaresinol (see Magnoliacea), lyoniresinol, and lyoniside (fig. 14). 2,6-Dimethoxybenzoquinone is probably formed by free radical oxidation of syringyllignans. Neither flavonols nor their glycosides could be detected. However, color tests suggested that several esters of hydroxycinnamic, vanillic, and syringic acids were present as well as glucosides, arabinosides, and xylosides. The inner bark was very different from either the sapwood or the heartwood. Although no gallic or ellagic acids were present, tannin esters, catechin, flavonoids, and lyoniside were tentatively identified. The general chemistry of this bark has been studied (**55**), as has that of chestnut oak (**34**). Tartaric acid has been suggested as the cause of toxicity of red, black, northern pin, and bur oak heartwood extracts against oak wilt fungus (**32**). A few cases of sensitivity to oak wood dust have been reported (**386**), but the allergen is unknown.

Northern red oak is a valuable commercial wood, but its value is often degraded by a variety of stains, most of which are due to the phenolics in the wood. Thus, contact of the wet wood with sources of iron such as concrete, steel wool, and other abrasives can lead to formation of blue-black iron tannates (**364**). Fortunately, these are usually readily bleached with oxalic acid. Other stains develop from air oxidation of the phenolics in the wet wood, perhaps with the help of enzymes. These stains often can be prevented by high-temperature steaming. Extraordinarily high concentrations


S
6% ACETIC ACID - ACETONE (95:5)
BAW
S-1
S-2
S-3
S-4
S-5
S-6
S-7
S-10
S-11
S-12
S-16
S-17
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H
6% ACETIC ACID - ACETONE (95:5)
BAW
H-1
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H-3
H-5
H-6
H-7
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H-76
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H-78
H-79a
H-79b
H-80
H-81
H-82
H-83
H-84
H-85
H-86
H-87
H-88
H-90
H-91
H-98
H-99
PRINCIPAL SPOTS
TRACE SPOTS
•• TO ••••• RELATIVE STRENGTH
TANNIN SPOTS

Spot No.[1]	Compound	Isolated from heartwood, H, and sapwood, S
1	Ellagic acid	H and S
20	Hamamelitannin	H and S
40	Gallic acid	H and S
42	Sinapaldehyde	H and S
43	Coniferaldehyde	H and S
50	Catechin	S
75	Scopoletin	H
76	Syringaldehyde	H and S
77	Propioguaiacone (propiovanillone)	H
78	Vanillin	H and S
80	Lyoniside	H and S
90	*rac*-Lyoniresinol	H
*	2,6-Dimethoxybenzoquinone	H
*	Resorcinol	H
*	Syringaresinol	H and S
*	*p*-Hydroxybenzaldehyde	S

[1] *, Location on chromatograms unknown; probably masked under other spots.

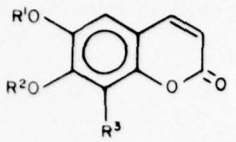
Figure 12.—Two-dimensional paper chromatography of acetone-water extractives of *Quercus rubra*. Top, sapwood (S); bottom, heartwood (H) M 146 192

of heartwood phenols can cause other stains around defects and injuries in the wood. Still other stains result from microbiological attack or fall into the category of "mineral stains."

A full understanding of the phenomena of stain development in oak wood will be attainable only when information on the chemistry of oak heartwood extractives has progressed considerably. However, catechin and gallocatechin moieties are undoubtedly involved because they are relatively easily oxidized to deeply colored quinones. The quinones can be bleached by reducing agents to the less colored hydroquinones or oxidatively bleached by cleavage of the quinoid ring. Because these bleaching agents are not completely successful in decolorizing stained oak wood, other factors must be involved such as different chemical chromophores or quinoid groups protected as insoluble complexes.

The general chemistry of white oak bark has been investigated (**55**). The heartwood was found to contain scopoletin (**14**); gallic and ellagic acids; gallotannins and ellagitannins; sitosterol; stigmasterol; campesterol; stigmastanol; lignoceryl ferulate and related esters; triglycerides of linoleic, oleic and palmitic acids; and coniferaldehyde (**57**). Vanillin, syringaldehyde, and sinapaldehyde had been found earlier in the wood (**36**). Coniferaldehyde and sinapaldehyde have also been reported in post oak wood; these simple phenolics are probably very common (**36**). The corresponding ferulic and sinapic acids and salicylic and gentisic acids as well as pyrogallol, *p*-hydroxybenzaldehyde, eugenol, and *D*-mannitol have been reported in various foreign oaks. Many of the typical bark components have also been reported in the wood.

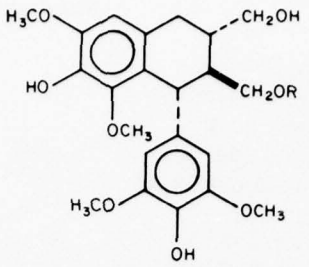
White oak is also a general commercial name for a group of oaks that include *Quercus alba, Q. bicolor, Q. lyrata, Q. macrocarpa, Q. michauxii, Q. muehlenbergii, Q. prinus, Q. stellata,* and *Q. virginiana*. In general the vessels of these oaks are plugged with tyloses making the wood difficult to treat with preservatives. However, the tyloses also make white oaks watertight, thus ideal for liquor and wine barrels. Eugenol and two *Quercus* lactones (diastereoisomers of 3-methyl-4-octanolide) have been found in an unidentified member of this white oak group (**217**). The lactones were also found in aged whiskey and are responsible for the woody odor of whiskey. Vanillin, syringaldehyde, and related phenolics derived from lignin also are important in the desirable odor contributed by oak barrels to whiskey and wine (**324**). Old (extractive-rich) oak bonds relatively poorly



	R^1	R^2	R^3
Esculetin	H	H	H
Esculin	Glucose	H	H
Scopoletin	CH_3	H	H
Scopolin	CH_3	Glucose	H
Fraxetin	CH_3	H	OH
Fraxin	CH_3	H	O-Glucose

Figure 13.—Some natural coumarins.

M 146 170



Lyoniresinol (R = H)

Lyoniside (R = xyloside)

Lyoniresinol 2α-O-rhamnoside (R = rhamnoside)

Figure 14.—Oak lignans.

M 146 169

with phenol-formaldehyde adhesives. Water, or even more efficient, sodium carbonate extraction, has removed interfering materials. Since the addition of extra sodium hydroxide improves bonding, the deleterious effect may be predominately caused by acidity of the extractives (**297**).

Although relatively little information has been published on eastern oaks, if what is known is combined with extensive studies on foreign oaks, a pattern does indeed emerge.

HAMAMELIDACEAE

Liquidambar styraciflua L., sweetgum

Sweetgum is the most common hardwood species in the Southeast. The comparative phenology, physiology, and biochemistry of populations of this species have been investigated (**377**). Sweetgum is the source of an exudate known locally as sweet gum and commercially as American storax (styrax); it sells for just under $1.50 per pound. Although current production is small ($150,000/yr, Clark Co., Ala.), this was a significant industry during and after World War I (**117,211**). American storax, essentially identical to Oriental storax from *Liquidambar orientalis* in Turkey, has been used in perfumery, chewing gum, incense, tobacco, adhesives, pharmaceutical preparations as well as in folk medicine (**187**).

Storax is obtained by collecting the exudate from cuts made through the bark. Yields are up to 1 pound per tree per year, most of which is collected during the mid-June to mid-October growing period. Very little storax is stored in normal wood or bark. Apparently storax is formed in traumatic resin ducts near a wound. The most recent references (**72,329**) and a number of articles in the popular press have contained little scientific data. Surprisingly, no work has been reported on the chemistry of American storax since 1921, when even earlier work reporting the presence of cinnamyl cinnamate and related esters was confirmed (**125**). American storax is a true balsam. The natural products chemistry of this material might be worthy of further study. Oriental storax has been found to contain oleanolic, 3-epi-oleanolic (first time in nature), and oleanonic acids (**163**).

Sweetgum heartwood is difficult to glue, has intermediate decay resistance, and is relatively impermeable. Although in the early part of this century an ether extract of the heartwood was reported to cause dermatitis (**307,386**), this does not seem to be a problem with this species. The quantities of extractives in the wood

apparently are highly variable (**167,368**). The ether extractives of the wood contained the usual fatty acids and esters as well as β-sitosterol (**368**).

Sweetgum sapwood has been extensively studied and found to contain a large amount of vanillic and syringic acids plus 3,4-dihydroxyphenyl, galloyl, and related hydrolyzable tannins. Lesser components included vanillin, syringaldehyde, coniferaldehyde, sinapaldehyde, *m*-coumaraldehyde, gallic acid, dihydroquercetin, glucose, fructose, and soluble lignin fragments (**180,332**). Ellagic acid plus related methyl ethers and glycosides are also indicated (**332**). Polymeric phenolic glycosides predominate and apparently in the heartwood are heavily polymerized and oxidized to colored nontannin polymers. The heartwood has recently been shown to contain quercetin (**332**).

The general chemistry of the bark has been studied (**55**). Successive extractions with benzene, 95 percent ethanol, hot water, and 1 percent sodium hydroxide dissolved 1.5 percent, 17.7 percent, 7.4 percent, and 21.3 percent, respectively. In contrast to the wood with very little tannin, the bark has been reported to contain 7.6 percent tannin. Hot-water extracts of the bark produce large amounts of precipitate with gelatin or with formaldehyde-hydrochloric acid (**55**). Hegnauer reported Plouvier (**143**) found that the bark contains 0.1 percent shikimic acid, and that both the wood and bark contain the monoterpene iridioside, monotropein (fig. 9) (**215**). The phenolics in the bark apparently are closely related to those in the sapwood and include large amounts of gallic and ellagic acids plus 3,3′-di-*O*-methylellagic acid, other methylated ellagic acids, related glycosides, and ellagitannins and gallotannins (**332**). Although there are many similarities between the bark and the sapwood extractives, distributions of the individual components are different.

The tannin-rich leaves of the sweetgum tree are still used today as a folk remedy to relieve sore throat and diarrhea. The dry, spiny mature fruit is burned, and the ash applied to sores and burns (**226**).

HIPPOCASTANACEAE

Aesculus glabra Willd., Ohio buckeye
A. octandra Marsh., yellow buckeye
A. parviflora Walt., bottlebrush buckeye
A. pavia L., red buckeye
A. sylvatica Bartr., painted buckeye

Almost nothing is known about the extractives of eastern buckeyes. The wood is of limited commercial significance, has essentially no color, odor, or taste, and is of low durability. These facts suggest that study of the extractives of the wood and the bark of this genus would not be particularly rewarding, although the barks of some other *Aesculus* species have had limited pharmaceutical use. Yellow and red buckeye woods have been reported to contain no tannin, although yellow buckeye bark contains 28 percent and red buckeye bark, an insignificant amount (**304**).

The general chemistry of the Hippocastanaceae has been summarized (**143**). Most reports on this genus deal with the European horse chestnut, *Aesculus hippocastanum*, the chemistry of which has been reviewed (**154**).

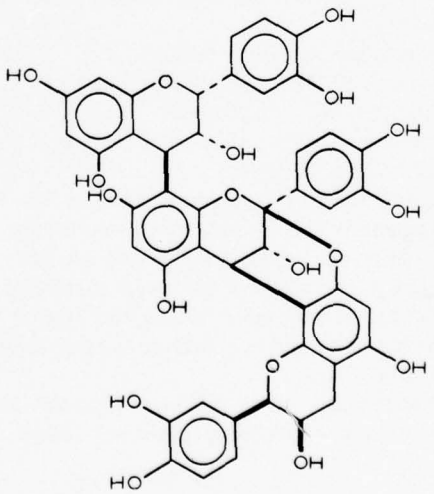


Figure 15.—Proanthocyanidin (-)-epicatechin-A2. M 146 168

Aescin, the triterpene glycoside saponin of horse chestnut seeds, also occurs in the bark. Therefore, triterpene saponins may also be present in eastern U.S. buckeye barks, although no more than traces were detected in bottlebrush buckeye bark. Coumarins are found in the wood, and especially in the bark of this genus. They account for the fluorescence of the aqueous bark extracts, although bottlebrush buckeye bark lacks this fluorescence. Yellow buckeye bark contains a polar coumarin of unknown structure (**109**). All of the coumarins esculetin, esculin, scopoletin, scopolin, fraxetin, and fraxin (fig. 13), have been found in the barks of *Aesculus* species.

Horse chestnut husks, and to a lesser extent the bark, contain simple flavonoids and condensed tannins. The structures of several dimeric and trimeric condensed tannins [*e.g.*, proanthocyanidin (-)-epicatechin-A2 (fig. 15)] have been elucidated (**168**).

Twigs of red buckeye contain traces of quebrachitol that apparently is widespread in this genus. Allantoin and allantoic acid apparently are common sap constituents analogous to the Aceraceae, which has many chemical similarities to this family.

JUGLANDACEAE

Carya aquatica (Michx. f.) Nutt., water hickory
C. cordiformis (Wangenh.) K. Koch, bitternut hickory
C. floridana Sarg., scrub hickory
C. glabra (Mill.) Sweet, pignut hickory
C. illinoensis (Wangenh.) K. Koch, pecan
C. laciniosa (Michx. f.) Loud., shellbark hickory
C. myristicaeformis (Michx. f.) Nutt., nutmeg hickory
C. ovata (Mill.) K. Koch, shagbark hickory
C. pallida (Ashe) Engl. and Graebn., sand hickory
C. texana Buckl., black hickory
C. tomentosa Nutt., mockernut hickory
Juglans cinerea L., butternut
J. microcarpa Berlandier, little walnut
J. nigra L., black walnut

Extractives of *Carya* species have had little investigation. The chemistry of this family has been reviewed (**103,143**); there is an early report on the chemistry of hickory inclusive of pecan (**223**). An extensive review has been made of the chemistry and the biochemistry of walnut trees (**81**).

Tannin content of hickory and pecan barks are given in the following tabulation (**304**).

Species	*Percent*
Hickory:	
Bitternut	7.8
Mockernut	Insignificant, 5.0-9.8
Pignut	7.6-10.0
Sand	6.7
Shagbark	0
Shellbark	4.7, 6.7
Pecan	5.7

All woods were reported as not containing tannin, although young whole pecan plants contain 11.5 percent tannin (**127**). It is intriguing that in a survey of the general chemistry of pecan bark, the benzene-extracted bark had an extraordinarily large amount of ethanol extract, 18.1 percent (**55**). Pecan bark contains azaleatin (quercetin 5-methyl ether); the new flavonol, caryatin (quercetin 3,5-dimethyl ether) (**308**), and juglone.

The occurrence of juglone apparently is characteristic of the barks (especially the husks) of this family, and probably explains both the use of pecan bark by Mexican Indians to stupefy fish (**280**) and of the hickory bark to repell insects (see Ulmaceae). Juglone is also a purgative (butternut and black walnut bark have been used to make a laxative (**187**)). Juglone can cause blackening, blistering, and peeling of the skin; is a tranquilizer and sedative (**28,374**); has antitumor activity (**29**); is fungitoxic and an antibiotic; and is allelopathic (**330**). Unquestionably, this is a significant compound.

Juglone or a precursor is probably the active substance responsible for dermatitis from the nutshells, roots, and bark of black walnut. Juglone has not been reported in the wood and no cases of skin or mucosal irritation by the wood have been found (**386**). Juglone is formed

in a tree from dihydrojuglone-4-glucoside *via* dihydrojuglone (fig. 16) and readily polymerizes to brown-black pigments. Apparently it is part of the wound response mechanism, although it is not reported in the wood.

Black walnut is the most valuable eastern hardwood, is highly decay resistant, and is prized for its dark color. The influence of light on the color of the wood has been studied (**220**). The American Indians used the roots as a source of a black dye and the leaves, husks, and nuts as the source of a brown dye. The heartwood contains only about 10 percent total extractives (**70**), the function of which has been discussed (**235**). The bark has been found to contain the flavonoids myricetin, myricitrin (myricetin-3-rhamnoside), sakuranetin and sakurenin (sakuranetin-5-glucoside); the chalcone glucoside neosakuranin; and juglone and dihydrojuglone-4-glucoside (**126**). Neither the wood nor the bark contains tannins. However, the wood contains appreciable amounts of gallic acid as well as ellagic acid, glucose, and a dark violet polymer (**126,316**). The oxidation and the condensation of gallic acid and its derivatives into soluble polymers is a well-known phenomenon. The compounds responsible for the durability of the heartwood have not yet been identified. The bark components apparently are absent from the wood. Ellagic acid is a sedative and tranquilizer (**28**) and has antitumor activity (**29**). In one case a dog chewed on a black walnut statue and fell into a deep sleep, much to the distress of the owner. After 48 hours, the dog awoke with no apparent ill effects. Both black walnut and butternut woods contain coniferaldehyde and sinapaldehyde (**36**).

Butternut wood also contains large amounts of gallic acid, ellagic acid, and two gallotannin-like compounds (**316**). However, the wood is reported to contain only insignificant amounts of tannin; the bark contains 7.9 percent (**304**). The heartwood is nondurable, without odor or taste, and darkens on exposure to light. It is rich in gallic acid and also contains ellagic acid, proanthocyanidins, and gallotannin-like compounds. β-Sitosterol and gallic acid were found in butternut bark (**316**). A patent has been issued for an antibiotic isolated from the root bark for use as a food preservative (**170**). The American Indians used the husks for a brown dye.

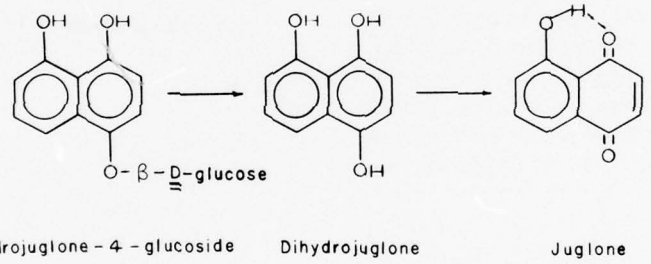


Figure 16.—Formation of juglone.

M 146 167

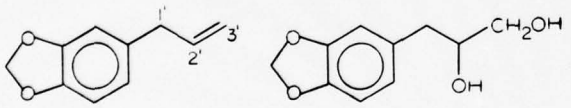
LAURACEAE

Sassafras albidum (Nutt.) Nees, sassafras

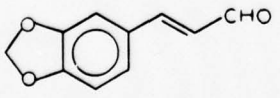
This family is most attractive chemotaxonomically because of the number of unusual extractives. These extractives are discussed in a recent excellent review (**122**) as well as in earlier reviews (**103,143**). The only eastern member of this family, sassafras, reportedly contains 8.5 percent tannin in the bark, but no tannin in the wood (**304**). A water-soluble polysaccharide of the twigs is pharmaceutically active (**333**). Researchers of the Forest Service at the Southern Forest Experiment Station are investigating termiticidal components in sassafras.

The literature back to the early 19th century contains numerous references to sassafrass, mostly because of the pharmaceutical use of the oil of the root bark that contains safrole (80 pct of the oil) (fig. 17). The volatile constituents from the root bark oil also include α-pinene, camphor, α- and β-phellandrene, *l*-menthone, thujone, anethole, copaene, caryophyllene, eugenol, 5-methoxyeugenol, elemicin, coniferaldehyde, myristicin, asaron, piperonylacrolein, syringaldehyde, and apiol (**318**). The root bark contains the aporphine alkaloids boldine, norboldine, and isoboldine and the 1-benzyl-1,2,3,4-tetrahydroisoquinoline alkaloids norcinnamolaurine, cinnamolaurine, and reticuline (**63**) (fig. 18). The methylene chloride extract of sassafras root (wood) contained the lignans *D*-sesamin and desmethoxyashantin (fig. 19), as well as β-sitosterol, piperonylacrolein, and (+)-safrolglycol (**151**).

Sassafras oil, one of the oldest and best known American essential oils and one of New England's first plant-derived exports, is obtained in 6 to 9 percent yield by steam distillation. In colonial days, it was used for a tea, a sudorific for colds and a spring tonic to "get the winter sluggishness out of the blood." The tea has been used in folk medicine as a diaphoretic, stimulant, diuretic, carminative, and to treat bronchitis (**187**). The most important 20th-century uses of the oil have been in flavoring, especially sarsaparilla and root beer. Safrole was for many years the chief flavoring ingredient in root beer. If root beer no longer has the



Safrole Safrolglycol



Piperonylacrolein

Figure 17.—Safrole and related compounds from *Sassafras albidum*.

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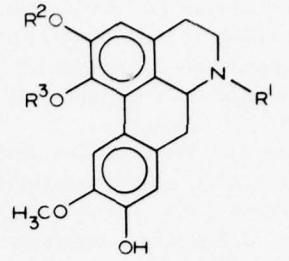
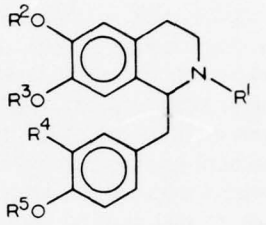


	R^1	R^2	R^3
Boldine	CH_3	H	CH_3
Norboldine	H	H	CH_3
Isoboldine	CH_3	CH_3	H



	R^1	R^2	R^3	R^4	R^5
Norcinnamolaurine	H	$-CH_2-$		H	H
Cinnamolaurine	CH_3	$-CH_2-$		H	H
Reticuline	CH_3	CH_3	H	OH	CH_3

Figure 18.—Alkaloids from *Sassafras albidum*.

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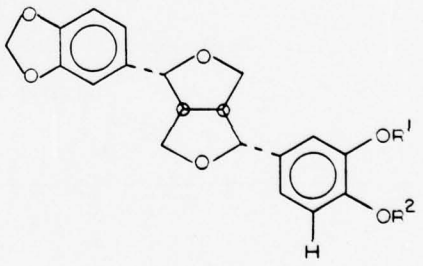

	R^1	R^2
(+)–D–sesamin	$-CH_2-$	
Desmethoxyaschantin	CH_3	CH_3

Figure 19.—Lignans from *Sassafras albidum*.

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kick it had, it may be because the Food and Drug Administration in 1960 banned the use of safrole. The ban resulted from long-term, rat-feeding studies that showed safrole could cause liver cancer. In 1976 FDA banned sassafras bark intended primarily as a vehicle for sassafras tea. However, safrole-free sassafras bark (and leaf) extracts can still be used.

The carcinogenicity of safrole is due to its metabolic conversion to 1′-hydroxysafrole, a proximate carcinogen (**37,38**). Further activation for carcinogenesis and mutagenesis can occur by either esterification of the 1′-hydroxy group or by epoxidation of the 2′,3′-double bond (**379,380**).

LEGUMINOSAE

Gleditsia aquatica Marsh., waterlocust
G. triacanthos L., honeylocust
Robinia kelseyi Hutchins., Kelsey locust
R. pseudoacacia L., black locust
R. viscosa Vent., clammy locust

In recent literature (**130,132**), the chemistry of the Leguminosae is discussed in detail. Honeylocust is the only eastern *Gleditsia* species investigated; this has involved mostly leaves and fruit. Indeed, this tree is named after the sweet succulent pulp found in the seed pod. D-Fustin [(2*R*,3*R*)-3,3′,4′,7-tetrahydroxyflavanone] and fisetin (3,3′,4′,7-tetrahydroxyflavone) are the major extractives in the heartwood (**54**). Roy and Prudy, University of Toronto, have told us that some 20 minor phenolics are detectable by thin-layer chromatography including vanillin, triacontanyl ferulate and related ester, and other flavonoids.

Black locust is the only eastern true locust that has had wood and bark extractive content investigated. Although tannins have been reported absent in both the wood and the bark of honeylocust and black locust (**304**), black locust wood has been reported to contain 1.5 percent tannin and the bark, 1.6 percent (**169**). These are apparently condensed tannins (polyleucorobinetinidins) similar to those in wattle (**130,300**). The flavonoids have been thoroughly investigated (**188,300,301**). Essentially the same flavonoids were detected in the heartwood and the sapwood, but the heartwood contained considerably larger quantities. The flavonoids found include the chalcones robtein (2′,3,4,4′,5-pentahydroxychalcone), butein (2′,3,4,4′-tetrahydroxychalcone), and 2′,4,4′-trihydroxychalcone; the flavanones *L*-robtin [(2*S*)-3′,4′,5′,7-tetrahydroxyflavanone], *L*-butin [(2*S*)-3′,4′,7-trihydroxyflavanone] and liquiritigenin [(2*S*)-4′,7-dihydroxyflavanone]; the flavanonols *D*-dihydrorobinetin [(2*R*, 3*R*)-3,3′,4′,5′,7-pentahydroxyflavanone], which is the major component (4-5 pct) found in the heartwood, and *D*-fustin; the flavonols robinetin (3,3′,4′,5′,7-pentahydroxyflavone) and fisetin; the flavan-3-ol *L*-robinetinidol (3,3′,4′,5′,7-pentahydroxy-2,3-*trans*-flavan); and the flavan-3,4-diols leucorobinetinidin and *D*-3,3′,4,4′,7-pentahydroxy-2,3-*trans*-3,4-*cis*-flavan. In addition the heartwood contained β-resorcylic acid and methyl β-resorcylate (**188**).

The compounds responsible for the luminescence and in part for the very high decay resistance of this wood are extractable with ethanol (**209**). Dihydrorobinetin inhibits growth of fungi, thus must contribute to the wood's durability (**108**). However, the fungicidal phytoalexins common in this family are considered to be pterocarpans such as have been reported in black locust (**147**). The flavonoids also have been implicated for causing an eczema from contact with this wood (**386**). Although discolored sapwood near wounds resembles heartwood, this wood differs chemically from heartwood (**135**). Nucleic acids and their components are present in the sievetube sap (**389**), and the wood and the leaves contain the antibiotic, *trans*-2-hexen-1-al.

Black locust bark has been the subject of numerous studies. Early work has shown the presence of stigmasterol, choline, syringenin, starch, and simple sugars, and related metabolites. However, most interest has centered on the high-protein content of the bark. In 1890 a phytohaemagglutin, robin, was isolated from the bark (**132**). The bark contains up to 4.5 percent of water-soluble protein that can be readily isolated due to the low amount of tannin in the bark. These proteins vary seasonally and are implicated in frost hardiness (**100,323**). The bark phospholipids also vary seasonally; phospholipids have been detected in the wood by staining (**73**).

MAGNOLIACEAE

Liriodendron tulipifera L., yellow-poplar
Magnolia acuminata L., cucumbertree
M. ashei Weatherby, Ashe magnolia
M. fraseri Walt., Fraser magnolia
M. grandiflora L., southern magnolia
M. macrophylla Michx., bigleaf magnolia
M. pyramidata Bartr., pyramid magnolia
M. virginiana L., sweetbay

The chemistry of the Magnoliaceae has been reviewed (**103,143**). The pale color of yellow-poplar heartwood, the low durability, the low extractives content, and the fact that yellow-poplar containers do not impart taste or odor to foodstuffs suggest the extractives may not be of interest. This is not true.

Yellow-poplar is the most toxic of all of the woods reviewed in this paper; it causes severe dermatitis on contact with either the green or the wet wood, and is even more severe, after contact with the bark (**314,386**). Fresh bark should probably not be used as a mulch or a soil conditioner because the bark appreciably retards the growth of garden pea seedlings (**11**) and is toxic to seed germination according to E. G. Scott, West Virginia University, Morgantown.

The extractives from wood, bark, and leaves of yellow-poplar have been investigated. They include alkaloids (fig. 20A, B), sesquiterpenes (fig. 21), and lignans (fig. 22). No significant tannin was found in either bark or wood (**304**).

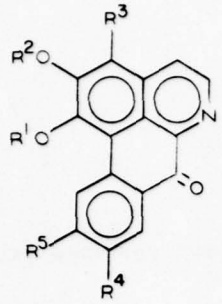
Yellow-poplar is a rich source of aporphine alkaloids. The wood, bark, cortex, leaves, and seeds contain alkaloids (**357,358,395**). The alkaloids in the bark probably explain why bark extracts were used medicinally for treating malaria during the War of Independence. The alkaloid glaucine is used as an antitussive in the Soviet Union. Recent investigations have shown that the heartwood alkaloid fraction has antimicrobial activity (**162**).

An extensive investigation of the alkaloids in yellow-poplar wood was conducted by Chen and others (**58,60,62,315**), who studied sapwood, discolored sapwood formed after injury, heartwood, and discolored heartwood infested by micro-organisms. Glaucine, the only alkaloid detected in sapwood, was the major alkaloid in the heartwood and the discolored sapwood. Other alkaloids in the heartwood and the discolored sapwood included dehydroglaucine, norglaucine, liriodenine [identical with spermatheridine, oxoushinsunsine, and michéline B (**344**)], *O*-methylatheroline (oxoglaucine), nuciferine, nornuciferine, *N*-acetylnornuciferine, norushinsunsine, asimilobine, and *N*-acetylasimilobine. At least two unidentified 1-benzyltetrahydroisoquinoline type alkaloids were found in the heartwood. Except for the oxoaporphine pigments liriodendronine and corunnine, the compounds isolated from the discolored heartwood were similar to those found in the normal heartwood. In contrast the discolored sapwood contained not only liriodendronine, corunnine, and the compounds mentioned, but in addition, thaliporphine, predicentrine, *N*-methyllaurotetanine, lirioferine, and liriotulipiferine that were not detected in either normal heartwood or discolored heartwood infested by micro-organisms. Thus the formation of these phenolic aporphines in the discolored sapwood probably did not result from microbial metabolism of glaucine, although the microbial *N*- and *O*-dealkylation of glaucine has been reported (**74**).

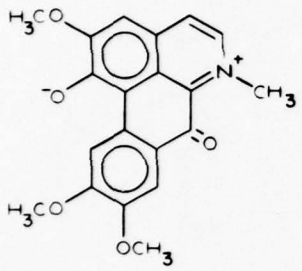
Production of aporphine alkaloids is stimulated by injury—apparently to inhibit the growth of invading micro-organisms. Thus glaucine, *N*-methyllaurotetanine, lirioferine, and liriotulipiferine have been found to have antimicrobial activity against fungi but not bacteria inhabiting the wood of yellow-poplar (**158**). In addition, dehydroglaucine and liriodenine, a known cytotoxin (**371**), have been identified as antimicrobial agents (**61,162**).

Liriodenine and *O*-methylatheroline, which can be formed by auto-oxidation of glaucine, are responsible for the yellowish-green color of normal heartwood of yellow-poplar (**43,60,68**). Liriodendronine and corunnine are responsible in part for the discoloration of injured wood (**62,315**), which ranges from yellow-green to pink, red, purple, blue, brown, and even black. In addition, other investigations showed the presence of *N*-acetylnornantenine (**161**), 3-methoxy-*N*-acetylnornantenine (**161**), ushinsunsine (michelabine) (**162**), *N*-acetylanonaine (**160**), and tuliferoline (**160**).

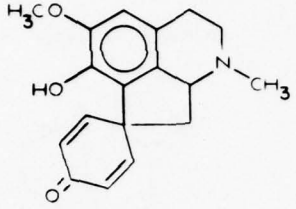
Extensive Russian investigations recently have been on the alkaloids in yellow-poplar



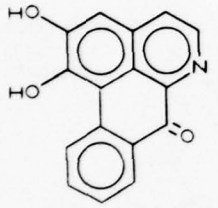
	R^1	R^2	R^3	R^4	R^5
Liriodenine	- CH_2 -		H	H	H
O-methylatheroline	CH_3	CH_3	H	OCH_3	OCH_3
Liridine	CH_3	CH_3	OCH_3	H	H
Lysicamine	CH_3	CH_3	H	H	H
Langinosine	- CH_2 -		H	OCH_3	H

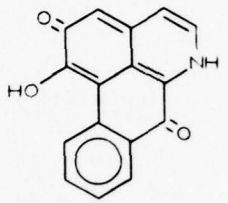


Corunnine

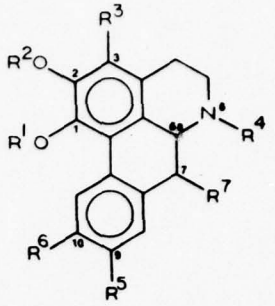


N-methylcrotsparine





Liriodendronine

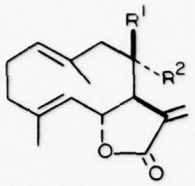


	R^1	R^2	R^3	R^4	R^5	R^6	R^7
(+)-Glaucine	CH_3	CH_3	H	CH_3	OCH_3	OCH_3	H
(+)-Norglaucine	CH_3	CH_3	H	H	OCH_3	OCH_3	H
(-)-Nuciferine	CH_3	CH_3	H	CH_3	H	H	H
(-)-Nornuciferine	CH_3	CH_3	H	H	H	H	H
(-)-*N*-acetylnornuciferine	CH_3	CH_3	H	Ac	H	H	H
(-)-Ushinsunsine	- CH_2 -		H	CH_3	H	H	OH
(-)-Norushinsunsine	- CH_2 -		H	H	H	H	OH
(-)-Asimilobine	CH_3	H	H	H	H	H	H
(-)-*N*-acetylasimilobine	CH_3	H	H	Ac	H	H	H
(+)-Thaliporphine	H	CH_3	H	CH_3	OCH_3	OCH_3	H
(+)-Predicentrine	CH_3	H	H	CH_3	OCH_3	OCH_3	H
(+)-Lirioferine	CH_3	CH_3	H	CH_3	OCH_3	OH	H
(+)-*N*-methyllaurotetanine	CH_3	CH_3	H	CH_3	OH	OCH_3	H
(+)-Liriotulipiferine	CH_3	OH	H	CH_3	OCH_3	OH	H
(+)-*N*-acetylnornantenine	CH_3	CH_3	H	Ac	$-CH_2$ -		H
(+)-3-Methoxy-*N*-acetylnornantenine	CH_3	CH_3	OCH_3	Ac	$-CH_2$ -		H
(-)-*N*-acetylanonaine	$-CH_2$ -		H	Ac	H	H	H
(-)-Tuliferoline	CH_3	CH_3	OCH_3	Ac	H	H	H
(+)-Lirinidine	H	CH_3	H	CH_3	H	H	H
(+)-Caaverine	H	CH_3	H	H	H	H	H
(+)-Isolaureline	- CH_2 -		H	CH_3	OCH_3	H	H
(+)-Isoroemerine	- CH_2 -		H	CH_3	H	H	H
(-)-Liridinine[1/]	CH_3	H	OCH_3	CH_3	H	H	H
(-)-Lirinine[1/]	H	CH_3	OCH_3	CH_3	H	H	H
(-)-Lirinine *O*-methyl ether	CH_3	CH_3	OCH_3	CH_3	H	H	H
(-)-Norlirinine *O*-methyl ether	CH_3	CH_3	OCH_3	H	H	H	H

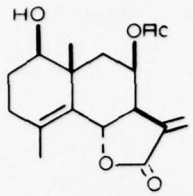
[1/] Structure for these compounds are interchangeable.

Figure 20.—Yellow-poplar alkaloids.

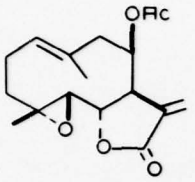
M 146 177
M 146 176



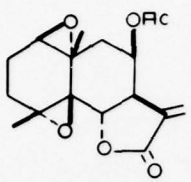
	R^1	R^2
Costunolide	H	H
Tulipinolide	H	OAc
Epitulipinolide	OAc	H



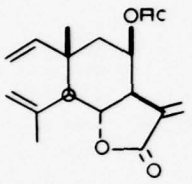
γ-Liriodenolide



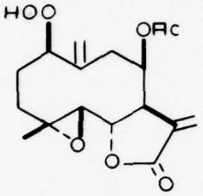
Lipiferolide



Epitulipinolide diepoxide



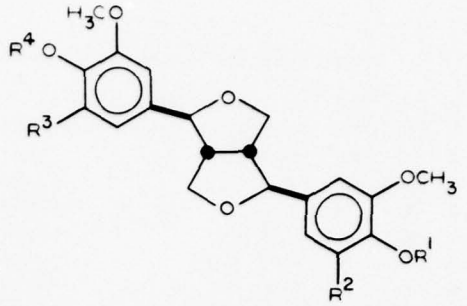
Epitulipdienolide



Peroxyferolide

Figure 21.—Yellow-popular sesquiterpenes.

M 146 178

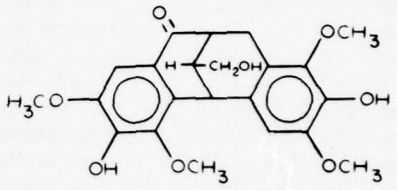


(+)-Syringaresinol ($R^1 = R^4 = H$, $R^2 = R^3 = OCH_3$)

(+)-Syringaresinol dimethyl ether ($R^1 = R^4 = CH_3$, $R^2 = R^3 = OCH_3$)

Liriodendrin ($R^1 = R^4 = \beta$-D-glucose, $R^2 = R^3 = OCH_3$)

(+)-Medioresinol ($R^1 = R^3 = R^4 = H$, $R^2 = OCH_3$)



Lirionol

Figure 22.—Yellow-poplar lignans.

M 146 179

leaves with limited work on the wood and the bark (**1,2,390-395**). The compounds that were isolated included liridine, caaverine, lirinidine (*N*-methylcaaverine), lirinine, lirinine *O*-methyl ether, lirinine *N*-oxide, isolaureline, lysicamine, isoroemerine, nornuciferine, languinosine, liridinine, and *N*-methylcrotsparine.

Lirinine and lirinine *O*-methyl ether were identified as 1-hydroxy-2, 9-dimethoxyaporphine and 1,2,9-trimethoxyaporphine, respectively, by Yunusov and others on the basis of spectroscopic analysis (**392**). However, the nuclear magnetic resonance (NMR) spectrum of lirinine is incompatible with the proposed structure (**58**). Of the two methoxyl resonances, the one at higher field (τ 6.37) corresponded to a C-1 methoxyl resonance (**30**). The aromatic region of the spectrum integrated for four hydrogens that constituted an ABCX spin-system corresponding to four adjacent aromatic hydrogens. An H-3 resonance around τ 3.50 was absent. In addition, the spectrum was almost identical to that of liridinine (**2**). Therefore, lirinine and liridinine should be isomers, *i.e.*, 3-hydroxy-1,2-dimethoxyaporphine and 2-hydroxy-1,3-dimethoxyaporphine, respectively, or *vice versa*. Lirinine *O*-methyl ether should then be 1,2,3-trimethoxyaporphine. Although the structure 2-hydroxy-1,3-dimethoxyaporphine was assigned to liridinine by the Russian authors on the basis of the NMR spectrum, C.-L. Chen, North Carolina University, Raleigh, believes that further research is required to establish the structures of lirinine and liridinine.

The isolation of the proaporphine alkaloid *N*-methylcrotsparine and the benzyltetrahydroisoquinoline alkaloids mentioned are interesting because compounds of this type are postulated as intermediates in the biosynthesis of aporphine alkaloids from phenylalanine and tyrosine (**17,122**).

The yellow-poplar bark (root) extractives contain a series of sesquiterpene lactones: Costunolide, tulipinolide, epitulipinolide, epitulipdienolide, and γ-liriodenolide (**83,84,87, 88,92**). The related compounds lipiferolide, epitulipinolide diepoxide, and peroxyferolide (the first naturally occurring germacranolide hydroperoxide) have been observed in the leaves (**90,91**). Most of these compounds are cytotoxic and inhibit feeding by gypsy moth larvae (*Porthetria dispar* L.) (**92**). Interestingly, Doskotch finds that the antifeeding activity is greater for mixtures of these compounds than for the individual compounds. In addition to the noraporphine alkaloids and sesquiterpene lactones, yellow-poplar bark extracts also contain large amounts of simple sugars, some phenolics and coloring materials, a pleasant smelling essential oil, esculetin dimethyl ether (fig. 13) (**358**), liriodendritol (mesoinositol-1,4-dimethyl ether) and methyl syringate (**58**). The amount of total alkaloids in the extract is insignificant although trace amounts of norlirinine *O*-methyl ether, nornuciferine, and *N*-(2-hydroxy-2-phenylethyl) benzamide were isolated from this fraction (**58**). The lignans (+)-pinoresinol (fig. 2), (+)-syringaresinol, the coniferyl-sinapyl analog (+)-medioresinol, and their monoglucosides and diglucosides *e.g.*, liriodendrin, as well as the unusual lignan lirionol were also found in the bark (**58,82,111**).

Liriodendrin is a derivative of (+)-syringaresinol (lirioresinol B) (**40,216**). Dickey's "lirioresinol C" was shown to be impure lirioresinol B (**40**). (+)-Syringaresinol, syringaresinol dimethl ether, and the simple phenol, syringaldehyde, were found in yellow-poplar heartwood (**60,62,162**). In studies on the biogenesis of the lignans in the bark (**110**), sinapyl alcohol was found, as expected, the best precursor. However, the free syringaresinol and the liriodendrin were, surprisingly, the (–) form in contrast to the (+)-isomers normally found. Apparently a tree can synthesize both antipodes. In addition to free syringaresinol and its monoglucoside, also found were the coniferyl analog, (+)-pinoresinol, and (+)-medioresinol.

Yellow-poplar contains a most unusual series of extractives including compounds of unusual structures as well as an extraordinary array of alkaloids, a class of extractives seldom found in temperate zone trees. The largest group of these are the aporphine alkaloids. They occur in two series depending on the stereochemistry at 6a. The compounds with a hydrogen at this position extending above the plane of the ring (*S*-absolute stereochemistry) are generally dextrorotatory [(+)]. Those with a hydrogen extending below the plane of the ring (R-absolute stereochemistry) are generally levorotatory [(–)].

The extractives of magnolia wood and bark are also characterized by lignans (fig. 23) and alkaloids, but are of a wider variety than are those of yellow-poplar. Thus, the alkaloids also

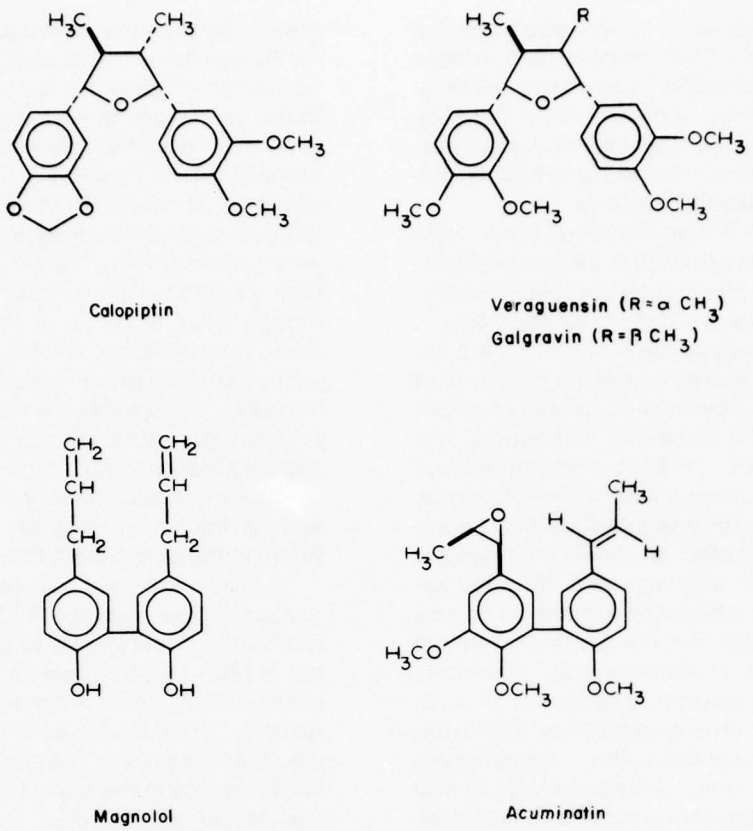


Figure 23.—Lignans of magnolias.

M 146 180

include phenylethylamine, benzylisoquinoline, and bisbenzylisoquinoline types. Most of the recent work on magnolias has been in Japan by groups such as Fujita's (**112-115**). The essential oil of the bark (especially on branches) of eastern magnolias should perhaps be studied.

The essential medicinal oils from Japanese magnolia barks consist of a mixture of monoterpenes and sesquiterpenes with a very high content of β-eudesmol in one species (**113**) and a high content of *trans*-anethole in another (**112**). Syringin is a common constituent of bark of *Magnolia* species. Lignans are also common in barks. Sweetbay contains a small amount of magnolol (**115**), whereas the bark (especially root bark) of the cucumbertree, used at one time as a drug in the treatment of malaria and rheumatism, contained the lignans calopiptin, galgravin, veraguensin, and acuminatin (**85**).

Alkaloids have been studied only in the cucumbertree and southern magnolia (**143**). The cucumbertree contains salicifoline and candicine in the roots and salicifoline and magnoflorine in the bark, whereas the magnolia contains choline, magnoflorine, salicifoline, magnocurarine, and *D-O*-methylarmepavine in the stem. More recently, the alkaloids of southern magnolia wood have been found to include anolobine, anonaine, *N*-nornuciferine, liridenine (**359**), and candicine (**296**). Many literature references in which magnoflorine has been identified may be in error because of the similarity in its properties to those of *N,N*-dimethyllindcarpine (**339,** footnote 5). The bark of southern magnolia has recently been shown to contain the glycosides magnolidin, magnolenin, and magnosidin (**296**).

Extracts of a cross between southern magnolia and sweetbay have yielded an extract in-

hibitory against both fungi and bacteria (**326**). A corn whiskey extract of bigleaf magnolia inner bark has been used in northeastern Alabama as a diuretic and to treat arthritis. Although corn whiskey alone would help relieve suffering, the alkaloids of the inner bark should be checked for physiological activity. Biologically active (cytotoxic) sesquiterpenes related to peroxyferolide have been obtained from southern magnolia (**96**). Neither the wood nor the bark of southern magnolia or sweetbay contains significant tannin (**304**).

MORACEAE

Maclura pomifera (Raf.) Schneid., Osage-orange
Morus rubra L., red mulberry
M. alba L., white mulberry

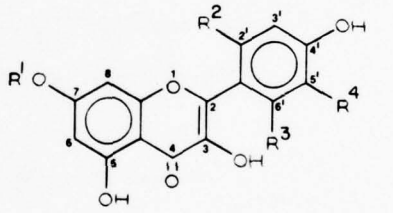
The extractives, particularly the phenolics, of the Moraceae have been reviewed (**362**). The flavonoids (fig. 24) and the stilbenes, which are the major types of compounds isolated from this family, may be useful chemotaxonomic markers. The wood and the bark of *Morus* species and the bark of Osage-orange do not contain significant tannin. The wood of Osage-orange contains 9.4 percent tannin (**304**).

Osage-orange is a small, rapid-growing tree; the wood is very dense, has high strength properties, and is resistant to decay. The general morphological and chemical difference between sapwood, discolored sapwood, and heartwood of Osage-orange has been studied (**135**). The mucilaginous sap of the wood causes dermatitis (**386**).

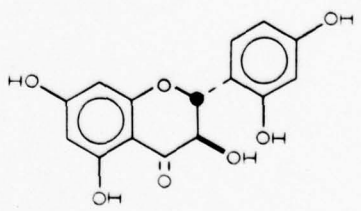
During World War I when imports of dyes were curtailed, Osage-orange wood was used as a dyestuff. After the War, Osage-orange became of minor importance as a dyewood because of the availability of imports and other sources of dyestuffs. Early studies indicated that the dyestuffs from the wood were morin (2′,4′,5,7-tetrahydroxyflavonol) and maclurin (2,3′,4,4′,6-pentahydroxybenzophenone) (**186**). Subsequent work (**16,381**) indicated that the heartwood contained the pigments morin, oxyresveratrol (2,3′,4,5′-tetrahydroxystilbene), and 1,3,6,7-tetrahydroxyxanthone, but the presence of maclurin was not confirmed (**16**). Oxyresveratrol is apparently the fungicidal (**16**) and termiticidal agent in Osage-orange wood responsible for its resistance to decay.

The root bark contains the pigments macluroxanthone, osajaxanthone, and alvaxanthone (**382-385**) (fig. 25). Macluroxanthone is the first natural product shown to contain the 1,1-dimethylallyl form of isoprenoid substitution. Macluroxanthone has antitermiticidal activity, whereas osajaxanthone and alvaxanthone are toxic to goldfish and mosquito larvae.

The heartwood of Osage-orange has also been reported to contain resorcinol, kaempferol, dihydrokaempferol, dihydrokaempferol-7-glucoside, quercetin, dihydroquercetin, and dihydromorin (**78,93,194**). It has been suggested (**194**) that since morin is produced by autoxidation of dihydromorin



	R^1	R^2	R^3	R^4
Kaempferol	H	H	H	H
Morin	H	H	OH	H
Norartocarpanone	CH_3	OH	H	H
Quercetin	H	H	H	OH



Dihydromorin

Figure 24.—Flavanoids from Moraceae.

M 146 181

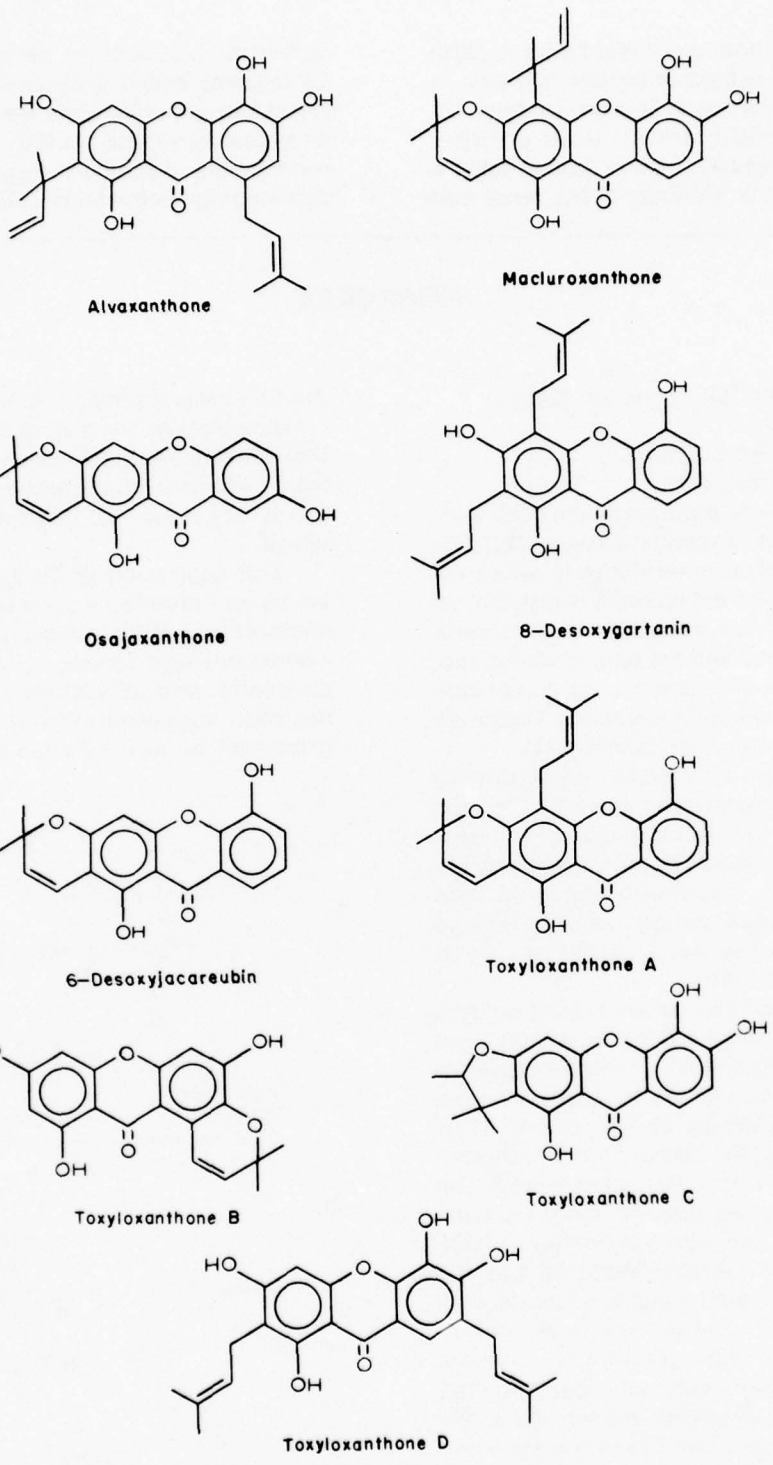


Figure 25.—Xanthones from Osage-orange (*Maclura pomifera*).

M 148 184

(**51**), some of the morin reported from the Moraceae may be an artifact produced during extraction and subsequent processing. However, Venkataraman, who has conducted much of the recent research on the extractives of the Moraceae, believes that this "certainly does not apply to [his] results," and morin is definitely present (**362**). Similarly quercetin and kaempferol can be formed by autoxidation of dihydroquercetin and dihydrokaempferol, respectively. Researchers should take sufficient care to avoid autoxidation if isolating dihydroflavonols.

The bark of Osage-orange contains 8-desoxygartanin, 6-desoxyjacareubin, osajaxanthone, and toxyloxanthones A, B, C, and D (**78**). The structure of toxyloxanthone B, the first naturally occurring 4,4-dimethylchromene, has recently been revised (**71**).

The roots of Osage-orange contain lupeol, butyrospermol, β-sitosterol, and lupane-3β, 20-diol (**94**). Similar triterpenes have been found in the fruit of female trees.

Morus species are small trees valued for their foliage as silkworm food, edible fruits, and for use as dyestuffs. The heartwood extractives of white mulberry and red mulberry have been reported to contain various simple phenolics, benzophenones, stilbenes, and flavonoids (Table 2,3; fig. 26). However the presence of benzophenones has not been confirmed (**194**). Alboctalol apparently is formed in vivo by a complex multistep dimerization process from oxyresveratrol or, alternately, alboctalol and oxyrsveratrol have a common biogenetic precursor (**363**). The original structure of alboctalol (**77**) has been revised recently (**363**). The heartwood of white mulberry also contains the sugars glucose, rhamnose, xylose, and mannose plus two unknown oligosaccharides (**184**). The seasonal variation of the sugars in the bark and the twigs of *M. alba* in relationship to frost hardness has been studied (**306**).

Bark of white mulberry contains α- and β-amyrin, betulinic acid, palmitic and stearic acids, and various sugars (**75,362**). β-Sitosterol was also present in the bark, and was the sole compound identified in callus tissue (**189**). In addition the barks of both white and red mulberry contain a variety of flavonoids (table 3). The flavonoid components in these barks differ markedly except for the occurrence of rubranol in the bark of both species. Rubranol and albanol are formed, at least conceptually, by dimerization of flavonoid intermediates. The rubraflavones are the first naturally occurring flavones with a geranyl substituent and rubraflavone A is the first flavone containing an alkenyl substituent in only the C-ring. The root bark of white mulberry has been

Table 2.—Heartwood extractives of *Morus alba* and *M. rubra*[1]

Compound	*M. alba*	*M. rubra*
Simple phenolics		
Resorcinol	+	+
β-Resorcylaldehyde	+	+
Protocatechualdehyde	+	–
Benzophenones		
Maclurin	+	–
2,4,4',6-Tetrahydroxy-benzophenone	+	–
Stilbenes		
Resveratrol	+	–
Oxyresveratrol	+	+
Dihydrooxyresveratrol	+	–
3,3',4,5'-Tetrahydroxy-stilbene ("piceatannol")	–	+
Flavonoids		
Kaempferol	–	+
Dihydrokaempferol	+	+
Norartocarpanone	+	+
Morin	+	+
Dihydromorin	+	+
Quercetin	+	+
Dihydroquercetin (taxifolin)	+	–
Other		
Alboctalol	+	–

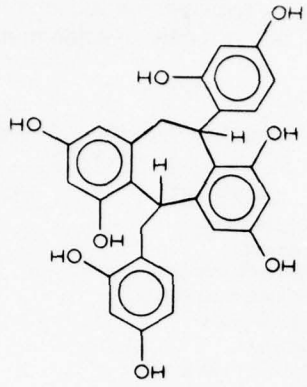
[1] +, Detected; –, not reported; data from literature cited **76, 77, 184, 194, 331, 362, 363.**

Table 3.—Flavonoids in the bark of *Morus alba* and *M. rubra*[1]

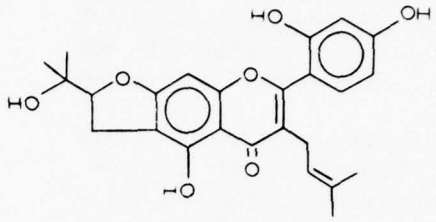
Compound	*M. alba*	*M. rubra*
Mulberrin	+	–
Mulberrochromene	+	–
Cyclomulberrin	+	–
Cyclomulberrochromene	+	–
Mulberranol	+	–
Albanol	+	–
Rubranol	+	+
Rubraflavone A	–	+
Rubraflavone B	–	+
Rubraflavone C	–	+
Rubraflavone D	–	+

[1] +, Detected; –, not reported; data from literature cited **75, 77, 79, 363.**

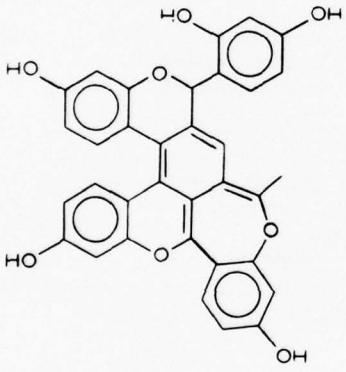
shown to contain β-tocopherol; α,β-dimontanylglycerol; morusin (an isomer of mulberrochromene); cyclomorusin (an isomer of cyclomulberrochromene); and another compound also related to cyclomulberrochromene (**182,239,319**).



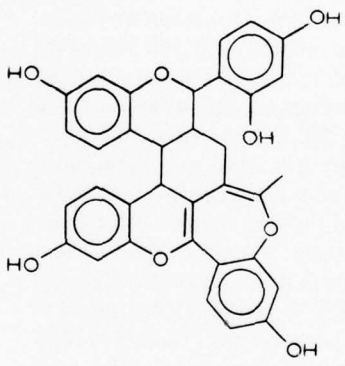
Alboctalol



Mulberranol

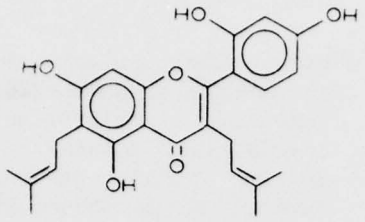


Albanol

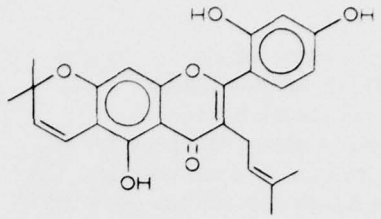


Rubranol

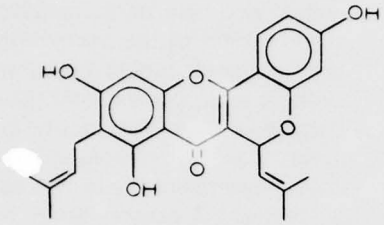
Figure 26.—Compounds from *Morus* species.
M 146 185
M 146 191



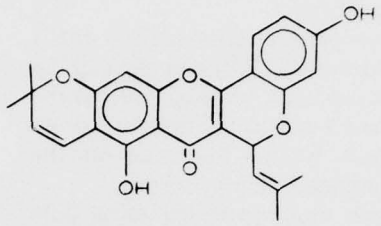
Mulberrin



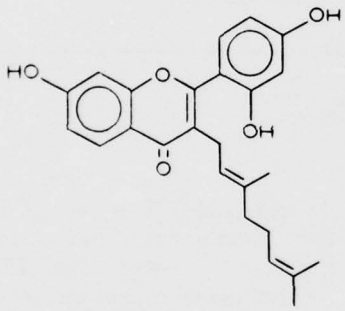
Mulberrochromene



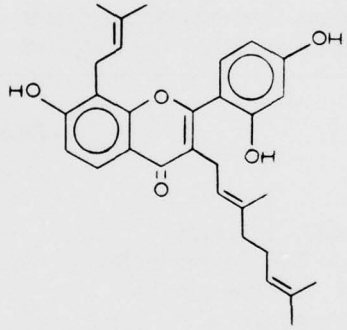
Cyclomulberrin



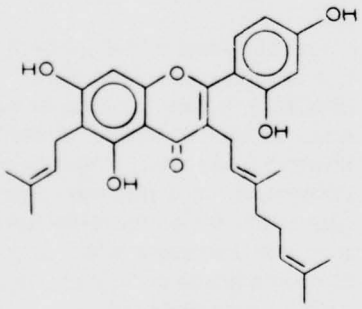
Cyclomulberrochromene



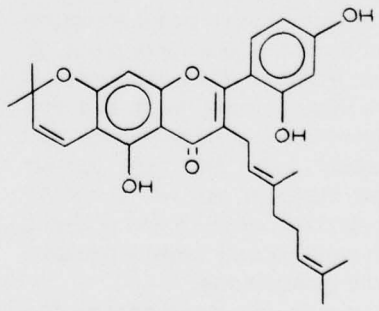
Rubraflavone A



Rubraflavone B



Rubraflavone C



Rubraflavone D

NYSSACEAE

Nyssa aquatica L., water tupelo
N. ogeche Bartr., Ogeechee tupelo
N. sylvatica Marsh., black tupelo

Tupelo wood is used principally for lumber, veneer, pulpwood, and railroad ties. The porous wood of *Nyssa* species has been used in certain surgical procedures (**224**). Tupelo wood lacks durability if conditions promote decay; the heartwood, however, is easily penetrated by preservatives.

Although the general chemistry of black and water tupelo woods (**368**) and of black tupelo bark (**55**) have been investigated, no detailed studies have been conducted on extractives of this genus. Neither the wood nor the bark has any significant tannin content.

Water tupelo heartwood contains 0.26 percent benzene extractives, 0.3 percent acetone extractives, and 1.6 percent methanol extractives. The acetone and methanol extracts gave positive tests for alkaloids. The methanol extract contained glucose, rhamnose, lactose, and phenolic glycosides (**363**). Column chromatography of the benzene and of an ethyl acetate extract resulted in three crystalline low-yield phenolics, the structures of which have not been determined (**363**).

Preliminary work on the extractives of black tupelo heartwood indicates the presence of an alkaloid in minute amounts, phenolics, and one or more flavones (**363**). The ether extract of the prehydrolysis pulping liquors of black tupelo contained vanillic acid, syringic acid, vanillin syringaldehyde, sinapaldehyde, and vanilloyl methyl ketone (**334**). The extractives of *Nyssa* species and indeed the entire Nyssaceae have not been investigated extensively. Because other members of this family contain pharmaceutically active alkaloids, future studies of these species may be rewarding.

OLEACEAE

Fraxinus americana L., white ash
F. berlandieriana A. DC., Berlandier ash
F. caroliniana Mill., Carolina ash
F. nigra Marsh., black ash
F. pennsylvanica Marsh., green ash
F. profunda (Bush) Bush, pumpkin ash
F. quadrangulata Michx., blue ash
F. texensis (A. Gray) Sarg., Texas ash

The white ash wood used commercially is primarily the white and the green ash, although blue ash is often included. Because commercial white ash is heavy, strong, hard, stiff, and has high resistance to shock, it is used for handles, oars, baseball bats, and other similar uses. Black and pumpkin ash are lighter in weight and are used for furniture and shipping containers. Ash wood is only slightly resistant to decay-promoting conditions.

A *Fraxinus* species reportedly caused dermatitis on a woodcutter's wife who developed it from contact with her husband's working clothes. However, the sensitivity was traced to the lichen *Lecanora conizaeoides* that grew on the bark (**386**). The bark of *F. americana* has been used in folk medicine in a tonic, as a diuretic, and to relieve fever (**187**).

Neither wood nor bark of ash contains any significant amounts of tannin, although white ash bark reportedly contains 4.5 to 4.8 percent tannin (**304**). Tannin and carbohydrate contents of white ash bark have been reported (**229**).

Stachyose and especially mannitol are characteristic sugars found in *Fraxinus* species (**244,284**). Indeed, manna of commerce is the dried exudation from *F. ornus*, the European flowering ash tree, which contains about 90 percent mannitol (manna sugar). However, the manna that fell on the Israelites is thought to be a lichen (*Lecanora* spp.) that in dry weather curls into flakes or balls that can be borne long distances on the wind.

Coumarins (fig. 13), flavonoids, simple phenolics, and their glycosides are generally characteristic extractives of *Fraxinus* species. The coumarin derivatives are responsible for

the blue to blue-green florescence of the water extract of the bark. Glycosides have been implicated as the active antibiotic substances found in barks of white, green, and black ash (**173**).

Bark of *Fraxinus* species commonly contains syringin and coumarin. The barks of white, green, and black ash contain syringoside and fraxin (**283,284**). The bark of blue ash is unique; it alone contains coniferoside (**284**). In addition to fraxin, fraxetin, esculin, and esculetin were isolated from both the wood and the bark of black ash (**247**). The novel chromenol pennsylvanol (fig. 27) has recently been isolated from the bark of green ash (**363**). The data obtained on the purified compound are best explained if pennsylvanol exists as a mixture of tautomers as shown (**363**).

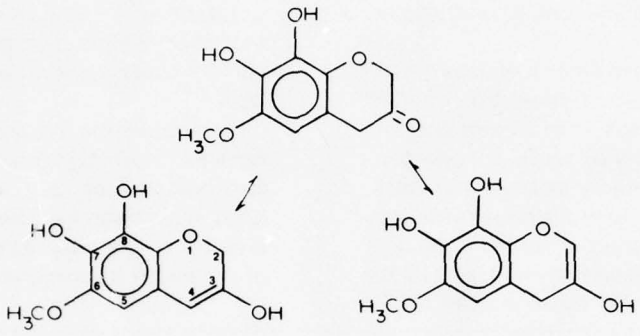


Figure 27.—Pennsylvanol.

M 146 190

PLATANACEAE

Platanus occidentalis L., American sycamore

American sycamore is used for lumber, veneer, railroad ties, and fenceposts. American sycamore causes woodcutter's eczema, and the down under the young leaves is an irritant to throat and eyes (**386**).

The general chemistry of the bark has been investigated (**55**). The wood does not contain tannins, but the bark is reported to contain 1.9 percent tannin (**304**). The wood and the bark of the Platanaceae are rich in triterpenes. Indeed American sycamore contains betulinic acid, betulinic aldehyde, β-sitosterol, and a new triterpene, platanic acid (3β-hydroxy-20-oxo-30-norlupan-28-oic acid) in the bark, and betulinic acid in the heartwood (**353,387**). Stearic and docosanoic acids have also been found in the bark (**353,387**).

RHIZOPHORACEAE

Rhizophora mangle L., mangrove

Mangrove is a principal part of the coastal vegetation throughout tropical and subtropical America. It fringes shores and estuaries and is of primary importance as a land retainer and builder. One of the largest mangrove forests in

the world is found in the Everglades National Park of Florida. Mangrove leaves have been studied as a supplement to cattle feeds and as a source of pharmaceuticals. An excellent review on the utilization of this species has been published (**225**). The bark, roots, young shoots, and leaves are a possible source of dyestuffs (**225**). The bark and the bark resin have been used as a native remedy for leprosy, elephantiasis, asthma, diarrhea, dysentery, and to treat lesions of various kinds. The bark has also been used as a substitute for quinine to alleviate fever (**225**).

Mangrove is best known as a source of tannin (**7,279,294**). The wood does not contain tannin, but the bark yields 11 to 23 percent hot-water extract containing 37 to 56 percent tannin. The tannin is primarily in the inner bark. Mangrove tannin has several undesirable features: Causes cracky grain in leather due to its astringency; has a high salt content; and its intense red color has little trade appeal (**225**). These difficulties can be overcome partly by blending with other tannins to reduce the astringency and the salt content, and by eliminating the color chemically (**279,305**). Mangrove tannins (**325**) and tannins from related species (**282**) show promise in the formulation of adhesives. Chemically, mangrove tannin is probably similar to that of the closely related species, *Rhizophora mucronata*. D. G. Roux, University of the Orange-Free State, South Africa, told us this tannin consists predominately of highly condensed 4,8-linked leucocyanidin tannins that readily yield cyanidin and traces of a flavan-3,4-diol precursor on reaction with mineral acid.

Because the extractives of mangrove have not been studied in any detail and because certain compounds, *e.g.*, sulfur-containing alkaloids, have been reported from related species, a study of the chemistry of this species might prove highly informative.

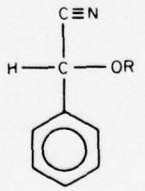
ROSACEAE

Prunus alleghaniensis Porter, Allegheny plum
P. americana Marsh., American plum
P. angustifolia Marsh., Chickasaw plum
P. caroliniana (Mill.) Ait., Carolina laurelcherry
P. hortulana Bailey, hortulan plum
P. mexicana S. Wats., Mexican plum
P. munsoniana Wight and Hedr., wildgoose plum
P. myrtifolia (L.) Urban, myrtle laurelcherry
P. nigra Ait., Canada plum
P. pensylvanica L. f., pin cherry
P. serotina Ehrh., black cherry
P. umbellata Ell., flatwoods plum
P. virginiana L., common chokecherry

The Rosaceae consists of approximately 4,000 species, so that the *Prunus* species reviewed here represent only a small segment of the family. *P. serotina* is the only native species of commercial importance for lumber production. The fruits of this and other species have been collected for food.

A folk remedy for dispelling chills is a whiskey drink in which the inner bark of *Prunus serotina* has been steeped until the bitter properties are extracted (**226**). The inner bark is used commercially as a flavoring agent for medicaments and has been used as an antitussive (**187,335**).

The American Indians used the inner bark of *P. virginiana* as a source of a red dye. Because the wood and the bark of *P. serotina* and *P. angustifolia* inhibit seed germination in a variety of plants (**178**), *Prunus* species wood and bark chips probably should not be used as a mulch on seedbeds.



Prunasin (R=β–Glucosyl)
Amygdalin (R=β–Gentiobiosyl)

Figure 28.—Cyanogenetic glycosides.

M 146 189

The extractives of the Rosaceae have been reviewed (**143**). The characteristic compounds found in this family generally have included cyanogenetic glycosides (fig. 28), polyphenols, and pentacyclic triterpenes. The chemotaxonomic classification of *Prunus* by the flavonoids found in the wood has been studied (**136**).

The cyanogenetic glycoside prunasin is found in all tissues of *Prunus* species (**143**). Amygdalin, a compound closely related to prunasin, is also found in some *Prunus* species, and is used in the preparation of laetrile. The cyanogenic glycosides, especially in the fruit stones and foliage of the Rosaceae, can be of dangerous levels and are responsible not only for the loss of livestock but also of human lives (**179**). The toxicity of the glycoside is due to its rapid hydrolysis to free hydrogen cyanide after ingestion. Thus the bark of *P. capuli* was used by the Mexicans as a fish poison (**280**). For safety the foliage and fruit pits of all *Prunus* species should be treated as potentially dangerous (**179**).

The wood of *Prunus* species has been reported to contain up to 4.5 percent tannin. The bark contains approximately 3 to 8 percent tannin (**304**). Tannin of *P. serotina* bark consisted of tannins that contained monomeric and polymeric leucocyanidin (3,3′,4,4′,5,7-hexahydroxyflavanol) units (**42**).

The heartwood of *Prunus serotina* contained (+)-catechin, naringenin, and 3-hydroxynaringenin (**281**). In addition to prunasin, the bark contained scopoletin, benzoic acid, trimethylgallic acid, *p*-coumaric acid, and phytosterols (**289**). The leaves of *P. serotina* contained the pentacyclic triterpenes ursolic acid, ursol aldehyde, and the new triterpene, 2α,3α-dihydroxy-12-ursen-28-oic acid (**31**).

Several *Prunus* species are known to produce bark gums that give simple sugars on hydrolysis (**292**). This gum production is stimulated by wounding the tree, and is the typical wound response of these species. Hillis (**149**) recently reported that treatment of *Prunus* species with chloroethylphosphoric acid, which liberates ethylene above pH 4, produced massive amounts of carbohydrate gum exudate containing only small amounts of polyphenols. The amount of gum produced was many times that produced as a typical wound response. Fungal attack of *Prunus* species caused the accumulation of isoolivil (a lignan) and scopoletin in the sapwood (**137,150**).

SALICACEAE

Populus balsamifera L., balsam poplar
P. deltoides Bartr., eastern cottonwood
P. grandidentata Michx., bigtooth aspen
P. heterophylla L., swamp cottonwood
P. tremuloides Michx., quaking aspen
Salix amygdaloides Anderss., peachleaf willow
S. bebbiana Sarg., Bebb willow
S. caroliniana Michx., Coastal Plain willow
S. discolor Mühl., pussy willow
S. exigua Nutt., coyote willow
S. floridana Chapm., Florida willow
S. interior Rowlee, sandbar willow
S. lucida Mühl., shining willow
S. lutea Nutt., yellow willow
S. nigra Marsh., black willow
S. pellita Anderss.,_____
S. petiolaris J. E. Sm., meadow willow
S. pyrifolia Anderss., balsam willow
S. rigida Mühl., Missouri River willow
S. sericea Marsh., silky willow

The genus *Salix* contains about 300 species (**65**); approximately 100 are found in North America (**206**). The willows range from small plants to large trees, and generally grow along the banks of streams or on lake shores. The willows that grow to tree size are used in limited quantities for veneer, pulpwood, artificial limbs, boxes and various containers, and for furniture parts.

The most widely studied extractable constituents in the genus *Salix* are the phenolic glycosides (**349**) (fig. 29). The phenolic glycoside salicin is of widespread occurrence in this genus and has been used medicinally as an analgesic (**335**). This probably explains the use of *S. nigra* bark tea as a folk remedy in treating colds accompanied by fever (**187,226**). Salicin and its derivatives are responsible for the bitterness of willow leaves; as a result high levels of these compounds correlate well with the resistance

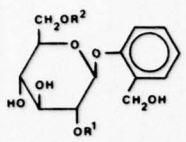
of willows to opossum attack (**214**). Other compounds reported include the leucoanthocyanidins and the anthocyanins in leaves and bark (**20,33,39**).

Of the willows found in the eastern United States, only the extractives of *Salix nigra* wood and *S. petiolaris* bark have been studied. The general chemistry of *S. nigra* bark has been examined (**55**). The wood does not contain significant tannin, although the bark contains approximately 5 percent (**304**). The acetone and the ethanol extract of *S. petiolaris* bark was shown to contain the glycosides salicin, picein, vimalin, salicyloylsalicin, salireposide, grandidentatin, populin, tremulacin or tremuloidin (or both), and salicyloylsalicin-2-*O*-benzoate, (+)-catechin, and β-sitosterol (**338**).

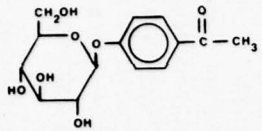
Pearl and coworkers (**273,275**) extracted *Salix nigra* wood with 75 percent *n*-propanol and identified *p*-hydroxybenzoic acid in the extractives. The extractives were hydrolyzed with alkali and fractionated to yield *p*-hydroxybenzoic acid as the major component and smaller amounts of syringic acid, vanillic acid, ferulic acid, syringaldehyde, vanillin, acetosyringone, and acetovanillone. Acid hydrolysis (**272**) of the propanol extractives gave vanillic and syringic acids as the major hydrolytic products with lesser amounts of *p*-hydroxybenzoic acid, vanillin, and syringaldehyde. In addition, after hydrolysis, galactose, glucose, and mannose were found in quantity, whereas before hydrolysis only glucose and mannose occurred, in small amounts. Thus, apparently the acids and the phenols obtained on hydrolysis of the extractives of *S. nigra* are present as both esters and glycosides. The higher yields of *p*-hydroxybenzoic acid, vanillin, and syringaldehyde in the alkaline hydrolysis products suggest that these components are present predominantly as esters; whereas, the relatively higher yields of vanillic and syringic acids in the acid hydrolyzates suggest that these acids are present primarily as glycosides.

The genus *Populus* includes the aspens and the cottonwoods. Aspen wood when well seasoned does not impart odor or taste to foodstuffs. Aspen and cottonwood are used for lumber, veneer, pulpwood, boxes, and crates. Balm-of-Gilead, used in cough medicine, is derived from the buds of balsam poplar. The extractives of *Populus* species bark and wood have been reviewed (**197,250**). A literature survey of *Populus* species with emphasis on *P. tremuloides* has been compiled (**293**). An important class of extractives in the bark and the leaves of this genus are the phenolic glycosides (**350,351**). A gas-liquid chromatographic screening method for detecting phenolic glycosides has been described as a chemotaxonomic aid in the botanical classification of *Populus* species (**336,337**). The extractives of the bark and the leaves often contain antimicrobial activity (**47,124,181,204,208,218,369**). Trichocarpin is important as a decay resistance factor in poplar bark (**208**). The general chemistry of the bark of *P. tremuloides* and *P. heterophylla* has been studied (**55**). Although the wood of *Populus* species does not contain tannins, the bark has been reported to contain approximately 2 percent tannin.

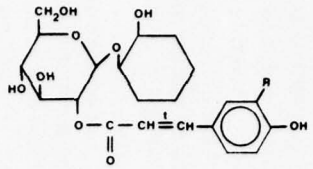
Wood of *Populus tremuloides* has been extensively investigated (**269**). Saponification and fractionation of the neutrals from the benzene extract gave linoleic acid, oleic acid and a homologous series of wax acids from C_{12} to C_{28} including the odd-numbered acids except C_{27} (**269**). The major alcohols found were glycerol and the C_{24}, C_{26}, and C_{27} wax alcohols. An impure β-sitosterol apparently was present as well as an unknown steroid later shown to be citrostadienol (**44**). Petroleum ether extraction of heartwood of *P. tremuloides* followed by saponification confirmed the presence of the C_{16}-C_{28} wax acids (**6**). Acetone extraction of the heartwood also yielded sitosterol glucoside in the insoluble fraction. On saponification the acetone extract yielded a hydrocarbon fraction containing C_{14}-C_{29} normal paraffins; C_{24}, C_{26}, and C_{28} wax alcohols; 3,5-stigmastadien-7-one (tremulone); and β-sitosterol (**6**). In addition the heartwood extractives contained α- and β-amyrin, butyrospermol, 24-methylenecycloartanol, lupeol, and α-amyrenonol (**4**). Steam distillation of the heartwood gave benzyl alcohol, *p*-ethylphenol, phenol, β-phenylethanol, *n*-hexanol, and *n*-heptanol (**3**). The methanol extractives of *P. tremuloides* wood were shown to contain phenylalanine, tyrosine, serine, glycine, sinapaldehyde (**227**), sucrose, glucose, fructose, *O*-α-*D*- glucopyranosyl-(1→2)-*O*-β-*D*- fructofuranosyl-(1→2)-β-*D*-fructofuranoside, and traces of xylose and raffinose (**291**). A spent sulfite liquor from pulping *P. tremuloides* was extracted with ether and fractionated to yield several stereoisomeric forms of syringaresinol and its stereoisomer, lirioresinol (**271**).



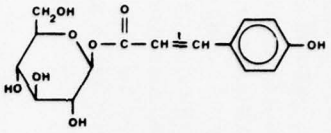
Salicin R^1=H, R^2=H
Tremuloidin R^1=C_6H_5CO-, R^2=H
Populin R^1=H, R^2=C_6H_5CO-



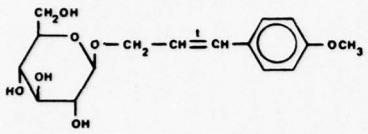
Picein



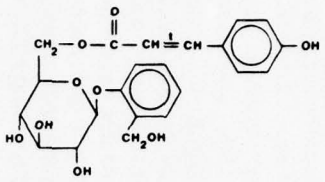
Grandidentatin R=H
Grandidentoside R=OH



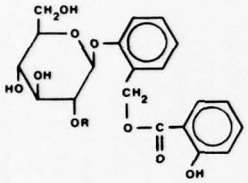
1-O-*p*-Coumaroyl-β-D-glucoside



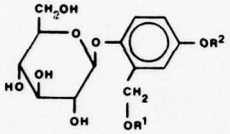
Vimalin



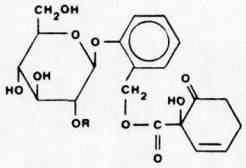
Trichocarposide



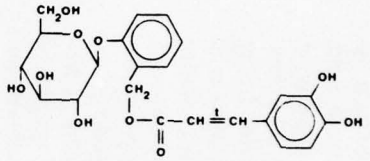
Salicyloylsalicin R=H
Salicyloyltremuloidin R=C_6H_5CO-



Salireposide R^1=C_6H_5CO-, R^2=H
Trichocarpin R^1=$C_6H_5CH_2$-, R^2=H
Trichoside R^1=$C_6H_5CH_2$-, R^2=CH_3



Salicortin R=H
Tremulacin R=C_6H_5CO-



Populoside

Figure 29.—Phenylglycosides from Salicaceae.

M 146 182
M 146 183

The *n*-propanol extractives of *Populus tremuloides* wood were investigated after alkaline or acid hydrolysis (**272,273,275**). The major hydrolytic product was *p*-hydroxybenzoic acid. Alkaline hydrolysis also yielded syringic acid, vanillic acid, syringaldehyde, vanillin, *p*-hydroxybenzaldehyde, and acetosyringone. These same components were also found after acid hydrolysis, but in somewhat different relative amounts. Of the *Populus* species reviewed, only *P. tremuloides* extractives gave *p*-hydroxybenzaldehyde on hydrolysis. Because no *p*-coumaric acid was found in the alkaline hydrolyzate, the *p*-hydroxybenzaldehyde could not be formed from it by oxidative alkaline cleavage, but must have been formed by a reverse aldol from a *p*-hydroxyphenyl moiety containing an aldol or protected aldol configuration (**367**) or by hydrolysis of a glycoside or ester. Acid hydrolysis also gave galactose, glucose, mannose, and xylose.

The bark of *Populus tremuloides* has also been investigated extensively. The petroleum ether extractives contained lignoceric acid, linoleic acid, β-sitosterol, ceryl alcohol, glycerol, and an unknown sterol (**155**). From the physical properties given, the unknown sterol is probably citrostadienol. The methanol extractives contained pyrocatechol, benzoic acid, vanillic acid, *p*-hydroxybenzoic acid, *p*-coumaric acid, ferulic acid, salireposide, salicin, populin, tremuloidin, glucose, sucrose, and fructose (**101**). Pyrocatechol has been shown to be the fungistatic agent from *P. tremuloides* bark (**159**). The benzene-ethanol extractives contained benzoic and salicylic acids (**156**). An arabinan of molecular weight 15,000 was found in the aqueous-methanol extractives (**172**). Alkaline hydrolysis of *P. tremuloides* bark yielded a large amount of *p*-coumaric acid with lesser amounts of ferulic acid, vanillic acid, *p*-hydroxybenzoic acid, vanillin, syringaldehyde, acetovanillone, acetosyringone, and *p*-hydroxybenzaldehyde (**276**). Further studies on the hot-water extractives of this bark indicated quantities of salicin, tremuloidin, and salireposide (**251,252,278**). In addition to these glucosides, salicyl alcohol, gentisyl alcohol, benzoic acid, sucrose, fructose, and glucose were identified as important components of these extractives along with minor amounts of mannose and galactose. Pearl subsequently demonstrated that under the influence of mild alkaline conditions (e.g., excess lead subacetate, lime, magnesium oxide, ammonium hydroxide) used for the isolation of the phenolic glycosides, the benzoyl group at the 2-position of the glucose in tremuloidin and salicyloylsalicin-2-benzoate (salicyloyltremuloidin) would migrate to the 6-position to give populin or salicyloylsalicin-6-benzoate, respectively. By adjusting the alkalinity of the isolation procedures, the proportions of these compounds could be changed. These studies made suspect all isolations of populin and salicyloylsalicin-6-benzoate from *Populus* and *Salix* species in which alkaline purification procedures were employed (**254,255,268,274**).

The application of polyamide column chromatography to bark extractives fractions not subjected to previous alkaline treatment of any type resulted in isolating bark components that could not be artifacts of isolation procedures. The inherent resolving power of the polyamide column technique also resulted in separating and isolating many new components that could not be isolated by procedures used earlier. By this means, 1-*O*-*p*-coumaroyl-β-*D*-glucose was isolated and demonstrated to be a major component in the hot-water extractives of *Populus tremuloides* bark (**256**). Pyrocatechol was also isolated.

The mass spectral fragmentation pattern of salireposide acetate demonstrated conclusively that the structure of salireposide was not hydroxypopulin as accepted for many years, but was 2-benzoyloxymethyl-4-hydroxyphenyl-β-*D*-glucoside (**261**). Mass spectral fragmentation of glucosides of unequivocally known structures yielded background information that could be applied to the structure elucidation of unknown glucosides (**258**).

Continued development of procedures for isolating components without change from the extractives of *Populus tremuloides* bark resulted in isolating quantities of salicortin and tremulacin (**264,266**), two labile complex glucosides previously isolated but not characterized by Thieme and coworkers from *Salix purpurea* bark (**348**) and *P. tremula* bark (**352**), respectively. By means of hydrogenolysis and acid and alkaline hydrolysis and by infrared, nuclear magnetic resonance, and mass spectrometry, Pearl and Darling (**266**) proved the structure of salicortin to be the ω-(1-hydroxy-6-oxo-2-cyclohexene-1-carboxylic acid ester) of salicin and the structure of tremulacin the 2-*O*-

benzoyl ester of salicortin. Studies on these two labile glucosides suggest that they are the precursors of salicin, tremuloidin, or populin or of all three that have been isolated from *P. tremuloides* bark. Acid hydrolysis of salicortin yields salicyloylsalicin that yields salicin and salicylic acid on alkaline hydrolysis. However, direct alkaline hydrolysis of salicortin yields salicin and pyrocatechol with no trace of salicylic acid. Similarly, acid hydrolysis of tremulacin yields salicyloyltremuloidin that, in turn, will give salicylic acid, tremuloidin, populin, or all three depending on the alkalinity of the solution. Thus apparently many of the compounds reported in the barks of *P. tremuloides* (and other *Populus* and *Salix* species) were artifacts of processing procedures. Many flavonoid compounds were also noted in the polyamide chromatograms of *P. tremuloides* bark extractives, but were not characterized further.

Propanol extractives of *Populus grandidentata* wood on alkaline and acid hydrolysis gave results similar to those obtained with *Salix nigra* wood except no ferulic acid was detected (**272,273,275**). Methanol extraction of the wood gave sucrose, glucose, fructose, *O*-α-*D*-glucopyranosyl-(1→2)-*O*-β-*D*-fructofuranosyl-(1→2)-β-*D*-fructofuranoside, and traces of xylose and raffinose (**291**). The bark extractives of this species have received the same attention given to *P. tremuloides* (**253-255,276-278**). If subjected to alkaline hydrolysis the bark extractives yielded the same compounds given by *P. tremuloides*, but syringic acid was the major hydrolytic product, a situation unique to this species (**276**). In early studies of the hot-water extractives of this bark, fractionation yielded all of the compounds previously reported for *P. tremuloides* bark plus *cis*-cyclohexanediol and its 2-*O*-*p*-coumaroyl-β-*D*-glucoside, grandidentatin (**253,277**). Interestingly, cyclohexanediol has been found in the scent glands of beavers. Controlled acid hydrolysis of *P. grandidentata* bark extractives gave salicyloylsalicin and salicyloyltremuloidin in the same manner reported for *P. tremuloides* (**254,255**). Polyamide column chromatography yielded salicortin and two new glucosides containing the caffeic acid moiety, populoside and grandidentoside. Populoside was identified as the ω-caffeoyl ester of salicin, and grandidentoside was identified as the caffeoyl analog of grandidentatin, *cis*-cyclohexanediol-2-*O*-caffeoyl-β-*D*-glucoside (**97,98**).

Propanol extractives of *Populus balsamifera* wood gave on hydrolysis compounds similar to those reported for *Salix nigra*, except acetovanillone was not found in the alkaline hydrolyzate (**272,273,275**). The pattern of fatty acids in *P. balsamifera* bark was investigated by gas-liquid chromatography at monthly intervals for a year (**190**). The most important compounds were palmitic, oleic, linoleic, linolenic myristoleic and behenic acids.

Alkaline hydrolysis of the bark of *Populus balsamifera* yielded the same components as did *P. tremuloides* bark (**276**); preliminary evaluation of the crude hot-water extractives yielded salicin, salicyl alcohol, and gentisyl alcohol (**278**). Polyamide column fractionation (**270**) demonstrated quantities of salireposide and the glucoside trichocarpin isolated earlier by Loeschcke and Francksen (**208**) from *P. trichocarpa* bark and proved to be the β-glucoside of the benzyl ester of gentisic acid. Continued polyamide column fractionation yielded further extractives including 2,6-dimethoxy-*p*-benzoquinone, azelaic acid, cinnamic acid (**257**), gentisyl alcohol, trichoside, trichocarpigenin (benzyl gentisate) (**262**), trichocarposide, populoside, and dihydromyricetin (**263**). Trichocarpigenin, trichoside, and trichocarposide had been isolated previously from *P. trichocarpa* (**99,259,260**).

Acetone extraction of the bark of *Populus balsamifera* gave neutral and acidic material (**5**). Saponification of the neutral material gave palmitic, palmitoleic, stearic, oleic, linolenic, 11-eicosenoic, behenic, lignoceric and cerotic acids. Also isolated were the even-numbered wax alcohols C_{18}-C_{26} plus the C_{27} wax alcohol. Saponification of the acidic material gave *p*-hydroxybenzoic, vanillic, *p*-coumaric, ferulic, caprylic, pelargonic, capric, tridecyclic, palmitic, stearic, and arachidic acids. Phenolic aldehydes and ketones were not detected.

Hydrolysis of *Populus deltoides* wood propanol extractives gave results that were identical to those obtained with *P. grandidentata* (**272,273,275**).

Bark extractives of *Populus deltoides* on alkaline hydrolysis yielded the same compounds obtained from the other *Populus* species, but the green bark did not yield *p*-hydroxybenzaldehyde; the brown furrowed bark did (**276**). Preliminary evaluation of the hot-water extractives of this bark indicated the presence

of salicin, salireposide, salicyl alcohol, and gentisyl alcohol (**278**). In addition, polyamide column chromatographic fractionation yielded salicortin, pyrocatechol, grandidentatin, grandidentoside, populoside, trichocarposide, and 6-methyldihydroquercetin (**265**).

Propanol extractives of *Populus heterophylla* wood on alkaline hydrolysis gave results qualitatively similar to those from *Salix nigra* wood extractives. However, acid hydrolysis yielded more vanillic and syringic acids than did alkaline hydrolysis suggesting that these acids are probably linked glycosidically in the propanol extractives (**272,273,275**). In contrast, the yield of *p*-hydroxybenzoic acid from acid hydrolysis was much lower than that from alkaline hydrolysis suggesting that this acid for the most part is ester-linked, a hypothesis first noted by Smith for *P. tremula* (**328**).

The extractives of *Populus heterophylla* bark, if hydrolyzed with alkali, gave the same compounds as did the barks of other *Populus* species, but was the only one of these barks to give *p*-hydroxybenzoic acid as the most important hydrolytic product (**276**). Preliminary evaluation of the hot-water extractives of this bark indicated the presence of salicin, salireposide, salicyl alcohol, gentisyl alcohol, and syringic acid (**278**).

C-Glycosyl flavones such as vitexin and orientin were reported in the leaves of *Populus heterophylla*; this is the first reported isolation of compounds of this type from the family Salicaceae. A new diterpenoid, heterophyllin, was the major water-soluble extractive of the leaves (**267**).

TILIACEAE

Tilia americana L., American basswood
T. caroliniana Mill., Carolina basswood
T. floridana Small, Florida basswood
T. heterophylla Vent., white basswood

The genus *Tilia* is distributed throughout the world. The exact number of species has been disputed for more than 150 years because of the variability of the leaf characteristics (**206**). Thus the exact number of recognized North American species has varied over the years from 3 to 15. A recent investigation showed that the variations in *Tilia* leaf flavonoids and the morphological characteristics were continuous across the North American range of this genus; this suggested the genus as represented in eastern North America should be considered one species, *T. americana* L. (**146**). American Indians made thongs, rope, string, and thread from the strong inner bark of *T. americana*. In addition the Indians used the bark mucilage characteristic of this species as well as other Tiliaceae as a remedy for wounds. Various decoctions of the leaves, flowers, bark, and wood are reported in American folk medicine to have been used for disorders of the bile and liver (**335**). Indeed the wood of *Tilia* species is of interest as a source of useful pharmaceuticals (**48,49**). The water extract of the obscure *T. alburnum* has antispasmodic, vasodilative, and cholepoietic properties that were patented (**192,193**).

Although *Tilia americana* was reported to contain no tannin in the wood and only insignificant amounts in the bark (**304**), the barks of several Tiliaceae have been used as a tanning material. The tannins from European Tiliaceae consist primarily of condensed tannins that cooccur with lesser amounts of gallotannins and ellagitannins.

The chemistry of the extractives from the Tiliaceae has been reviewed (**143**). The compounds characteristic of *Tilia* species include tannins, flavonoids, coumarins, triterpenes, and sterols. Work on American *Tilia* spp. has shown the presence of fraxin (**286**) in twigs from *T. americana* and *T. heterophylla* and that of fatty acids (**67**) in the heartwood and the sapwood of *T. americana*. Because of the limited work with American species and of the medicinal properties reported for other *Tilia* species, the extractives chemistry of *T. americana* and its closely related American species might be rewarding.

ULMACEAE

Celtis occidentalis L., hackberry
C. laevigata Willd., sugarberry
C. lindheimeri Engelm., Lindheimer hackberry
C. tenuifolia Nutt., Georgia hackberry
Ulmus alata Michx., winged elm
U. americana L., American elm
U. crassifolia Nutt., cedar elm
U. rubra Mühl., slippery elm
U. serotina Sarg., September elm
U. thomasii Sarg., rock elm

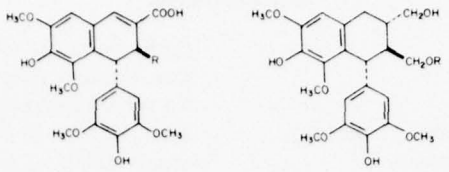
In the eastern United States the Ulmaceae consist of hackberries and elms. *Celtis occidentalis* and *C. laevigata* are the sources of lumber known commercially as hackberry. Most of this lumber is used for furniture and some for various types of containers. The elms were considered an excellent wood for houses and boats by both the American Indians and the English settlers. The Indians fashioned canoes from the bark of *Ulmus americana* and stopped the cracks with the crushed bark of *U. rubra*. The inner bark of *U. rubra* has been chewed as a soothing remedy and used as a laxative and an emollient for external inflamation (**187**). For commercial purposes the elms are divided into two categories: Hard (rock) elms (*U. alata, U. crassifolia, U. serotina,* and *U. thomasii*) and the soft elms (*U. americana* and *U. rubra*). Other uses of elm lumber are for manufacturing boxes and crates and furniture. A poultry farmer told us that using bedding of elm leads to high mortality for turkeys, but not for chickens. Elm wood can cause woodcutter's eczema; the leaves have irritant hairs on their undersurfaces (**386**).

The extractives chemistry of *Celtis* species has not been studied in detail. Preliminary work showed that the wood and the bark of *C. laevigata* were almost devoid of any phenolic extractives. Only triterpenoid acids, fatty acids, and glucose were detected (**316**). These findings contrast with those for *C. australis* bark that contained betulin, 3,3′-di-*O*-methylellagic acid and its glycoside, gallic acid, and quebrachitol (**56**).

The American elms are threatened by two diseases, phloem necrosis and Dutch elm disease. Phloem necrosis is apparently caused by mycoplasma bodies; the symptoms are suppressed by injecting tetracycline, an antibiotic (**105**). Dutch elm disease is caused by the fungus *Ceratocystis ulmi*; the fungus is carried from tree to tree by the smaller European elm bark beetle *Scolytus multistriatus* and to a much lesser extent by the native elm bark beetle *Hylurgopinus rufipes*. The fungus can also spread from diseased to healthy trees by root grafts between neighboring elms. Trees affected by Dutch elm disease form tyloses that block water-conducting vessels of the wood, thus killing the tree.

Although research on preventing Dutch elm disease has not been fully successful, the disease is now better understood as are the intricate relationships between the host tree and the beetle and fungus that attack it. Thus methods that apparently have promise in controlling Dutch elm disease include the early (but still necessary) control methods—removing the diseased tree and using insecticides to control the beetle (**50,310**). The control methods also include the possibility of using repellant chemicals that deter beetle feeding and are derived from tree species not attacked by the beetle (**13,119,120,240-243**); using systemic fungicides, e.g., benomyl and lignasan (**290,327**); and using pheromones (sex attractants) elicited by the female beetle for baiting traps (**248,249,366**).

Because of the intricate relation of extractives chemistry to Dutch elm disease, the extractives of the elms are important. Elm wood extractives (**197**) and the extractives chemistry of the Ulmaceae (**143**) have been reviewed. The general chemistry of the bark has been investigated (**55**). The characteristic compounds isolated thus far from this family include a mucilage from the bark, flavanoids, tannins, lignans (table 4), aromatic sequiterpenes (table 5), sterols, and triterpenes. The structure of the bark mucilage of *Ulmus rubra* has been studied (**26,27**) as has the hemicellulose obtained from *U. americana* wood (**121**). Although neither the wood nor the bark of the Ulmaceae reviewed here was reported to contain significant amounts of tannin (**304**); the bark of *C. occidentalis* has been used as a tanbark, and that of the elms at one time as a source of dyes and tannins (**221**). The bark tannins of European elms contained leucoanthocyanidins and catechin units (**21**).

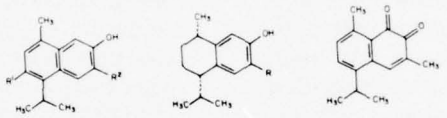


(1) R = CH_2OH
(2) R = COOH
(3) R = H
(4) R = rhamnoside

Table 4.—Lignans in Ulmus heartwood

Compound	*Ulmus* species[1]					
	alata	*americana*	*crassifolia*	*rubra*	*serotina*	*thomasii*
Thomasic Acid (1)	+	–	±	–	+	+ + +
Thomasidioic Acid (2)	+	–	–	–	±	+
Lyoniresinol (3)	±	–	±	–	+	+ + +
(+)-*Lyoniresinol-2a-O*-rhamnoside (4)	+	–	+	–	+ +	+ +

[1] –, Not detected; ±, possibly minute amounts; +, small amounts; + +, moderate amounts; + + +, major amounts.



(1) R^1 = H, R^2 = COH
(2) R^1 = CH_3O, R^2 = CHO
(3) R^1 = H, R^2 = CH_3
(4) R = CHO
(5) R = CH_3
(6)

Table 5.—Sesquiterpenes in Ulmus heartwood

Compound	*Ulmus* species[1]					
	alata	*americana*	*crassifolia*	*rubra*	*serotina*	*thomasii*
7-Hydroxycadalenal (1)	–	–	±	+ + +	–	–
7-Hydroxy-3-methoxycadalenal (2)	–	–	–	+	–	–
7-Hydroxycadalene (3)	–	+	–	+	–	±
(-)-7-Hydroxycalamenenal (4)	±	–	±	+ +	–	–
(-)-7-Hydroxycalamenene (5)	+ +	+ + +	+ +	+	+ +	+ + +
Mansonone C (6)	–	+ +	±	–	+	±

[1] –, Not detected; ±, possibly minute amounts; +, small amounts; + +, moderate amounts; + + +, major amounts.

The extractives of *Ulmus thomasii* heartwood contained the lignans (table 4), thomasic acid, thomasidioic acid, lyoniresinol, and (+)-lyoniresinol-2a-*O*-rhamnoside (**157,312**), as well as 6-hydroxy-5,7-dimethoxy-2-napthoic acid (**59**), 6-hydroxy-3-hydroxymethyl-5,7-dimethoxy-2-napthoic acid lactone (**59**), and 2,6-dimethoxy-*p*-benzoquinone (**157**). The napthoic acids and the benzoquinone can be regarded as *in vivo* cleavage products of thomasic acid. The original structure proposed for thomasic acid (**312**), responsible for the fluorescence of wet *U. thomasii* wood, was revised (**157,370**).

Furniture manufacturers have repeatedly experienced difficulties with a yellow-colored stain in their finishes on *Ulmus rubra* wood. (See cover) This yellow color will even migrate into vinyl plastic overlays. Research on this staining showed that the compound responsi-

ble for the yellow discoloration was the new, lipophilic sesquiterpene, 7-hydroxycadalenal. This compound is accompanied by a series of related sesquiterpenes, 7-hydroxy-3-methoxycadalenal, 7-hydroxycadalene, and (-)-7-hydroxycalamenenal (**106**). The yellow stain is deepest in outer heartwood. Bleaching the wood with peroxide oxidizes the yellow sesquiterpene found at the wood surface to a colorless compound. However, because of the slight volatility of the sesquiterpene, the yellow stain returns as sesquiterpene slowly migrates from the interior of the wood to the wood surface. 7-Hydroxycalamenene, first isolated from *U. thomasii* (**302**), apparently is ubiquitous in elm heartwood (**303**). Mansonone *C* has also been detected in heartwood of various elms (**303**).

7-Hydroxycalamene and 7-hydroxcadalene were found toxic to many micro-organisms and are produced in *Ulmus americana* in response to wounding (**15**). The total phenolic content among the various elm species can apparently be correlated with their susceptibility to Dutch elm disease (**303**). The free sterols found in *Ulmus thomasii* heartwood contained large amounts of sitosterol, and smaller amounts of cholesterol, campesterol, stigmasterol, 24-methylenelophenol, and citrostadienol. The free sterols of *U. rubra* were similar except 24-methylenelophenol was not detected. The esterified sterols from *U. rubra* were mostly sitosterol and citrostadienol with lesser amounts of the other sterols except stigmasterol. Sitosterol and campesterol also were found in *U. americana* (**303**). Saponification of the esters obtained from *U. rubra* heartwood gave wax alcohols, fatty acids, and dolichols (dihydro-*cis*-betulaprenol-5) in addition to the various sterols mentioned (**106**). This was the first reported occurrence of dolichols in a plant species.

The extractives in the bark of *Ulmus americana* have been investigated with particular emphasis on Dutch elm disease. Thus lupeyl cerotate and catechin-7-β-xylopyranoside (**86,89**) as well as friedelan-3β-ol (**12**) have been reported to stimulate feeding of the smaller European elm bark beetle. Interestingly, juglone, which can be isolated from shagbark hickory (*Carya ovata*), as well as other napthoquinones deter bark beetles from feeding (**120,240-242**). Chemical deterrents to elm bark beetle feeding have also been found in another nonhost tree, the white oak (*Quercus alba*) (**119**). Several sugars in elm bark failed to stimulate feeding (**243**).

The elm bark beetle aggregation pheromone is composed of three components: (-)-4-Methyl-3-heptanol; 2-*endo*,4-*endo*-dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane (multistriatin); and (-)-α-cubebene (**249**). α-Cubebene is a naturally occurring sesquiterpene in elm bark. Structurally multistriatin, the synthesis of which was recently reported (**53**), is closely related to frontalin, an aggregating pheromone of the southern pine beetle (**228**), and brevicomin, the principal component of the western pine beetle pheromone (**23**). Bait tests with a mixture of the synthetic pheromones of elm bark beetle (multilur) have been successful in Europe (**366**).

This Review concludes with the elms. This is fortunate because the research on this species, especially the inclusion of Dutch elm disease, exemplifies the intricate relationships that wood and bark extractives can have in utilization and preservation of trees. The work on this species also demonstrates a need for further research in extractives chemistry.

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Literature Cited

1. Abdusamatov, A., R. Ziyaev, and S. Yu. Yunusov.
   1974. Alkaloids of *Liriodendron tulipifera* wood. Khim. Prir. Soedin. 10(1):112-113.

2. Abdusamatov, A., R. Ziyaev, and S. Yu. Yunusov.
   1975. Alkaloids of *biodendron tulipifera*. Khim. Prir. Soedin. 11(6):812-814.

3. Abramovitch, R. A., and O. A. Koleoso.
   1966. Some steam volatile components of the extractives from *Populus tremuloides* heartwood. Can. J. Chem. 44:2913-2915.

4. Abramovitch, R. A., and R. G. Micetich.
   1963. Extractives from *Populus tremuloides* heartwood. The triterpene alcohols. Can. J. Chem. 41:2362-2367.

5. Abramovitch, R. A., R. T. Coutts, and E. E. Knaus.
   1967. Some extractives from the bark of *Populus balsamifera*. Can. J. Pharm. Sci. 2:71-74.

6. Abramovitch, R. A., R. G. Micetich, and S. J. Smith.
   1963. Extractives from *Populus tremuloides* (aspen poplar) heartwood. Tappi 46:37-40.

7. Acosta Solis, M.
   1959. The mangroves of Ecuador. Contrib. Inst. Ecuatoriano de Cienc. Nat. Quito, 29.

8. Adams, G. A.
   1964. Water-soluble polysaccharides of sugar maple. Svensk Papperstidn. 67(3):82-88.

9. Adams, G. A., and C. T. Bishop
   1960. Constitution of an arabinogalactan from maple sap. Can. J. Chem. 38:2380-2386.

10. Ahn, B. Z.
    1974. Catechin trimer from oak bark. Arch. Pharm. 307(3):186-197. Weinheim, Ger.

11. Allison, F. E.
    1965. Decomposition of wood and bark sawdusts in soil: Nitrogen requirement and effects on plants. 58 p. USDA, ARS Tech. Bull. 1332.

12. Baker, J. E., and D. M. Norris.
    1967. A feeding stimulant for *Scolytus multistriatus* isolated from the bark of *Ulmus americana*. Ann. Entomol. Soc. Amer. 60:1213-1215.

13. Baker, J. E., D. P. Rainey, D. M. Norris, and F. N. Strong.
    1968. *p*-Hydroxybenzaldehyde and other phenolics as feeding stimulants for the smaller European bark beetle. Forest Sci. 14:91-95.

14. Baldwin, S., R. A. Black, A. A. Andreasen, and S. L. Adams.
    1967. Aromatic congener formation in maturation of alcohol distillates. Agric. Food Chem. 15:381-385.

15. Balsillie, D.
    1972. The formation of heartwood phenols in red pine (*Pinus resinosa* Ait.) and white elm (*Ulmus americana* L.) Ph.D. thesis, Univ. Toronto, Toronto, Ont.

16. Barnes, R. A., and N. N. Gerber.
    1955. The antifungal agent from Osage orange wood. J. Amer. Chem. Soc. 77:3259-3262.

17. Barton, D.H.R., D. S. Bhakuni, G. M. Chapman, and G. W. Kirby.
    1967. Phenol oxidation and biosynthesis. Part XV. The biosynthesis of roemerine, anonaine, and mecambrine. J. Chem. Soc.:2134-2140.

18. Bates, R. B., A. D. Brewer, B. R. Knights, and J. W. Rowe.
    1968. Double bond configurations of 24-ethylidine sterols. Tetrahedron Lett. 59:6163-6167.

19. Bate-Smith, E. C.
    1975. Phytochemistry of proanthocyanidins. Phytochemistry 14:1107-1113.

20. Bate-Smith, E. C., and N. H. Lerner.
1954. Leuco-anthocyanins 2. Systematic distribution of leuco-anthocyanins in leaves. Biochem. J. 58:126-132.

21. Bednarska, D.
1963. Tannin content of domestic species of the genus *Ulmus*. III. Chromatographic analysis. Diss. Pharm. 15:87-93.

22. Beebe, C. W., F. P. Luvisi, and M. L. Happich.
1953. Tennessee Valley oak bark as a source of tannin. J. Amer. Leather Chem. Assoc. 48:32-41.

23. Bellas, T. E., R. G. Brownlee, and R. M. Silverstein.
1969. Synthesis of brevicomin, principal sex attractant in the frass of the female western pine beetle. Tetrahedron 25:5149-5153.

24. Bergman, J.
1965. Yellowing of pulp extractives. Svensk Papperstidn. 68(9):339-347.

25. Bergman, J., B. O. Lindgren, and C. Svahn.
1965. Triterpenes and α-methylsterols in birchwood. Acta Chem. Scand. 19(7):1661-1666.

26. Beveridge, R. J., J.K.N. Jones, R. W. Lowe, and W. A. Szarek.
1971. Structure of slippery elm mucilage (*Ulmus fulva*). J. Polymer Sci. (C. Polym. Symp.) 36:461-466.

27. Beveridge, R. J., J. F. Stoddart, W. A. Szarek, and J.K.N. Jones.
1969. Some structural features of the mucilage from the bark of *Ulmus fulva* (slippery elm mucilage). Carbohydr. Res. 9:429-439.

28. Bhargava, U. C.
1967. Pharmacology of ellagic acid from black walnut. Ph.D. thesis, Univ. Miss., 366 p.

29. Bhargava, U. C., and B. A. Westfall.
1968. Antitumor activity of *Juglas nigra* (black walnut) extractives. J. Pharm. Sci. 57(10):1674-1677.

30. Bick, I.R.C., J. Harley-Mason, N. Sheppard, and M. J. Vernengo.
1961. Structural correlations in the nuclear magnetic resonance spectra of bisbenzylisoquinoline and aporphine alkaloids. J. Chem. Soc.: 1896-1903.

31. Biessels, H.W.A., A. C. van der Kerk-van Hoof, J. J. Kettenes-van den Bosch, and C. A. Salemink.
1974. Triterpenes of *Prunus serotina* and *P. lusitanica*. Phytochemistry 13:203-207.

32. Bilbruck, J. D.
1959. Toxicity of oak heartwood and oak heartwood water extracts to the oak wilt fungus. Plant Dis. Reporter 43(8):936-941.

33. Binns, W. W., G. Blunden, and D. L. Woods.
1968. Distribution of leucoanthocyanins, phenolic glycosides and imino-acids in leaves of *Salix* species. Phytochemistry 7:1577-1581.

34. Binotto, A. P., and W. K. Murphy.
1975. Season and height variation in extractives and cell wall components of chestnut oak bark. Wood Sci. 7(3):185-190.

35. Bjeldanes, L. F., and G. W. Chang.
1977. Mutagenic activity of quercetin and related compounds. Science 197:577-578.

36. Black, R. A., A. A. Rosen, and S. L. Adams.
1953. The chromatographic separation of hardwood extractive components giving color reactions with phloroglucinol. J. Amer. Chem. Soc. 75:5344-5346.

37. Borchert, P., J. A. Miller, E. C. Miller, and T. K. Shires.
1973. 1′-Hydroxysafrole, a proximate carcinogenic metabolite of safrole in the rat and mouse. Cancer Res. 33:590-600.

38. Borchert, P., P. G. Wislocki, J. A. Miller, and E. C. Miller.
1973. The metabolism of the naturally occurring hepatocarcinogen safrole to 1′-hydroxysafrole and the electrophilic reactivity of 1′-acetoxysafrole. Cancer Res. 33:575-589.

39. Bridle, P., K. G. Stott, and C. F. Timberlake.
1970. Anthocyanins in *Salix* species. Phytochemistry 9:1097-1098.

40. Briggs, L. H., R. C. Cambie, and R.A.F. Couch.
1968. Lirioresinol-C dimethyl ether, a diaxially substituted 3,7-dioxabicyclo [3,3,0] octane lignan from *Macropiper excelsum* (Forst. f.) Miq. J. Chem. Soc. (C):3042-3045.

41. Buch, M. L.
1960. A bibliography of organic acids in higher plants. USDA Agric. Res. Serv. Agric. Handb. 164, U.S. Gov. Print. Off., Washington, D.C.

42. Buchalter, L.
1968. Identification of monomeric and polymeric 5,7,3′,4′-tetrahydroxyflavan-3,4-diol from tannin extract of wild cherry bark USP, *Prunus serotina*. J. Pharm. Sci. 58:1272-1273.

43. Buchanan, M. A., and E. E. Dickey.
1960. Liriodenine, a nitrogen-containing pigment of yellow poplar heartwood (*Liriodendron tulipifera* L.). J. Org. Chem. 25:1389-1391.

44. Buchanan, M. A., S. L. Burson, Jr., and C. H. Springer.
1961. The neutral fatty materials in paper birchwood, *Betula papyrifera* Marsh. Tappi 44:576-580.

45. Buchanan, M. A., R. V. Sinnett, and J. A. Jappe.
1959. The fatty acids of some American pulpwoods. Tappi 42:578-583.

46. Büchi, G., and R. E. Manning.
1962. Constitution of verbenalin. Tetrahedron 29:1049-1059.

47. Butin, H., and V. Loeschke.
1960. Fungistatic substances in the bark of various poplars. Naturwissenschaften 47:451-452.

48. Cahen, R., and C. Hirsch.
1960. Pharmacodynamic study on the sapwood of *Tilia cordata*. C. R. Acad. Sci. 251:161-163. Paris.

49. Cahen, R., C. Hirsch, and A. Pessonnier.
1960. Pharmacodynamic study of sapwood of *Tilia cordata:* Merchanism of the intestinal spasmolytic effect. C. R. Acad. Sci. 251:1433-1435. Paris.

50. Cannon, W. N., Jr., and D. P. Worley.
1976. Dutch elm disease control: Performance and cost. USDA For. Serv. Res. Pap. NE-345.

51. Carruthers, W. R., R. H. Farmer, and R. A. Laidlaw.
1957. Dihydromorin from east African mulberry (*Morus lactea* Mildbr.). J. Chem. Soc.: 4440-4444.

52. Carter, F. L., A. M. Garlo, and J. B. Stanley.
Termiticidal components of wood extracts: 7-Methyljuglone from *Diospyros virginiana*. J. Agr. Food Chem. [In press.]

53. Cernigliaro, G. J., and P. J. Kocienski.
1977. A synthesis of (-)-α-multistriatin. J. Org. Chem. 42:3622-3624.

54. Chadenson, M., L. Molho-Lacroix, D. Molho, and C. Mentzer.
1955. Flavonoid constituents of locust (*Gleditsia triacanthos*). Compt. Rend. 249:1362-1364.

55. Chang, Y.-P., and R. L. Mitchell.
1955. Chemical composition of common North American pulpwood barks. Tappi 38:315-320.

56. Chari, V. M., S. Neelakantan, and T. R. Seshadri.
1968. Chemical components of *Betula utilis* and *Celtis australis*. Indian J. Chem. 6:231-234.

57. Chen, C.-L.
1970. Constituents of *Quercus alba*. Phytochemistry 9:1149.

58. Chen, C.-L., and H.-M. Chang.
Lignans and aporphine alkaloids in bark of *Liriodendron tulipifera*. Phytochemistry. [In press.]

59. Chen, C.-L., and F. D. Hostetter.
1969. Phenolic constituents of elm wood. 2-Naphthoic acid derivatives from *Ulmus thomasii*. Tetrahedron 25:3223-3229.

60. Chen, C.-L., H.-M. Chang, and E. B. Cowling.
1976. Aporphine alkaloids and lignans in heartwood of *Liriodendron tulipifera*. Phytochemistry 15:547-550.

61. Chen, C. R., J. L. Beal, R. W. Doskotch, L. A. Mitscher, and G. H. Svoboda.
1974. Phytochemical study of *Doryphora sassafras*. II. Isolation of eleven crystalline alkaloids from the bark. Lloydia 37(3):493-500.

62. Chen, C.-L., H.-M. Chang, E. B. Cowling, C.-Y. Huang Hsu, and R. P. Gates.
1976. Aporphine alkaloids and lignans formed in response to injury of sapwood in *Liriodendron tulipifera*. Phytochemistry. 15:1161-1167.

63. Chowdhury, B. K., M. L. Sethi, H. A. Lloyd, and G. J. Kapadia.
1976. Aporphine and tetrahydrobenzylisoquinoline alkaloids in *Sassafras albidum*. Phytochemistry 15:1803-1804.

64. Chu, J.-H., S.-H. Hung, and Y.-H. Wang.
1958. Glucosides of the Chinese drug, Chen-Pi-Ying (*Ilex*). Hua Hsueh Hsueh Pao 22:128-132.

65. Clapham, A. R., J. G. Tutin, and E. F. Warburg.
1962. Flora of the British Isles, 2d ed. Cambridge Univ. Press, Cambridge.

66. Clausen, K. E.
1963. Characteristics of a hybrid birch and its parent species. Can. J. Bot. 41:441-458.

67. Clermont, L. P.
1961. The fatty acids of aspen, poplar, basswood, yellow birch, and white birch. Pulp Paper Mag. Can. 62:T511-T514.

68. Cohen, J., W. von Langenthal, and W. I. Taylor.
1961. The alkaloids of *Liriodendron tulipifera* L. The structure and synthesis of the unnamed yellow alkaloid and the isolation of D-glaucine. J. Org. Chem. 26(10):4143-4144.

69. Cooke, G. B.
1961. Cork and the cork tree. Int. Ser. Monogr. Pure and Appl. Biol., Vol. 4. 121 p. Pergamon Press, New York.

70. Cooper, G. A.
1971. Black walnut extractives availability is influenced by thawing-to-extraction time. For. Prod. J. 21(10):44-45.

71. Cotterill, P. J., and F. Scheinmann.
1975. A revised structure for toxyloxanthone. J. Chem. Soc. (Chem. Comm.): 664-665.

72. Crown, H.
1962. Storax is magic word for Alabama tree farmers. For. World, p. 31-32. (Oct.-Nov.)

73. Czaninski, Y.
1965. Application of the Baker method to show the phospholipids and chondriome in some plant tissues. C. R. Acad. Sci. 261(14):2705-2708. Paris.

74. Davis, D. J., D. Wiese, and J. P. Rosazza.
1977. Microbial transformations of glaucine. J. Chem. Soc. (Perkin I): 1-6.

75. Deshpande, V. H., D. C. Parthasarathy, and K. Venkataraman.
1968. Four analogues of artocarpin and cycloartocarpin from *Morus alba*. Tetrahedron Lett.: 1715-1719.

76. Deshpande, V. H., R. Srinivasan, and A.V.R. Rao.
1975. Wood phenolics of *Morus* species. IV. Phenolics of the heartwood of five *Morus* species. Indian J. Chem. 13:453-457.

77. Deshpande, V. H., P. V. Wakharkar, and A.V.R. Rao.
1976. Wood phenolics of *Morus* species: part V—Isolation of a new flavone, mulberranol, and a novel phenol, alboctalol, from *Morus alba*. Indian J. Chem. 14B:647-650.

78. Deshpande, V. H., A.V.R. Rao, M. Varadan, and K. Venkataraman.
1973. Wood and bark phenolics of *Maclura pomifera:* Four new xanthones. Indian J. Chem. 11:518-524.

79. Deshpande, V. H., A.V.R. Rao, K. Venkataraman, and P. V. Wakharkar.
1974. Wood phenolics of *Morus* species: Part III—Phenolic constituents of *Morus rubra* bark. Indian J. Chem. 12:431-436.

80. Devon, T. K., and A. I. Scott.
1972-75. Handbook of naturally occurring compounds. Vols. I, II. Academic Press, New York.

81. Dhar, D. N.
1968. Chemistry and biochemistry of walnut trees. Mono. 54 p. (Eng.) Indian Inst. Technol., Kanpur, India.

82. Dickey, E. E.
1958. Liriodendrin, a new lignan diglucoside from the inner bark of yellow poplar (*Liriodendron tulipifera* L.). J. Org. Chem. 23:179-184.

83. Doskotch, R. W., and F. S. El-Feraly.
1969. Antitumor agents II. Tulipinolide, a new germacranolide sesquiterpene, and costunolide. Two cytotoxic substances from *Liriodendron tulipifera.* J. Pharm. Sci. 58:877-880.

84. Doskotch, R. W., and F. S. El-Feraly.
1970. Antitumor agents IV. Structure of tulipinolide and epitulipinolide cytotoxic sesquiterpenes from *Liriodendron tulipifera* L. J. Org. Chem. 35:1928-1936.

85. Doskotch, R. W., and M. S. Flom.
1972. Acuminatin, a new *bis*-phenylpropide from *Magnolia acuminata* L. Tetrahedron 28:4711-4717.

86. Doskotch, R. W., S. K. Chatterji, and J. W. Peacock.
1970. Elm bark derived feeding stimulants for the smaller European elm bark beetle. Science 167:380-382.

87. Doskotch, R. W., C. D. Hufford, and F. S. El-Feraly.
1972. Antitumor agents. VI. Sesquiterpene lactones tulipinolide and epitulipinolide from *Liriodendron tulipifera* J. Org. Chem. 37:2740-2744.

88. Doskotch, R. W., S. L. Keely, Jr., and C. D. Hufford.
1972. Lipiferolide, a cytotoxic germacranolide, and γ-liriodenolide, two new sesquiterpene lactones from *Liriodendron tulipifera.* J. Chem. Soc. (Chem. Comm.): 1137-1138.

89. Doskotch, R. W., A. A. Mikhail, and S. K. Chatterji.
1973. Structure of the water-soluble feeding stimulant for *Scolytus multistriatus:* A revision. Phytochemistry 12:1153-1155.

90. Doskotch, R. W., F. S. El-Feraly, E. H. Fairchild, and C.-T. Huang.
1976. Peroxyferolide: A cytotoxic germacranolide hydroperoxide from *Liriodendron tulipifera.* J. Chem. Soc. (Chem. Comm.): 402-403.

91. Doskotch, R. W., F. S. El-Feraly, E. H. Fairchild, and C.-T. Huang.
1977. Isolation and characterization of peroxyferolide, a hydroperoxy sesquiterpene lactone from *Liriodendron tulipifera.* J. Org. Chem. 42:3614-3618.

92. Doskotch, R. W., S. L. Keely, Jr., C. D. Hufford, and F. S. El-Feraly.
1975. New sesquiterpene lactones from *Liriodendron tulipifera.* Phytochemistry 14:769-773.

93. Drost, K., M. Olszak, and L. Skrzypczak.
1967. Kaempferol 7-glucoside from *Maclura aurantiaca.* Planta Med. 15:264-268.

94. Douglas, G. K., and K. G. Lewis.
1966. Triterpene constituents of Osage orange, *Maclura pomifera.* Aust. J. Chem. 19:175-178.

95. Ekimova, T., N. Gerasimova, and M. Pesheva.
1964. Determination of the influence of sulfites on the extraction of tannins from oakwood (*Quercus conferta*) and oak bark (*Quercus sessiliflora*) and on the quality of extracts obtained. Khim.-Ind. 36(3):90-95. Sofia.

96. El-Feraly, F. S., Y.-M. Chan, E. H. Fairchild, and R. W. Doskotch.
1977. Peroxycostunolide and peroxyparthenolide two cytotoxic germacranolide hydroperoxides from *Magnolia grandiflora*. Structural revision of verlotorin and artemorin. Tetrahedron Lett.: 1973.

97. Erickson, R. L., I. A. Pearl, and S. F. Darling.
1970. Further investigations of the hot water extractives of *Populus grandidentata* Michx. bark. Tappi 53:240-244.

98. Erickson, R. L., I. A. Pearl, and S. F. Darling.
1970. Populoside and grandidentoside from the bark of *Populus grandidentata*. Phytochemistry 9:857-863.

99. Estes, T. K., and I. A. Pearl.
1967. Hot water extractives of the green bark of *Populus trichocarpa*. Tappi 50:318-324.

100. Ewart, M. H., D. Siminovitch, and D. R. Briggs.
1954. The chemistry of the living bark of the black locust in relation to its frost hardiness. VIII. Possible enzymic processes involved in starch-sucrose interconversions. Plant Physiol. 29:407-413.

101. Faber, H. B., Jr.
1960. The methanol extractable aromatic materials in the inner bark of *P. tremuloides*. Tappi 43:406-413.

102. Fallas, A. L., and R. H. Thomson.
1968. Ebenaceae extractives. Part III. Binaphtaquinones from *Diospyros* species. J. Chem. Soc. (C):2279-2282.

103. Farnsworth, N. R., R. N. Blomster, M. W. Quimby, and J. W. Schermerhorn, eds.
1969-1974. The Lynn index. A bibliography of phytochemistry. Vols. VI-VIII. 412 p. Coll. Pharm., Univer. Ill., Chicago, Ill. 60612.

104. Fieser, L. F., and M. Fieser.
1959. Steroids. Reinhold Publishing Corp. New York.

105. Filer, T. H., Jr.
1973. Suppression of elm phloem necrosis symptoms with tetracycline antibiotics. Plant Dis. Rep. 57:341-343.

106. Fracheboud, M., J. W. Rowe, R. W. Scott, S. M. Fanega, A. J. Buhl and J. K. Toda.
1968. New sesquiterpenes from yellow wood of slippery elm. For Prod. J. 18:37-40.

107. Frei, J. K.
1972. Effect of bark extractives on orchids. Ph.D. thesis, Univ. of Miami, [Fla.]

108. Freudenberg, K., and L. Hartmann.
1953. Constituents from *Robinia pseudoacacia*. Naturwissenschaften 40:413.

109. Friedrich, H., and E. Zeruhn.
1971. Occurrence of coumarins in the bark of *Aesculus* varieties. Pharm. Weekbl. 106(12):198-206.

110. Fujimoto, H., and T. Higuchi.
1977. Biosynthesis of liriodendron by *Liriodendron tulipifera*. Wood Res. Bull., Wood Res. Inst., Kyoto Univ., 62, p. 1-10.

111. Fujimoto, H. and T. Higuchi.
1977. Lignans from the bark of yellow poplar (*Liriodendron tulipifera* L.). J. Jap. Wood Res. Soc. 23:405-410.

112. Fujita, S., and Y. Fujita.
1974. Miscellaneous contributions to the essential oils of the plants from various territories. XXXIV. Comparative biochemical and chemotaxonomical studies of the essential oil of *Magnolia salicifolia*. II. Chem. Pharm. Bull. 22(3): 707-709.

113. Fujita, M., H. Itokawa, and Y. Sashida.
1973. Components of *Magnolia obovata*. I. Components of the essential oil of the bark. J. Pharm. Soc. Japan 93(4):415-421.

114. Fujita, M., H. Itokawa, and Y. Sashida.
1973. Components of *Magnolia obovata*. II. Components of the methanol extract of the bark. J. Pharm. Soc. Japan 93(4): 422-428.

115. Fujita, M., H. Itokawa, and Y. Sashida.
1973. Components of *Magnolia obovata*. III. Occurrence of magnolol and honokiol in *M. obovata* and other allied plants. J. Pharm. Soc. Japan 93(4):429-434.

116. Geissman, T. A.
1962. The chemistry of flavonoid compounds. 666 p. Macmillan Co., New York.

117. Gerry, E.
1921. American storax production: Results of different methods of tapping red gum trees. J. For. 19(1):1-10.

118. Gibbs, R. D.
1974. Chemotaxonomy of flowering plants. Vols. I-IV. McGill-Queens Univ. press, Montreal.

119. Gilbert, B. L., and D. M. Norris.
1968. A chemical basis for bark beetle (*Scolytus*) distinction between host and nonhost trees. J. Insect Physiol. 14:1063-1068.

120. Gilbert, B. L., J. E. Baker, and D. M. Norris.
1967. Juglone (5-Hydroxy-1,4-Napthoquinone) from *Carya ovata*, a deterrent to feeding by *Scolytus multistriatus*. J. Insect Physiol. 13:1453-1459.

121. Gillham, J. K., and T. E. Timell.
1958. The hemicellulose of white elm (*Ulmus americana*) 1. Identification of 2-O-(4-*O*-methyl-*D*-glucopyranosyluronic acid)-*D*-xylopyranose. Can. J. Chem. 36:410-413.

122. Gottlieb, O. R.
1972. Chemosystematics of the Lauraceae. Phytochemistry. 11:1537-1570.

123. Gough, D. P., and F. W. Hemming.
1970. The stecochemistry of betulaprenol biosynthesis. Biochem. J. 117:309-317.

124. Grosjean, J.
1950. Substances with fungicidal activity in the bark of deciduous trees. Nature 165:853-854.

125. Guenther, E.
1952. The essential oils. Vol. 5. p. 254. van Nostrand, New York.

126. Gupta, S. R., B. Ravindranath, and T. R. Seshadri.
1972. Polyphenols of *Juglans nigra*. Phytochemistry. 11:2634-2636.

127. Happich, M. L., C. W. Beebe, and J. S. Rogers.
1954. Tannin evaluation of one hundred sixty-three species of plants. J. Amer. Leather Chem. Assoc. 49:760-773.

128. Haq, S., and G. A. Adams.
1961. Oligosaccharides from the sap of sugar maple. Can. J. Chem. 39:1165-1170.

129. Haq, S., and G. A. Adams.
1962. Oligosaccharides of birch sap. Can. J. Biochem. Physiol. 40:989-999.

130. Harborne, J. B.
1963. Comparative biochemistry of the Leguminosae. Nature 200:1055-1056.

131. Harborne, J. B.
1977. Flavonoids and the evolution of the angiosperms. Biochem. Syst. Ecol. 5:7-22.

132. Harborne, J. B., D. Boulter, and B. L. Turner.
1971. Chemotaxonomy of the Leguminosae. 612 p. Academic Press, New York.

133. Harborne, J. B., T. J. Mabry, and H. Mabry, eds.
1975. The flavonoids. Vols. I,II. Academic Press, New York.

134. Harkin, J. M., and J. W. Rowe.
1971. Bark and its possible uses. USDA For. Serv. Res. Note FPL-091, For. Prod. Lab., Madison, Wis.

135. Hart, J. H.
1968. Morphological and chemical differences between sapwood, discolored sapwood, and heartwood in black locust and Osage orange. For. Sci. 14(3):334-338.

136. Hasegawa, M.
1958. On the flavonoids contained in *Prunus* woods. J. Jap. For. Soc. 40:111-112.

137. Hasegawa, M., and T. Shirato.
1959. Abnormal constituents of *Prunus* wood: Isoolivil from the wood of *Prunus jamasakura*. J. Jap. For. Soc. 41:1-4.

138. Haslam, E.
1977. Symmetry and promiscuity in procyanidin biochemistry. Phytochemistry. 16:1625-1640.

139. Haslam, E., C. T. Opie, and L. J. Porter.
1977. Procyanidin metabolism—A hypothesis. Phytochemistry. 16:99-102.

140. Hass, H. B.
1977. Leaves of autumn. Chemtech 7(9):525-528.

141. Hathway, D. E.
1958. Oak-bark tannins. Biochem J. 70:34-42.

142. Hathway, D. E.
1959. Experiments on the origin of oak-bark tannin. Biochem. J. 71:533-537.

143. Hegnauer, R.
1964-1973. Chemotaxonomie der Pflanzen, Vols. 3-6. Birkhaeuser Verlag, Basel and Stuttgart.

144. Hemming, F. W.
1967. Polyisoprenoid alcohols (prenols). *In* Terpenoids in plants, J. B. Pridham, ed., p. 223-239, Academic Press, New York.

145. Hemmingway, R. W.
1969. Thermal instability of fats relative to surface wettability of yellow birchwood (*Betula lutea*). Tappi 52:2149-2155.

146. Hickok, L. G., and J. C. Anway.
1972. A morphological and chemical analysis of geographical variation in *Tilia* L. of eastern North America. Brittonia 24:2-8.

147. Hijwegen, T.
1973. Autonomous and induced pterocarpanoid formation in the Leguminosae. Phytochemistry. 12:375-380.

148. Hillis, W. E.
1962. Wood extractives and their significance to the pulp and paper industries. 513 p., Academic Press, New York.

149. Hillis, W. E.
1977. Secondary wood changes and the involvement of ethylene. *In* Recent advances in phytochemistry. Vol. II, F. A. Loewus and V. C. Runeckles, eds. Plenum Press, New York.

150. Hillis, W. E., and T. Swain.
1959. Phenolic constituents of *Prunus domestica*. III. Identification of the major constituents in the tissues of victoria plum. J. Sci. Food Agr. 10:533-537.

151. Hoke, M., and R. Hansel.
1972. A new investigation on sassafras root. Arch. Pharm. 305:33-39.

152. Holmbom, B., and E. Avela.
1971. Studies on tall oil from pine and birch. Acta Acad. Aboe., Ser. B 31(13):1-14.

153. Hoover, J. D., S. H. Wender, and E. G. Smith.
1977. Effect of phenolic compounds on glucose-6-phosphate dehydrogenase isoenzymes. Phytochemistry 16:199-201.

154. Horvath, T.
1968. Therapeutic utilization of *Aesculus hippocastianum*. I. Chemistry of the active compounds. Rev. Med. 14(1):75-79. Targu-Mures.

155. Hossfeld, R. L., and W. T. Hunter.
1956. The petroleum ether extractives of aspen bark. Tappi 41:359-362.

156. Hossfeld, R. L., and F. H. Kaufert.
1957. Structure and composition of aspen bark. For. Prod. J. 7:437-439.

157. Hostettler, F. D., and M. K. Seikel.
1969. Lignans of *Ulmus thomasii* heartwood. II. Lignans related to thomasic acid. Tetrahedron 25:2325-2337.

158. Huang Hsu, C.-Y.
1976. M.S. Thesis, North Carolina State University, Raleigh.

159. Hubbes, M.
1962. Inhibition of *Hypoxylon pruinatum* by pyrocatechol isolated from bark of aspen. Science 136:156.

160. Hufford, C. D.
1976. Four new *N*-acetylnoraporphine alkaloids from *Liriodendron tulipifera*. Phytochemistry 15:1169-1171.

161. Hufford, C. D., and J. J. Funderburk.
1974. Nonbasic aporphine alkaloids from *Liriodendron tulipifera*. J. Pharm. Sci. 63(8):1338-1339.

162. Hufford, C. D., M. J. Funderburk, J. M. Morgan, and L. W. Robertson.
1975. Two antimicrobial alkaloids from heartwood of *Liriodendron tulipifera* L. J. Pharm. Sci. 64(5):789-792.

163. Huneck, S.
1963. Triterpene acids of *Liquidambar orientalis*. Tetrahedron 19:479-482.

164. Huystee, R. B. van.
1965. Cold acclimation and accompanying metabolic changes in red-osier dogwood with emphasis on proteins. Diss. Abstr. 25(9):4898-4899.

165. Imamura, H., and M. Suda.
1962. Wood extractives. III. Constituents of *Catalpa ovata* wood., J. Jap. Wood Res. Soc. 8:127-130.

166. Inouye, H., T. Okuda, and T. Hayashi.
1971. Naphthoquinone derivatives from *Catalpa ovata* G. Don. Tetrahedron Lett. 39:3615-3618.

167. Isenberg, I. H., M. A. Buchanan, and L. E. Wise.
1946, 1957. Extraneous components of American pulpwoods. Pap. Ind. 28:816-822; 38:945-946, 1042-1046, 1098.

168. Jacques, D., E. Haslam, G. R. Bedford, and D. Greatbanks.
1974. Plant proanthocyanidins. Part II. Proanthocyanidin-A2 and its derivatives. J. Chem. Soc. (Perkin I):2663-2671.

169. Jayme, G., and H. Semmler.
1957. Production of tannin and pulp from young black locust wood. Das Pap. 11: 396-398.

170. Jensen, L. B., and J. E. Sherman.
1951. Antibiotic from the butternut tree as a food preservative. U. S. Pat. 2,550,268 (Apr. 24).

171. Jensen, S. R., A. Kjaer, and B. J. Nielsen.
1973. Dihydrocornin, a novel natural iridoid glucoside. Acta Chem. Scand. 27(7):2581-2585.

172. Jiang, K. S., and T. E. Timell.
1972. Polysaccharides in the bark of aspen (*Populus tremuloides*). II. Isolation and structure of an arabinan. Cellul. Chem. Technol. 6:499-502.

173. Jung, J., and M. Hubbes.
1965. Growth inhibition of *Bacillus cereus* in vitro by glycosidal substances extracted from bark of *Fraxinus*. Can. J. Bot. 43:469-474.

174. Kahila, S. K.
1966. Influence of birchwood extract on tall oil. Pap. Puu 48(11):677-679, 681-682.

175. Kahila, S. K.
1966. On the extractives of birch wood. Pap. Puu 48(9):529-534.

176. Darchesy, J. J., M. L. Laver, D. F. Barofsky, and E. Barofsky.
1974. Structure of oregonin, natural diarylheptanoid xyloside. J. Chem. Soc. (Chem. Comm.):649-650.

177. Karrer, W.
1977. Konstitution und Vorkommen der Organischen Pflanzenstoffe. 1,038 p. Birkhaeuser Verlag, Basel and Stuttgart.

178. KenKnight, G.
1952. Germination inhibiter in wood and bark of peach and wild *Prunus*. Phytopathology 42:285.

179. Kingsbury, J. M.
1964. Poisonous plants of the United States and Canada. Prentice-Hall, Inc., Englewood Cliffs, N.J.

180. Kirk, T. K., and K. Lundquist.
1970. Comparison of sound and white-rotted sapwood of sweetgum with respect to properties of the lignin and composition of extractives. Svensk Paperstidn. 73:294-306.

181. Klimczak, M., W. Kahl, and Z. Grodzinska-Zachwieja.
1972. Phenolic acids, derivatives of cinnamic acid, in plants. Diss. Pharm. Pharmacol. 24:181-185.

182. Kondo, Y., and T. Takemoto.
1973. New diglyceride from root-bark of *Morus alba* L. Chem. Pharm. Bull. 21:2265-2267.

183. Kondo, T., H. Ito, and M. Suda.
1957. Extractives from insect-infested woody tissue of *Acer negundo*. J. Jap. Wood Res. Soc. 3:151-153.

184. Kondo, T., H. Ito, and M. Suda.
1958. Wood extractives. VII. Wood components of *Morus bambycis*, Nippon Nogei-Kagaku Kaishi 32:1-4.

185. Koran, Z., and K.-C. Yang.
1972. Gum distribution in yellow birch. Wood. Sci. 5(2):95-101.

186. Kressman, F. W.
1914. Osage-orange—Its value as a commercial dyestuff. J. Ind. Eng. Chem. 6:462-464.

187. Krochmal, A., R. S. Walters, and R. M. Doughty.
1969. A guide to medicinal plants of Appalachia. USDA For. Serv. Res. Pap. NE-138, Northeast. Forest Exp. Sta., Upper Darby, Pa.

188. Kubota, T., and T. Hase.
1966. Constituents of *Robinia pseudoacacia*. I. Constituents of the heartwood of *Robinia pseudoacacia*. J. Chem. Soc. Jap., Pure Chem. Sect. 87(11):1201-1205.

189. Kulkarni, D. D., D. D. Ghugale, and R. Narasimhan.
1970. Chemical investigations of plant tissues grown *in vitro*: Isolation of β-sitosterol from *Morus alba* (mulberry) callus tissue. Indian J. Exp. Biol. 8:347.

190. Kull, U., and K. Jeremias.
1972. Fatty acid composition of saponifiable lipids from barks of *Populus balsamifera* during the course of a year. Z. Pflanzenphysiol. 68:55-62.

191. Kupchan, S. M., M. Takasugi, R. M. Smith, and P. S. Steyn.
1971. Tumor inhibitors. LXII. The structures of acerotin and acerocin, novel triterpene ester aglycones from the tumor inhibitory saponins of *Acer negundo*. J. Org. Chem. 36:1972-1976.

192. Lafon, L.
1962. Brit. Patent 912,971 (to Orsymonde, S.A.).

193. Lafon, L.
1962. U. S. Patent 3,030,271 (to Orsymonde, S.A.).

194. Laidlaw, R. A., and G. A. Smith.
1959. Heartwood extractives of some timbers of the family Moraceae. Chem. Ind.:1604-1605.

195. Lanuza, J. M. de.
1964. The cork of *Quercus suber*. Instit. For. Invest. Exper. 35:7-138. Madrid.

196. Levitin, N.
1970. Chemical composition of clear and mineral-stained maple. Bimon. Res. Notes, Environ. Can., For. Serv. 26(6):57.

197. Levitin, N.
1970. The extractives of birch, aspen, elm, and maple: Review and discussion. Pulp Pap. Mag. Can. 71(16):T361-T364.

198. Levitin, N.
1972. The coloring of mineral-stained maple. Wood Sci. 5(2):87-94.

199. Levitin, N.
1974. Bleaching mineral-stained maple. Forest Prod. J. 24(8):28-32.

200. Lillie, T. J., and O. C. Musgrave.
1977. Ebenaceae extractives. Part 7. Use of hydroxy-proton shifts of juglone derivatives in structure elucidation. J. Chem. Soc. (Perkin I):355-358.

201. Lillie, T. J., O. C. Musgrave, and D. Skoyles.
1976. Ebenaceae extractives. Part V. New diospyrin derivatives from *Diospyros montana* Roxb. J. Chem. Soc. (Perkin I):2155-2161.

202. Lillie, T. J., O. C. Musgrave, and D. Skoyles.
1976. Ebenaceae extractives. Part 6. Ehretione, a bisnaphthoquinone derived from plumbagin and 7-methyljuglone. J. Chem. Soc. (Perkin I):2546.

203. Lillie, T. J., O. C. Musgrave, and R. H. Thomson.
1973. Diosquinone, a naphthoquinoylnaphthoquinone epoxide. J. Chem. Soc. (Chem. Comm.):463-464.

204. Lindeberg, G.
1971. Aromatic substances in leaves of *Populus tremula* as inhibitors of mycorrhizal fungi. Physiol. plant. 25:122-129.

205. Lindgren, B. O.
1965. Homologous aliphatic 30-45C terpenols in birchwood. Acta Chem. Scand. 19(6):1317-1326.

206. Little, E. L., Jr.
1953. Check list of native and naturalized trees of the United States (including Alaska). Agric. Handb. 41, Supt. Doc., U.S. Gov. Print. Off., Washington, D.C.

207. Little, E. L. Jr.
1971. Atlas of United States trees. Vol. 1. Conifers and important hardwoods. USDA Misc. Public. 1146. Supt. Doc., U.S. Gov. Print. Off., Washington, D.C.

208. Loeschcke, V., and H. Francksen.
1964. Trichocarpin, a new phenol glycoside from poplar bark significant as a resistance factor. Naturwissenschaften 51:140.

209. Lutomski, K., and J. Surminski.
1965. The effect of the substances causing the luminescence of *Robinia pseudoacacia* wood on its natural durability. For. Abst. 26(3):470.

210. Mabry, T. J., K. R. Markham, and M. B. Thomas.
1970. The systematic identification of flavonoids. Springer-Verlag, New York.

211. Mahood, S. A., and E. Gerry.
1921. The production of American storax. Drug. Cir., 3 p. [Jan.].

212. Manske, R. H. F., ed.
1950-1973. The alkaloids. Chemistry and physiology. Vol. 1-14. Academic Press, New York.

213. Manville, J. F., and N. Levitin.
1974. Anti-fungal coumarins from mineral stained maple. Bimon. Res. Notes, Environ. Can., For. Serv. 30(1):3-4.

214. Markham, K. R.
1971. Chemotaxonomic approach to the selection of opossum-resistant willows and poplars for use in soil conservation. N. Z. J. Sci. 14:179-186.

215. Masaki, N., M. Hirabayashi, K. Fuji, K. Osaki, and H. Inouye.
1967. Monoterpene glycosides. V. The X-ray investigation of the monotropein molecule. Tetrahedron Lett. (25):2367-2370.

216. Maslen, E. N., C. Nockolds, and M. Paton.
1962. The stereochemistry of lirioresinol-B. Aust. J. Chem. 15:161-162.

217. Masuda, M., and K. Nishimura.
1971. Branched nonalactones from some *Quercus* species. Phytochemistry 10:1401-1402.

218. Mathes, M. C.
1963. Antimicrobial substances from aspen tissue grown in vitro. Science 140:1101-1102.

219. Mayer, W., H. Seitz, J. C. Jochims, K. Schauerte, and G. Schilling.
1971. Tanning compounds from the chestnut and oak wood. VI. Structure of vescalagin. Justus Liebigs Ann. Chem. 751:60-68.

220. McGinnes, E. A., Jr.
1975. Influence of incandescent and fluorescent light on the color of unfinished heartwood of black walnut and eastern red cedar. Wood Sci. 7:270-279.

221. Mell, C. D.
1939. Dyes and tans from the bark of the elm tree. Textile Color. 61:127.

222. Miller, L. P., ed.
1973. Phytochemistry. Vols. I-III. Van Nostrand Reinhold Co., New York.

223. Mitchell, R. L.
1955. Chemistry of hickory. Hickory task force Rep. 2, 14 p., U.S. Forest Prod. Lab., Madison, Wis.

224. Moeller, J.
1883. Lignum tupelo (tupelo wood). Pharm. Zentralhalle 24:545.

225. Morton, J. F.
1965. Can the red mangrove provide food, feed, and fertilizer? Econ. Bot. 19:113-123.

226. Morton, J. F.
1973. Plant products and occupational materials ingested by esophageal cancer victims in South Carolina. Q. J. Crude Drug Res. 13:2005-2022.

227. Mugg, J. B.
1959. The methanol-extractable materials in newly formed aspenwood. Tappi 42:289-294.

228. Mundy, B. P., R. D. Otzenberger, and A. R. De Bernardis.
1971. A synthesis of frontalin and brevicomin. J. Org. Chem. 36:2390.

229. Murko, D.
1966. The extractives from bark of indigenous *Fraxinus* Spp. Pregl. Naurnoteh. Rad. Inf. Zavod Teh. Drveta, 3:43-46. Sarajevo.

230. Musgrave, O. C., and D. Skoyles.
1974. Ebenaceae extractives. Part IV. Diosindigo A, a blue pigment from several *Diospyros* species. J. Chem. Soc. (Perkin I):1128-1131.

231. Mutton, D. B.
1958. Hardwood resin. Tappi 41:632-643.

232. Nair, G. V., and G. von Rudloff.
1960. Isolation of hyperin from red-osier dogwood. Can. J. Chem. 38(12):2531-2533.

233. Narayanan, V., and T. R. Seshadri.
1969. Chemical components of *Acer rubrum* wood and bark: Occurrence of procyanidin dimer and trimer. Indian J. Chem. 7(3):213-214.

234. Neelands, R. W.
1974. Important trees of eastern forests. USDA, For. Serv., South. Reg., Atlanta, Ga.

235. Nelson, N. C.
1975. Extractives produced during heartwood formation in relation to amounts of parenchyma in *Juglans nigra* and *Quercus rubra*. Can. J. For. Res., 5(2):291-301.

236. Newman, A. A.
1972. Chemistry of terpenes and terpenoids. 449 p. Academic Press, New York.

237. Nitsch, J. P., and C. Nitsch.
1965. The presence of phytokinins and other growth substances in sap of *Acer saccharum* and *Vitis vinifera*. Bull. Soc. Bot. Fr. 112(1/2):11-18.

238. Nomura, M., T. Tokoroyana, and T. Kubota.
1974. Three new cyclized C_9-C_1-C_9 compounds from *Alnus japonica* Steud. J. Chem. Soc. (Chem. Comm.):65-66.

239. Nomura, T., T. Fukai, S. Yamada, and M. Katayanagi.
1976. Phenolic constituents of the cultivated mulberry tree (*Morus alba* L.). Chem. Pharm. Bull. 24:2898-2900.

240. Norris, D. M.
1969. Mechanism of olfactory and gustatory stimulation of the nervous system in *Scolytus multistriatus*. Univ. Wis., For. Res. Notes, 147.

241. Norris, D. M.
1970. Chemical deterrence of feeding by insect pests. Soap Chem. Spec. 46:48-50.

242. Norris, D. M.
1970. Quinol stimulation and quinone deterrency of gustation by *Scolytus multistriatus*. Ann. Entomol. Soc. Amer. 63:476-478.

243. Norris, D. M., and J. E. Baker.
1967. Feeding responses of the beetle *Scolytus* to chemical stimuli in the bark of *Ulmus*. J. Insect Physiol. 13:955-962.

244. Oesch, F.
1969. The low molecular weight carbohydrates and polyphenols in the cambial sap of European beech and some other deciduous trees. Planta 87(4):360-380.

245. Paasonen, P. K.
1967. Extractives of birchwood and birch sulfate pulp. Pap. Puu 49(1):3-15.

246. Paasonen, P. K.
1967. Location and behavior of birch extractives in the cell system of the tree. Pap. Puu 49(8):503-508.

247. Paris, R. R., and A. Stambouli.
1960. The heterosides of the ash tree *Fraxinus excelsior* and some closely related species, particularly *Fraxinus ornus*. Ann. Pharm. Fr. 18:873-887.

248. Pearce, G. T., W. E. Gore, and R. M. Silverstein.
1976. Synthesis and absolute configuration of multistriatin. J. Org. Chem. 41:2797-2803.

249. Pearce, G. T., W. E. Gore, R. M. Silverstein, J. W. Peacock, R. A. Cuthbert, G. N. Lanier, and J. B. Simeone.
1975. Chemical attractants for the smaller European elm bark beetle *Scolytus multistriatus* (Coleoptera, Scolytidae). J. Chem. Ecol. 1:115-124.

250. Pearl, I. W.
1969. Water extractives of American Populus pulpwood species barks—A review. Tappi 52:428-431.

251. Pearl, I. A., and S. F. Darling.
1959. Studies on the barks of the family Salicaceae. II. Salireposide from the bark of *Populus tremuloides*. J. Org. Chem. 24:1616.

252. Pearl, I. A., and S. F. Darling.
1959. Tremuloidin, a new glucoside from the bark of *Populus tremuloides*. J. Org. Chem. 24:731-735.

253. Pearl, I. A., and S. F. Darling.
1962. Grandidentatin, a new glucoside from the bark of *Populus grandidentata*. J. Org. Chem. 27:1806-1809.

254. Pearl, I. A., and S. F. Darling.
1964. Further studies on the isolation of glucosides from the barks and leaves of *Populus tremuloides* and *Populus grandidentata*. Tappi 47:377-380.

255. Pearl, I. A., and S. F. Darling.
1965. Benzoates and salicyloyl salicin from the barks and leaves of *Populus grandidentata* and *Populus tremuloides*. Tappi 48:506-508.

256. Pearl, I. A., and S. F. Darling.
1967. Further studies on the bark of triploid *Populus tremuloides*. Tappi 50:324-329.

257. Pearl, I. A., and S. F. Darling.
1968. Continued studies on the hot water extractives of *Populus balsamifera* bark. Phytochemistry 7:1851-1853.

258. Pearl, I. A., and S. F. Darling.
1968. Mass spectrometry as an aid for determining structures of natural glucosides. Phytochemistry 7:831-837.

259. Pearl, I. A., and S. F. Darling.
1968. Studies on the barks of the family Salicaceae. (17) Trichoside, a new glucoside from the bark of *Populus trichocarpa*. Phytochemistry 7:825-829.

260. Pearl, I. A., and S. F. Darling.
1968. Studies on the hot water extractives of the brown bark of *Populus trichocarpa*. Tappi 51:537-539.

261. Pearl, I. A., and S. F. Darling.
1968. The structure of salireposide. Phytochemistry 7:821-824.

262. Pearl, I. A., and S. F. Darling.
1968. Variations in the hot water extractives of *Populus balsamifera* bark. Phytochemistry 7:1855-1860.

263. Pearl, I. A., and S. F. Darling.
1969. Investigation of the hot water extractives of *Populus balsamifera* bark. Phytochemistry 8:2393-2396.

264. Pearl, I. A., and S. F. Darling.
1971. Hot water phenolic extractives of the bark and leaves of diploid *Populus tremuloides*. Phytochemistry 10:483-484.

265. Pearl, I. A., and S. F. Darling.
1971. Studies on the hot water extractives of the bark and leaves of *Populus deltoides* Bartr. Can. J. Chem. 49:49-55.

266. Pearl, I. A., and S. F. Darling.
1971. The structures of salicortin and tremulacin. Phytochemistry 10:3161-3166.

267. Pearl, I. A., and S. F. Darling.
1977. Hot-water extractives of the leaves of *Populus heterophylla* L. J. Agric. Food Chem. 25:730-734.

268. Pearl, I. A., and T. K. Estes.
1965. Studies on the hot water extractives of the brown bark of *Populus tremuloides*. Tappi 48:532-535.

269. Pearl, I. A., and J. A. Harrocks.
1961. Neutral materials from the benzene extractives of *Populus tremuloides*. J. Org. Chem. 26:1578-1583.

270. Pearl, I. A., and C. R. Pottenger.
1966. Studies on the green bark of *Populus balsamifera*. Tappi 49:152-155.

271. Pearl, I. A., D. L. Beyer, and E. E. Dickey.
1958. Studies on the chemistry of aspenwood. II. Lignans from aspen spent sulfite liquor. J. Org. Chem. 23:705-706.

272. Pearl, I. A., D. L. Beyer, and D. Laskowski.
1959. Acid hydrolysis of the extractives of representative hardwoods. Tappi 42:849-854.

273. Pearl, I. A., D. L. Beyer, and D. Whitney.
1961. Alkaline hydrolysis of representative hardwoods V. Tappi 44:656-661.

274. Pearl, I. A., S. F. Darling, and S. F. Heller.
1966. Glucosides from the barks and leaves of triploid varieties of *Populus* species. Tappi 49:278-280.

275. Pearl, I. A., D. L. Beyer, S. S. Lee, and D. Laskowski.
1959. Alkaline hydrolysis of representative hardwoods III. Tappi 42:61-67.

276. Pearl, I. A., D. L. Beyer, D. Laskowski, and D. Whitney.
1960. The alkaline hydrolysis of barks of several species of the genus *Populus*. Tappi 43:756-758.

277. Pearl, I. A., O. Justman, D. L. Beyer, and D. Whitney.
1962. Further studies on the hot water extractives of *Populus grandidentata* bark. Tappi 45:663-666.

278. Pearl, I. A., S. F. Darling, H. De Haas, B. A. Loving, D. A. Scott, R. H. Turley, and R. E. Werth.
1961. Preliminary evaluation for glycosides of barks of several species of the genus *Populus*. Tappi 44:475-478.

279. Pearman, R. W.
1957. Mangrove bark—its value as a tanning material. Leather Trades Rev. 125:315-316.

280. Pennington, C. W.
1958. Tarahumar fish stupefaction plants. Econ. Bot. 12:95-102.

281. Pew, J. C.
1948. A flavonone from Douglas-fir heartwood. J. Amer. Chem. Soc. 70:3031-3034.

282. Plomley, K. F., J. W. Gottstein, and W. E. Hillis.
1964. Tannin-formaldehyde adhesives for wood. Aust. J. Appl. Sci. 15:171-182.

283. Plouvier, V.
1952. New investigations on mannitol and syringoside of some Oleaceae. Compt. Rend. 234:1577-1579.

284. Plouvier, V.
1954. The heteroside composition of some *Fraxinus* (Oleaceae). Compt. Rend. 238:1835-1837.

285. Plouvier, V.
1964. L-inositol, L-quebrachitol, and D-pinitol in some botanical groups. The presence of shikimic acid in *Mammea americana*. Compt. Rend. 258:2921-2924.

286. Plouvier, V.
1968. Fraxoside and coumarin heterosides occurring in various botanical groups. Compt. Rend. 267:1883-1885.

287. Plouvier, V.
1971. Glycoside research: Catalpol of *Paulownia* and *Catalpa*, arbutoside of *Sorbaria*, knautioside and saponoside of *Knautia arvensis*. C. R. Acad. Sci., Ser. D, 272(10):1443-1446.

288. Pollock, J. R. A., and R. Steven, eds.
1965. Dictionary of organic compounds. Vols. 1-5 and Supp. Oxford Univ. Press, New York.

289. Power, F. B., and C. W. Moore.
1909. The constituents of the bark of *Prunus serotina*. Isolation of *l*-mandilonitrile glucoside. J. Chem. Soc. 95:243-261.

290. Prasad, R., and D. Travnick.
1974. Evaluation of fungicides for control of tree diseases. Screening against the dutch elm disease *Ceratocystis ulmi* (Buism) C. Moreau under laboratory conditions. Chem. Control Res. Inst., Inf. Rep. CC-X-75. Ottawa.

291. Pridham, J. B.
1960. Oligosaccharides and associated glycosidases in aspen tissues. Biochem. J. 76:13-17.

292. Pridham, J. B., and H. G. J. Worth.
1968. Gum exudates from the bark of cherry laurel. Chem. Ind. 1403. London.

293. Pronin, D., and C. L. Vaughan.
1968. A literature survey of *Populus* species with emphasis on *P. tremuloides*. U.S. Forest Serv. Res. Note FPL-0180 Rev. For. Prod. Lab., Madison, Wis.

294. Pustelnick, F. A.
1953. Analysis of the bark of *Rhizophora mangle* from eastern Venezuela, and its importance in the manufacture of solid tanning materials. Agron. Trop. 3:107-116. Maracay.

295. Raffauf, R. F.
1970. A handbook of alkaloids and alkaloid-containing plants. Wiley-Interscience, New York.

296. Rao, K. V.
1975. Glycosides of *Magnolia grandiflora*. I. Isolation of three crystalline glycosides. Planta Med. 27:31-36.

297. Roffael, W., and W. Rauch.
1974. Extractives of oak and their influence on bonding with alkaline phenol-formaldehyde resins. Holz Roh-Werks. 32(5):182-187.

298. Rogers, J. S., H. N. Calderwood, and C. W. Beebe.
1950. Study of the tannin contents of barks from the Florida scrub oaks *Quercus leavis* and *Q. cinerea*. J. Amer. Leather Chem. Assoc. 45:733-751.

299. Roux, D. G.
1972. Recent advances in the chemistry and chemical utilization of the natural condensed tannins. Phytochemistry 11:1219-1230.

300. Roux, D. G., and E. Paulus.
1962. Condensed tannins. 13. Interrelationships of flavonoid components from the heartwood of *Robinia pseudoacacia*. Biochem. J. 82:324-330.

301. Roux, D. G., and E. Paulus.
1962. Formation of (−)-3′,4′,5′,7-tetrahydroxyflavanone and (+)-3′,4′,5′,7-tetrahydroxyflavan-4-ol by interconversion from (+)-dihydrorobinetin, and synthesis of their racemates. Biochem. J. 84:416-421.

302. Rowe, J. W., and J. K. Toda.
1969. Absolute configuration at C-4 of calamenene, 7-hydroxycalamenal, and the new naturally occurring sesquiterpene, 7-hydroxycalamenene. Chem. Ind. 922-923. London.

303. Rowe, J. W., M. K. Seikel, D. N. Roy, and E. Jorgensen.
1972. Chemotaxonomy of *Ulmus*. Phytochemistry 11:2513-2517.

304. Russell, A., C. R. Vanneman, and W. E. Waddey.
1942-1945. Natural tanning materials of the Southeastern United States. Parts I-VIII. J. Amer. Leather Chem. Assoc. 37:340-356; 38:30-34, 144-148, 235-238, 355-358; 39:173-178; 40:110-121, 422-426.

305. Sagrario del, C. G.
1957. Recovery of tannin from mangrove bark and its conversion into a colorless tannin extract. Spanish Pat. 236,986 (Dec. 2).

306. Sakai, A.
1960. The frost-hardening process of woody plants. VI. Seasonal variations for sugars (I). J. Jap. For. Sci. 42:97-102.

307. Sandermann, W., and A.-W. Barghoorn.
1956. Gesundheitschädigende Hölzer. Holz Roh-Werks. 14(1):37-40; 14(3):87-94.

308. Sasaki, T.
1964 Components of pecan (*Carya pecan*). II. A new flavonol caryatin isolated from the bark of pecan and its structure. J. Pharm. Soc. Jap. 84:47-51.

309. Scheffer, T. C., and A. D. Chapman.
1934. Prevention of interior brown stain in persimmon sapwood during seasoning. Hardwood Rec. 72(11):17.

310. Schreiber, L. R., and J. W. Peacock.
1974. Dutch elm disease and its control. U.S. Dep. Agric., Agric. Inf. Bull. 193 rev.

311. Sears, K. D., R. L. Casebier, H. L. Hergert, G. H. Stout, and L. E. McCandlish.
1974. The structure of catechinic acid. A base rearrangement product of catechin. J. Org. Chem. 39(22):3244-3247.

312. Seikel, M. K., F. D. Hostettler, and D. B. Johnson.
1968. Lignans of *Ulmus thomasii* heartwood-I. Thomasic acid. Tetrahedron 24:1475-1488.

313. Seikel, M. K., F. D. Hostettler, and G. J. Niemann.
1971. Phenolics of *Quercus rubra* wood. Phytochemistry 10:2249-2251.

314. Senear, F. E.
1933. Dermatitus due to woods. J. Amer. Med. Assoc. 101(20):1527-1536.

315. Senter, P. D., and C.-L. Chen.
1977. Liriodendronine, an oxoaporphine from discolored wood of *Liriodendron tulipifera*. Phytochemistry 16:2015-2017.

316. Seshadri, T. R.
1973. An investigation of the phenolic constituents of certain woods and barks, including North American species and representatives of genera common to North America and India. (J. W. Rowe, USDA PL-480 Proj. FG-In-425, Forest Prod. Lab., Madison, Wis.).

317. Seshadri, T. R., and T. N. C. Vedantham.
1971. Chemical examination of the barks and heartwoods of *Betula* species of American origin. Phytochemistry 10:897-898.

318. Sethi, M. L., G. S. Rao, B. K. Chowdhury, J. F. Morton, and G. J. Kapadia.
1976. Identification of volatile constituents of *Sassafras albidum* root oil. Phytochemistry 15:1773-1775.

319. Shibata, H., I. Mikoshiba, and S. Shimyu.
1974. Constituents of the mulberry tree. I. Isolation of β-tocopherol from the root bark of the mulberry tree. Agric. Biol. Chem. 38:1745-1746.

320. Shim, C. S.
1954. A study on the effect of water-soluble extractives upon physical properties of wood. Coll. Theseon. (Sci. nat.), Univ. Seoul No. 1:117-162.

321. Shingu, T., T. Hayashi, and H. Inouye.
1971. On the stereochemistry of catalponols, an example of the use of shift reagents to elucidate configuration. Tetrahedron Lett. 39:3619-3621.

322. Siegle, H.
1967. Microbiological and biochemical aspects of heartwood stain in *Betula papyrifera*. Can. J. Bot. 45(2):147-154.

323. Siminovitch, D., and A. P. J. Chater.
1958. Biochemical processes in the living bark of the black locust tree in relation to frost hardiness and the seasonal cycle. *In* The physiology of forest trees. K. V. Thimann, W. B. Critchfield, and M. H. Zimmermann, eds. p. 219-250. Ronald Press Co., New York.

324. Singleton, V. L.
1974. Some aspects of the wooden container as a factor in wine maturation. *In* Advances in Chemistry No. 137: Chemistry of winemaking. Amer. Chem. Soc., Washington, D.C.

325. Slooten, H. J., van der.
1960. Resina De Fenol-Formaldehido Tanino De *Rhizophora mangle*. Bol. Inst. For. Lat. Amer. 6:34-39. Merida.

326. Smale, B. C., R. A. Wilson, and H. L. Keil.
1964. A survey of green plants for antimicrobial substances. (Abstr.) Phytopathology 54(7):748.

327. Smalley, E. B., C. J. Meyers, R. N. Johnson, B. C. Fluke, and R. Vieau.
1973. Benomyl for practical control of Dutch elm disease. Phytopathology 63:1239-1252.

328. Smith, D. C. C.
1955. *p*-Hydroxybenzoate groups in the lignin of aspen. J. Chem. Soc.:2347-2351.

329. Smith, W. A.
1960. New storax operation started. Tex. For. News 39(4):4,6.

330. Soderquist, C. J.
1973. Juglone and allelopathy. J. Chem. Educ. 50(11):782-783.

331. Spada, A., R. Cameroni, and M. T. Bernabei.
1956. The pigments of *Morus alba*. Gazz. Chim. Ital. 86:46-55.

332. Spencer, R. W., and E. T. Choong.
1977. Isolation and characterization of several extractives in the bark and wood of sweetgum. Holzforschung 31:25-31.

333. Springer, G. F.
1966. Relation of microbes to blood-group active substances. Angew. Chem. Internat. Ed. 5.909-920.

334. Stanek, D. A.
1958. A study of the low-molecular weight phenols formed upon hydrolysis of aspenwood. Tappi 41:601-609.

335. Stecher, P. G., ed.
1968. The Merck index. Merck and Co., Inc., Rahway, N.J.

336. Steele, J. W., and W. Ronald.
1973. Phytochemistry of the Salicaceae VI. The use of gas-liquid chromatographic screening test for the chemotaxonomy of *Populus* species. J. Chromatogr. 84:315-318.

337. Steele, J. W., W. Ronald, and M. Bolan.
1973. Phytochemistry of the Salicaceae V. The use of gas-liquid chromatographic screening test to detect phytochemical variations in *Populus deltoides* Marsh. J. Chromatogr. 84:309-314.

338. Steele, J. W., P. F. Weitzel, and R. C. S. Audette.
1972. Phytochemistry of the Salicacea. IV. Investigation of the bark of *Salix petiolaris* Sm. J. Chromatogr. 71:435-441.

339. Stermitz, F. R., and J. A. Adamovics.
1977. Alkaloids of *Caltha leptosepala* and *Caltha biflora*. Phytochemistry 16:500.

340. Stinson, E. E., C. J. Dooley, J. M. Purcell, and J. S. Ard.
1967. Quebrachitol—A new component of maple sap and sirup. J. Agric. Food Chem. 15(3):394-397.

341. Suga, T., Y. Asakawa, and N. Iwata.
1971. 1,7-Diphenyl-1,3-heptadien-5-one: A new ketone from *Alnus pendula* Chem. Ind.: 766. London.

342. Tannock, J.
1973. Naphthquinones from *Diospyros* and *Euclea* species. Phytochemistry 12:2066-2067.

343. Tattar, T. A., and A. E. Rich.
1973. Extractable phenols in clear, discolored and decayed woody tissues and bark of sugar maple and red maple. Phytopathology 63(1):167-169.

344. Taylor, W. I.
1961. The structure and synthesis of liriodenine, a new type of isoquinoline alkaloid. Tetrahedron 14:42-45.

345. Terazawa, M., S. Okuyama, and M. Miyake.
1973. Isolation of hirsutanonol and hirsutenone, two new diarylheptanoids from the green bark of keyamahannoki, *Alnus hirsuta* Turcz. Mokuzai Gakkaishi 19(1):45-46.

346. Terazawa, M., T. Koga, H. Okuyana, and M. Miyake.
1973. Isolation of platyphyllonol, a new diarylheptanoid from the green bark of shirakanba, *Betula platyphylla* Sukatch. var. *japonica* Hara. Mokuzai Gakkaishi 19(1):47-48.

347. Tezuka, M., C. Takahashi, M. Kuroyanagi, M. Satake, K. Yoshihira, and S. Natori.
1973. New naphthoquinones from *Diospyros*. Phytochemistry 12:175-183.

348. Thieme, H.
1964. Isolation of a new phenol glucoside from *Salix purpurea* L. Pharmazie 19:725.

349. Thieme, H.
1965. Phenolic glycosides of the Salicaceae. Planta Med. 13:431-438.

350. Thieme, H.
1967. Phenolic glycosides of the genus *Populus*. Planta Med. 15:35-40.

351. Thieme, H., and R. Benecke.
1971. Phenol glycosides of Salicaceae. 8. Glycoside accumulation in some central European species of *Populus*. Pharmazie 26:227-231.

352. Thieme, H., and R. Richter.
1966. Isolation of a new phenol glycoside from *Populus tremula* L. Pharmazie 21:251.

353. Thomas, A. F., and J. M. Müller.
1961. Some constituents of plane tree bark (*Platanus occidentalis* L.). Chem. and Ind.: 1794-1795.

354. Thompson, R. S., D. Jacques, E. Haslam, and R. J. N. Tanner.
1972. Plant proanthocyanidins. Part I. Introduction; The isolation, structure, and distribution in nature of plant procyanidins. J. Chem. Soc. (Perkin I): 1387-1399.

355. Thompson, M. J., S. J. Louloudes, W. E. Robbins, J. A. Waters, J. A. Steele, and E. Nosettig.
1962. Identity of the "House fly sterol." Biochem. Biophys. Res. Comm. 9:113-119.

356. Timell, T. E., and J. A. Mian.
1961. A study of the pectin present in the inner bark of white birch (*Betula papyrifera*). Tappi 44:788-793.

357. Tomita, M., and H. Furukawa.
1962. Studies on the alkaloids of magnoliaceous plants. XXVII. Alkaloids of *Liriodendron tulipifera* L. (1). J. Pharm. Soc. Jap. 82(4):616-618.

358. Tomita, M., and H. Furukawa.
1962. Studies on the alkaloids of magnoliaceous plants. XXXIV. Alkaloids of *Liriodendron tulipifera* L. (2). J. Pharm. Soc. Jap. 82(8):1199-1202.

359. Tomita, M., and M. Kozuka.
1967. Alkaloids of magnoliaceous plants XXXVIII. Alkaloids of *Magnolia grandiflora*. (4). J. Pharm. Soc. Jap. 87(9):1134-1137.

360. Urbas, B., G. A. Adams, and C. T. Bishop.
1964. Isolation and some structural features of a polysaccharide from birch sap. Can. J. Chem. 42(9):2093-2100.

361. Uvarova, N. I., G. I. Oshitok, A. K. Dzizenko, and G. B. Elyakov.
1970. 1,7-Diphenylheptane-3,5-diol from *Alnus fruticosa* and *A. manshurica*. Khim. Prir. Soedin. 6(4):463-464.

362. Venkataraman, K.
1972. Wood phenolics in the chemotaxonomy of the moraceae. Phytochemistry 11:1571-1586.

363. Venkataraman, K.
1977. Flavonoids, tannins, stilbenes, lignans, and quinones in some Indian forest trees. PL-480, Proj. A7-FS-70. [J. R. Rowe, Forest Prod. Lab., Madison, Wis.]

364. Vick, C. B., and M. A. Taras.
1969. Stain in red oak parquet flooring. For. Prod. J. 19(9):83-86.

365. Vijver, L. M. van der, and K. W. Gerritsma.
1974. Naphthoquinones of *Euclea* and *Diospyros* species. Phytochemistry 13:2322-2323.

366. Vite, J. P., R. Luehl, B. Gerken, and G. N. Lanier.
1976. Elm bark beetles: Bait test in the upper Rhine Valley using synthetic pheromones. Z. Pflanzenkr. Pflanzenschutz 83:166-171.

367. Wacek, A. V., and K. Kratzl.
1948. Constitution of the side chains of lignin. J. Polym. Sci. 3:359-548.

368. Walkup, J. H., R. I. Rush, and G. Haywood.
1956. The extractives of southern gum woods. Tappi 396:190A-193A.

369. Wall, R. E., and J. E. Kuntz.
1964. Water-soluble substances in dead branches of aspen (*Populus tremuloides* Michx.) and their effects on *Fomes igniarius*. Can. J. Bot. 42:969-977.

370. Wallis, A. F. A.
1968. Stereochemistry of cyclolignans—A revised structure for thomasic acid. Tetrahedron Lett.: 5287-5288.

371. Warthen, D., E. L. Gooden, and M. Jacobson.
1969. Tumor inhibitors: Liriodenine, a cytotoxic alkaloid from *Annona glabra*. J. Pharm. Sci. 58(5):637-638.

372. Weinges, K., W. Baehr, W. Ebert, K. Goeritz, and H. D. Marx.
1969. Constitution, formation, and significance of flavonoid tannins. Fortschr. Chem. Org. Naturst. 27:158-260.

373. West L. G., J. L. McLaughlin, and G. K. Eisenbeiss.
1977. Saponins and triterpenes from *Ilex opaca*. Phytochemistry 16:1846-1847.

374. Westfall, B. A., R. L. Russell, and T. K. Auyong.
1961. Depressant agent from walnut hulls. Science 134:1617-1618.

375. Willaman, J. J., and H. L. Li.
1970. Alkaloid-bearing plants and their contained alkaloids 1957-1968. Lloydia Suppl. 33(3A):1-286.

376. Willaman, J. J., and B. G. Schubert.
1961. Alkaloid-bearing plants and their contained alkaloids. USDA Agric. Res. Serv. Tech. Bull. 1234, 287 p., Supt. Doc., U.S. Gov. Print. Off., Washington, D.C.

377. Williams, G. J.
Comparative phenology, physiology, and biochemistry of populations of *Liquidambar styraciflua*. 103 p. Univ. Microfilms, Ann Arbor, Mich.

378. Willits, C. O.
1965. Maple sirup producers manual. Agric. Res. Serv. USDA Agric. Handb. 134. Repr. 1971, U.S. Gov. Print. Off., Washington, D.C.

379. Wislocki, P. G., P. Borchert, J. A. Miller, and E. C. Miller.
1976. The metabolic activation of the carcinogen 1′-hydroxysafrole *in vivo* and *in vitro* and the electrophilic reactivities of possible ultimate carcinogens. Cancer Res. 36:1686-1695.

380. Wislocki, P. G., E. C. Miller, J. A. Miller, E. C. McCoy, and H. S. Rosenkranz.
1977. Carcinogenic and mutagenic activities of safrol, 1′-hydroxysafrole, and some known or possible metabolites. Cancer Res. 37:1883-1891.

381. Wolfrom, M. L., and H. B. Bhat.
1965. Osage orange pigments XVII. 1,3,6,7-tetrahydroxyxanthone from the heartwood. Phytochemistry 4:765-768.

382. Wolfrom, M. L., F. Komitsky, Jr., and J. H. Looker.
1965. Osage orange pigments. XV. Structure of osajaxanthone. Synthesis of dihydroosajaxanthone monomethyl ether. J. Org. Chem. 30:144-149.

383. Wolfrom, M. L., F. Komitsky, Jr., and P. M. Mundell.
1965. Osage orange pigments. XVI. The structure of alvaxanthone. J. Org. Chem. 30:1088-1091.

384. Wolfrom, J. L., E. E. Dickey, P. McWain, A. Thompson, J. H. Looker, O. M. Windrath, and F. Komitsky, Jr.
1964. Osage orange pigments. XIII. Isolation of three new pigments from the root bark. J. Org. Chem. 29:689-691.

385. Wolfrom, M. L., F. Komitsky, Jr., G. Fraenkel, J. H. Looker, E. E. Dickey, P. McWain, A. Thompson, P. M. Mundell, and O. M. Windrath.
1964. Osage orange pigments. XIV. The structure of macluraxanthone. J. Org. Chem. 29:692-697.

386. Woods, B., and C. D. Calnan.
1976. Toxic woods. B. J. Derm. 94(Suppl. 13):1-97.

387. Yagishita, K., and S. Iseda.
1955. The triterpenic acid of *Platanus occidentalis*. Nippon Nogei-kagaku Kaishi 29:964-967.

388. Yasue, M.
1968. Studies on wood extractives of *Ostrya japonica*: Chemical structures of asadanin and related compounds. Bull. Gov. Forest Expt. Sta. 209:77-168. (Mar.). Tokyo.

389. Ziegler, H., and M. Kluge.
1962. Nucleic acids and their components in the sieve-tube sap of *Robinia pseudoacacia*. Planta 58(2):144-153.

390. Ziyaev, R., A. Abdusamatov, and S. Yu. Yunusov.
1973. Alkaloids of *Liriodendron tulipifera*. Khim. Prir. Soedin. 9(4):505-506.

391. Ziyaev, R., A. Abdusamatov, and S. Yu. Yunusov.
1973. D-Caaverine and the new alkaloid lirinidine from *Liriodendron tulipifera*. Khim. Prir. Soedin. 9(6):760-763.

392. Ziyaev, R., A. Abdusamatov, and S. Yu. Yunusov.
1973. Lirinine, a new alkaloid from *Liriodendron tulipifera*. Khim. Prir. Soedin. 9(1):67-70.

393. Ziyaev, R., A. Abdusamatov, and S. Yu. Yunusov.
1974. Alkaloids of *Liriodendron tulipifera*. Khim. Prir. Soedin. 10(1):108-109.

394. Ziyaev, R., A. Abdusamatov, and S. Yu. Yunusov.
1974. D-Isolaureline, a new alkaloid from *Liriodendron tulipifera*. Khim. Prir. Soedin. 10(5):685.

395. Ziyaev, R., A. Abdusamatov, and S. Yu. Yunusov.
1975. The dynamics of the accumulation and mutual transformation of alkaloids in *Liriodendron tulipifera*. Khim. Prir. Soedin. 11(4):478-481.

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