THE CHEMICAL COMPOSITION OF BARKS[1]

E. F. KURTH

Department of Chemistry, Oregon State College, Corvallis, Oregon

Received June 24, 1946

Bark analyses and components are tabulated and discussed. The standard wood analytical procedures for lignin and cellulose when applied to barks are often inadequate. The lignin fraction from barks usually contains materials low in methoxyl and, in some instances, carboxyl groups. There is evidence that the carbohydrate fraction in certain barks is chemically bound to the lignin fraction by bonds absent in wood. Barks contain hemicelluloses and cellulose; the sugars associated with the hemicelluloses are glucose, galactose, mannose, arabinose, and xylose, whereas the cellulose may have a large percentage of the alkali-resistant alpha cellulose. Chemically, little is known about the cork in barks. Numerous compounds have been isolated from bark extractives. These include representatives of the alkaloids, sterols and various alcohols, esters, glucosides, hydrocarbons, mucilages, proteins, saponins, sugars, tannins, and many types of acids and pigments. Ash, nitrogen, and the B.T.U. contents of barks are higher than for wood.

The literature on barks has been reviewed to the end of 1945.

The trunk of a mature tree is composed of a core of wood covered by a layer of bark on the outside. Inasmuch as the bark lies outside of the living cambium, it is pushed outward by the development of new tissue underneath. This increase in circumference to which the bark must accommodate itself often exceeds its ability to respond, with the result that the older tissues are broken and killed by exposure, and especially by the stoppage of food and water supplies. Thus two bark layers may be recognized: (*a*) the outer, dark-colored, dead portion that varies greatly in thickness, and (*b*) the inner, thin, light-colored, living portion. A roughening of the bark is held to indicate the inception of cork formation. Bark tissues may contain several types of cells, often designated as sieve, longitudinal parenchyma, ray parenchyma, stone, cork, fiber, etc., which may contribute to their different properties.

On the whole the available literature on barks gives too little information concerning their chemical composition, and much less is known of the properties of the actual components than one would normally expect. Millions of tons of bark from the lumber and pulp industries are wasted or destroyed annually. Wilson (80) has estimated that 209,000,000 cu. ft. of bark were developed in the manufacture of about 10.6 billion board feet of lumber at primary sawmilling operations in 1944 in the states of Oregon and Washington alone. About 12.5–14.7 per cent of the sawlogs in these states is bark. On the other hand, the chemical utilization of bark from cut timber is a field of research which has hardly been touched. Newer methods of bark removal from logs with the hydraulic barker give cleaner bark and will effect economies. It would appear that the availability of such large amounts of a natural raw material would stimulate a

---

[1] Published with Approval of the Monographs Publication Committee, Oregon State College, Research Paper No. 106, School of Science, Department of Chemistry.

great deal of research activity in the hope that such work will give rise to fuller utilization. In many instances the information needed for evaluation of barks having possible technological interest could be furnished by appropriate chemical analyses if these were available. In this connection the investigations of Zellner (81, 82, 83) and more recently of Sharkov (60–68) are particularly significant.

BARK ANALYSES

Our knowledge of the composition of barks is due preëminently to the application of analytical methods used for wood. That these procedures have not been entirely satisfactory when applied to barks is evident from the absence of cellulose and lignin determinations in table 1. No lignin determinations are reported for most barks, and what would ordinarily be reported as cellulose in wood analyses is designated as fiber because of questionable delignification. Table 2 lists extraneous organic compounds that were found to occur in the individual barks.

In the light of the information contained in tables 1 and 2, the principal components of bark with which the chemist is concerned are:

1. Lignin—the material insoluble in concentrated mineral acids
2. Cork—cutose, suberin, and suberic acid (1,6-hexanedicarboxylic acid)
3. Carbohydrates—holocellulose, the total carbohydrate fraction
    A. Cellulose
    B. Hemicelluloses—arabans, xylans, mannans, glucosans, galactans, and uronic acid substances
4. Extraneous materials
    A. Volatile acids and oils
    B. Non-volatile fatty oils (fats and fatty acids), higher alcohols, resins, and hydrocarbons
    C. Coloring matters
    D. Tannins and the related water-insoluble phlobaphenes
    E. Polysaccharides, glucosides, pectins, and sugars
    F. Organic nitrogen compounds
    G. Mineral matters
    H. Other organic components—saponins, mannitol, dulcitol, etc.

It can be readily understood that this classification indicates only types of the principal components present in barks and that in all cases, when not dealing with crystalline compounds, these components are likely to be of heterogeneous composition. As revealed in subsequent paragraphs, the composition will vary not only because of the inherent differences of the materials from the individual barks but also owing to the procedures employed for their isolation.

Although bark and wood tissues are formed side by side in the tree, their chemical nature is unlike. Bark differs from wood by a lower cellulosic content and in the type of lignin normally present in wood. The material in barks that appears as lignin varies in amount over a wide range, whereas the lignin content of both hardwoods and softwoods varies within rather narrow limits. Bark lignin is much lower in methoxyl than is wood lignin. Ash and nitrogen contents are higher than those for wood. No constant relation exists between the contents of the other components (cellulose, pentosans, volatile acids, etc.) in wood and in bark. Wood contains no cork or lignin with carboxyl groups. A summative analysis that includes ash, extractives, holocellulose, and lignin accounts for 100 per cent of the wood analyzed. Our knowledge of the various constituents of bark tissue is not sufficiently advanced to permit a scheme of summative analysis.

TABLE 1

Bark analyses

SPECIES	MOISTURE	SOLUBILITY				PENTOSAN	FIBER	NITROGEN	ASH	REFERENCE
		Ether	Alcohol	Water	Tannin					
Alder, *Alnus viridis*		3.6	23.1	31.3	16.5		26.6	1.2	3.2	(81)
Black alder, *Alnus glutinosa* L.		5.5	22.2		8.7		33.5	1.3	3.5	(81)
Balsam, *Abies balsamae*		14.0	2.0	14.0		6.7	36.7			(25)
Basswood, *Tilia platyphyllos*		2.3	12.3	18.1	7.3		49.3	1.5	1.9	(81)
Beech, *Fagus silvatica*		3.3	10.5	14.6	3.1	28.7	36.7	1.4	8.9	(11, 12, 81)
Beech, *F. grandifolia*		1.2	13.2	4.0		13.7			8.3	(58)
						14.2				
White birch, *B. papyrifera*		2.3	12.2			16.5				
		8.0	13.0	5.8		17.1			1.5	(58)
Yellow birch, *B. lutea*		1.7	12.3	5.9		16.6			2.9	(58)
						17.5				
Dogwood, *Cornus sanguinea*		4.2	21.8	25.5	13.0		31.3	1.8	6.2	(81)
Elder, *Sambucus nigra*		1.7	6.1	15.0	2.5		36.8	1.5	5.8	(81)
Elm, *Ulmus campestris* L.		2.4	14.6	20.5			59.2	0.2	6.83	(82)
Hemlock, Western, *T. heterophylla*	9.8			13.5		5.4	33.7		1.7	(33)
Hornbeam, *Carpinus betulus*		3.4	11.4	16.9	7.9		45.0	1.7	7.1	(81)
Horse chestnut, *Pavia rubra* Lam.		2.5	18.5	28.9			30.2	1.9	5.8	(83)
Oak, black	11.4			16.4		15.7	32.0		5.1	(33)
Oak, chestnut	11.9			11.1	4.6	13.4	30.4		4.3	(33, 41)
Oak, red	12.5			8.7	5.4–11.1	16.5	35.1		5.4	(33, 41)
Oak, white	12.6			10.5	2.3– 7.2	12.4	29.2		8.3	(33, 41)
Pine, European			12.3			5.7	21.5			(77)
Plane tree, *P. orientalis*		3.8	8.3	16.6	5.2		56.7	1.6	3.9	(82)
Privet, *Ligustrum vulgare*		2.6		38.3	7.0			2.3	4.4	(81)
Redwood fiber	0.0	0.2	3.1	4.6		7.7	92.6		0.3	(42)
Redwood dust	0.0	0.9	1.5	9.6		3.1				
Black spruce		2.3	4.1	10.5	6.6–12.2	8.8				(23)
		4.1	12.0	12.8		9.5			2.1	(41, 58)
Sugar maple, *A. saccharum*						9.1				
		1.9	20.3	4.6	0.4	12.6			4.3	(41)
Sycamore, *Acer pseudoplatanus*		0.9	11.5	20.7		11.4	50.5	2.0	10.5	(83)
Paper mulberry		4.8	3.9	17.3	5.5	12.9	36.4	1.0	6.7	(26)

The estimation of cellulose and lignin in bark often presents far greater difficulties than with wood, and the usual methods fail or are inadequate. Compli-

TABLE 2

Components of barks

Alder, *Alunus incana* L.	Protalnulin, p.m. 236°C.; alnulin, m.p. 260°C.; alniresinol, m.p.192–193°C.; resin acids; phlobaphenes; a sterol-like substance, m.p. 260°C.; and an unidentified substance p.m. 194–195°C. (21)
Alder, *Alnus viridis*	Protalnulin; ceryl alcohol, an alcohol $C_{33}H_{60}O_2$, m.p. 194°C., and an alcohol $C_{24}H_{42}O_2$, m.p. 250°C. (81)
Alder, black, *A. glutinosa* L.	Unidentified compounds: m.p. 83–84°C., 260°C., and 261°C. (82)
Ash, *Fraxinus excelsior*	7 per cent pectin; 20 per cent hemicelluloses (arabinose, mannose, galactose); ceryl alcohol and esters; phytosterols; resin; fats; carotenoid pigment; fraxin; mannitol; invert sugar (4, 9)
Ash, *F. silvatica*	Ceryl ester of an acid, $C_{20}H_{40}O_2$, m.p. 80°C., and a phytosterol (81)
Mountain ash, *Sorpus aucuparia* L.	Ceryl alcohol, $C_{26}H_{54}O$, m.p. 80°C.; an alcohol, $C_{35}H_{60}O$, m.p. 193°C.; an alcohol, $C_{16}H_{30}O_2$, m.p. 263°C.; resins; invert sugar; tannins; choline (15)
Aspen, sp.	Suberin (66)
Aspidosperma quirandy	Alkaloids; resins; a saponin; tannins (19)
Basswood, *P. platyphyllos*	Ceryl alcohol; sativinic acid, $C_{18}H_{36}O_6$; an alcohol, $C_{22}H_{38}O_3$, m.p. 285°C. (82)
Birch, white, *Betula alba* L.	Betulinol; tannin; gallic acid; pentosan; oil; glucoside; betuloside; betuligenol; yellow dye (73, 78)
Birch, sp. *Betulaceae*	Betulinol (75); tannins; carbohydrates; fats; waxes; alkaloids; phytosterol; fatty acids; volatile acids; pectin (60, 63, 68); suberin (12, 66)
Buckthorn	Frangularoside, $C_{21}H_{24}O_9$, m.p. 234°C., $(\alpha)_{5790} = 163°$; franguloside, $C_{21}H_{20}O_9$, m.p. 249°C., $(\alpha)_D = 134.4°$; and three glucosides containing emodol (5)
Calotropsis gigantea	Mudarol, m.p. 176–177°C.; β-amyrin, m.p. 196–197°C.; sterols; fatty acids C_{24} to C_{32}; α-calotropeol, m.p. 220–221°C.; giganteol, $C_{30}H_{50}O_2$, m.p. 224°C.; and other unidentified compounds (46)
Calycanthaceae	Fluorescent substances; a glucoside, calycanthin (43)
Chestnut, *Castanea sativa*, Mill	Ceryl alcohol; fatty acids; phlobaphenes; phytosterol, m.p. 133–135°C.; resins, invert sugar; tannins (15)
Chestnut, horse, *Pavia rubra* Lam.	A hydrocarbon; an alcohol, sitosterol; the glucoside esculetin; tannins (83)

Chuchuhuasha (So. America)	Alkaloids; a flavone pigment; a γ-pyran derivative; a catechol-type tannin; a phytosterol; vitamin C; rubber (50)
Dogwood, *Cornus sanguinea*	Phytosterol, $C_{26}H_{44}O$; platanalic acid, $C_{24}H_{40}O_3$; and a substance $C_{30}H_{52}O$, m.p. 251°C. (82)
Elder, *S. nigra*	An alcohol, $C_{23}H_{40}O_2$, m.p. 216°C.; an alcohol, $C_{27}H_{48}O$, m.p. 179°C. (81)
Elm, *Ulmus compestris* L.	$(C_{12}H_{24}O)_n$, m.p. 74–75°C.; $(C_{11}H_{20}O_2)_n$, decomposing at 240°C.; phlobaphene; phytosterol, $C_{27}H_{46}O$, m.p. 134°C. (82)
Elm, slippery, *Ulmus fulva*	Mucilage composed of galacturonic acid, *l*-rhamnose, *d*-galactose, and coloring matter (1, 22, 49)
Euonymus atropurpureus, "Wahoo"	Dulcitol; furan-β-monocarboxylic acid, $C_5H_4O_3$, m.p. 121–122°C.; euonymol, a new alcohol, $C_{21}H_{30}O_4$, m.p. 248–250°C.; tannin; coloring matter; monohydric alcohols; euonysterol, $C_{31}H_{52}O_2$, m.p. 137–138°C.; homoeuonysterol, $C_{40}H_{70}O_2$, m.p. 133–134°C.; a dihydric alcohol, atropurol, $C_{27}H_{44}(OH)_2$, m.p. 283–285°C.; citrullol, $C_{22}H_{36}O_2(OH)_2$; and palmitic, cerotic, oleic, and linoleic acids (57)
Fir, sp.	Pectin (60, 65); tannin (62); suberin (66)
Hawthorn, *Crataegus oxyacantha* L.	An alcohol, $C_{30}H_{50}O$ or $C_{31}H_{50}O$; palmitic and stearic acids; tannins; sucrose; oxalates and tartrates; and unidentified compounds $C_{26}H_{54}O$, $C_{43}H_{73}O$, and $C_{26}H_{44}O_2$ (83)
Hazel	A hydrocarbon, m.p. 16°C.; betulinol, m.p. 261°C.; lignoceryl alcohol, m.p. 76°C.; sitosterol, m.p. 135°C. (8)
Hornbeam, *Carpinus betulus* L.	Betulinol, $C_{30}H_{50}O_2$, m.p. 261°C., and phytosterol, m.p. 132°C. (7); ceryl alcohol; an alcohol, $C_{18}H_{34}O_2$, m.p. 249°C.; sativinic acid; dihydrostearic acid (82)
Larch, American	Starch; pentosans; catechol tannins; saponins; a resin; a white paraffin-like solid (37)
Locust, black, *Robina pseudacacia*	12.9–28.0 per cent protein in inner bark (30)
Lunasia *costulata* Miq.	Starch; fatty oil (stearic, palmitic, oleic, and linoleic acids, and unsaponifiable); alkaloids (16)
Mulberry, sp.	α-Amyrin, m.p. 185–195°C. (48)
Mulberry, paper, *Bronssonetia papyrifera*	Bast fibers 6.5–45.2 mm. long; resin and fatty acids; pectin; cutin; pentosan; tannin (26)
Mulberry, black, *Morus nigra* L.	Phytosterol, m.p. 132°C.; ceryl alcohol; stearic, myristic, and linolenic acids; glycerol; tannins and phlobaphenes; a sugar (21)

TABLE 2—*Continued*

Oak, sp.	Tannin (59a, 70); suberin (66)
Pine, sp.	Tannin and phlobaphenes (35, 74); pentosans, methyl pentosans, and cellulose (77); pectin (65, 68); suberin (66); fatty acid and resin acids (38); brown pigment $[C_{15}H_{13}O_5OCH_3]_x$ (39)
Australian pine, *C. calcarata* and *C. glauca*	Catechol tannins (13)
Pinus sylvestris	Lignoceric acid, $C_{24}H_{48}O_2$; palmitic, caproic, oleic, azelaic, pelargonic, and rosin acids; sitosterol, $C_{29}H_{50}O$, m.p. 137.5–138.5°C.; dihydrositosterol, m.p. 137.3–138°C.; carotene; $C_{29}H_{60}$, m.p. 59–61°C. (49).
Piscidia erythrina	Calcium oxalate (29)
Plane tree, *Platanus orientalis* L.	$C_{24}H_{42}O_2$, $C_{36}H_{74}$, $C_{24}H_{40}O_3$, and suberin (66, 82)
Privet, *Ligustrum vulgare* L.	Ceryl palmitate; ceryl alcohol; palmitic acid ester of an alcohol, $C_{25}H_{42}O$ (or $C_{26}H_{44}O$), m.p. 215°C.; phytosterol; and possible esters of behenic, arachidic, and platanolic acids (81)
Redwood, *Sequoia sempervirens*	"Bark fiber" and "bark dust"; lignin; a low-methoxyl phenolic acid; catechol tannins and phlobaphenes; a pectic acid gum; mannose, glucose, and xylose (42)
Spruce, *Picea excelsa*	Ceryl alcohol; palmiticand stearic acids; invert sugar; tannins (83)
Sycamore, *Acer pseudoplatanus* L.	An alcohol, $C_{26}H_{56}O$; phytosterol; tannins (83)
Walnut, *Juglans regina* L.	$C_{20}H_{36}O$, m.p. 63–64°C.; $C_{24}H_{42}$; $C_{22}H_{38}O$; $C_{17}H_{28}O_2$; tannin (82)
Willow, black	A glucoside (6)
Zizyphus, *Vulgaris* Lam.	Zeryl alcohol and esters; sterols; resin acids (4)

cations arise where cork and difficulty soluble extraneous materials are present or where a chemical union exists between the carbohydrates and lignin. Often the analytical results depend upon the methods used in extracting the bark prior to the actual determinations. The results of Heiduschka and Chang (26) indicate that inner bark tissues and the bark of some species may lend themselves to the application of conventional analytical procedures used for wood. Hay applied the standard wood analytical procedures to balsam bark, *Abies balsamae*, and the sum of the volatile oils, extractives, Cross and Bevan cellulose, lignin, and pentosans came to 99.7 per cent (25). Undoubtedly some duplication resulted in the Cross and Bevan cellulose and the pentosan values, which would lower the total. This duplication was off-set by the loss of hemicellulose material which occurs in the Cross and Bevan cellulose determination. No reports are made of the application of the wood holocellulose procedure to barks, and where a stable union exists between the cellulose and the lignin in bark this procedure is not applicable. The chemical analyses of inner and outer bark layers, because of changes brought about by exposure, parasitic growths, and other agents, are dissimilar.

BARK LIGNIN

There is little doubt that there is present in bark a mixture of substances that appear as lignin in the conventional analysis with the concentrated mineral acid methods. These have sufficiently dissimilar properties to enable some fractionation to be made. Most bark lignins have a relatively large amount of material with a low methoxyl content, as is evident from an examination of table 3. Some lignin fractions are relatively soluble in alkaline solutions and contain significant percentages of free carboxylic and phenolic hydroxyl groups to characterize them as high-molecular-weight phenolic acids or lignin acids (42).

TABLE 3

Lignin and pentosan values for bast fibers (28)

	PENTOSAN	LIGNIN	OCH_3 IN LIGNIN
	per cent	*per cent*	*per cent*
Spruce, *Picea excelsa*	5.7	6.2	7.4
Pine, *Pinus silvestris*	5.2	12.7	1.4
Taxus baccata	16.6	12.8	0.8
Ginkgo biloba	17.1	8.5	5.6
Thuja	9.4	33.7	7.8
Eucalyptus	20.1	25.6	9.2
Red beech, *F. silvatica*	12.4	21.5	14.3
White beech, *C. betulus*	21.3	20.2	12.3
Oak, *Q. pedunculata*	19.3	12.1	9.0
Linden, *T. ulmifolia*	19.3	8.9	12.5
Maple, *A. campestre*	21.7	21.2	14.6
Poplar, *P. alba*	19.8	17.5	13.2
Hazel, *Carylus arellana*	20.3	15.6	7.7
Elder, *S. nigra*		7.7	9.4
Willow, *Salix caprea*	17.4	12.1	13.2

At least a portion of the lignin in bark is similar to wood lignin (11, 42, 77). Oxidation with alkaline nitrobenzene yields a small amount of vanillin, indicating the presence of a lignin with phenolic hydroxyl groups (11, 77). Another difference is the amount of hydroxyl groups as compared with wood lignin. Sharkov and Kalnina (67) found that pine bark lignin contained 16 per cent of hydroxyl as compared with 20 per cent for pine wood lignin.

Studies at times have failed to differentiate sharply between lignin and other bark substances, with the result that some lignin values include products formed by treatment with strong acids. In this connection, the method used in removing the extraneous materials affects the lignin value. Wacek and Schön obtained 38.5–40.3 per cent of Klason lignin from spruce when the bark was extracted only with water. The same bark gave 30.3 per cent of lignin when extracted with methanol-benzene, and 19 per cent of lignin when it was extracted successively with water, alcohol, and finally with benzene. The application of the Willstätter lignin method to this extracted bark gave a lignin yield of 20.1 per cent. The methoxyl content of the Klason lignin was 5.6 per cent and that of the Willstätter lignin 5.05 per cent (77). Sharkov (62) extracted lignin fractions from spruce and fir and concluded that they were like the products formed by subjecting the corresponding tannin to 72 per cent sulfuric acid. He also found an accumulation of lignin-like substances in the change from living bark to dead bark (61). Suberin, the major constituent of cork cells, is insoluble in cold concentrated sulfuric acid, and hence interferes with a lignin determination. Zellner (81) and Krug (33) did not include lignin determinations in their bark analyses.

Clotofski and Junge (11) obtained widely varying lignin values from birch bark, depending upon the method used; cuprammonium solution gave the lowest yield of lignin with the highest methoxyl content.

Bark lignins undergo chlorination, methylation, and acetylation reactions by conventional lignin methods. Diazomethane in ether methylates only the acidic hydroxyls, whereas dimethyl sulfate with caustic methylates all hydroxyls except those whose methyl derivatives are saponified by the caustic solution (carboxylic hydroxyls). Acetic anhydride in pyridine reacts with all phenolic and alcoholic hydroxyls. Thus it is possible to determine the percentage of different types of hydroxyl groups in a lignin and to note contrasting characteristics. This is illustrated with the alkali lignins from redwood bark and spruce wood (42):

GROUP	REDWOOD BARK LIGNIN 1	REDWOOD BARK LIGNIN 2	SPRUCEWOOD LIGNIN
Methoxyl, per cent	11.6	2.7	14.9
Carboxyl, per cent	2.0	4.4	0.4
Phenolic, per cent	4.2	7.8	3.6
Alcoholic, per cent	3.9	2.1	5.5

Redwood bark, *Sequoia sempervirens*, is separated commercially into two fractions, the "bark fiber" and the "bark dust" (42). The bark fiber is inherently a cellulose fiber. In its raw state, the cellulose appears to be combined with lignin by a linkage which is very resistant to splitting either by caustic soda or by phenol and acid. A part of the lignin appears to be closely related structurally to sprucewood lignin and also to redwood wood lignin. Two other compounds may be associated with the fiber. One is a low-methoxyl phenolic acid; the other closely resembles lignin but contains a definite percentage of carboxyl groups. The first of these is readily soluble in alkali, whereas the second is somewhat more difficultly soluble. There is a possibility that these two compounds are merely mixtures of a phenolic acid containing no methoxyl groups whatever, with redwood bark lignins in different ratios. The bark dust represents a heterogeneous mixture of broken fibers and parenchyma cells, together with a large amount of the phenolic acid found in the fiber. This particular substance probably makes up 70–80 per cent of the bark dust. Because of its behavior in the lignin analytical method, it may appear as lignin in any determination made on redwood bark, thus giving a completely erroneous picture of the lignin content of the redwood bark. The purified product recovered from the bark dust is free of methoxyl groups; it possesses both phenolic and aliphatic hydroxyl and carboxyl groups.

Varying within broad limits are the lignin, methoxyl in lignin, and pentosan contents of some bast fibers isolated by Hilpert and Knackstedt (28). Their data (table 3) show no relationship between pentosan, lignin, or methoxyl in lignin. In this connection, there is no support for the assumption that pentosans are the precursor of lignin (51).

It is evident that the various bark lignins vary in composition, possibly by closely related and isomeric substances. Bark lignin when compared with wood lignin is of increased complexity, and yet may give information that, from a fresh viewpoint and approach, can aid in solving the wood lignin problem.

DELIGNIFICATION

A great resistance to delignification of barks by the chlorination (Cross and Bevan cellulose) and alkaline and acid pulping procedures is often experienced. A commercial sulfite liquor cook of redwood bark fiber gave a pulp with 31.8 per cent of lignin (42) and a recooked soda pulp from this bark retained 28.1 per cent of lignin. Such resistance to delignification is not observed with the wood from this species. This indicates that a stable lignin–carbohydrate linkage, which is absent in wood, actually exists in bark.

A lignin–carbohydrate union in wood has been claimed by several investigators (51). Whether any lignin is actually combined with the carbohydrates in wood cannot be stated with certainty but appears unlikely. For example, it has been assumed that lignin is associated with cellulose in wood by acetal, ester, and ether linkages. Of major importance in this connection is the fact that the holocellulose contains such linkages and is isolated from wood with these linkages intact. The wood lignin molecule contains few if any carboxyl groups, whether it is isolated by acid, alkaline, or inert solvent procedures. Therefore, any ester union of lignin and carbohydrates must originate with the uronic acid fractions, the least resistant substances, and not with the more resistant cellulose fractions. Any difference in the solubility of the isolated wood cellulose and the cellulose in wood can be due to a change in colloidal state and not to a hydrolysis of chemical bonds, whereas the tenacity with which lignin is held to the cellulose in bark is indicative of an actual chemical union.

Wacek and Schön (60) obtained the best results in isolating cellulose from pine and spruce barks by the method of Kürschner and Hoffer (36). The extracted bark was treated with four successive portions of a mixture of one part nitric acid and four parts alcohol. The cellulose so obtained was but faintly yellow and contained 42.2 per cent carbon, 6.4 per cent hydrogen, 0.85 per cent methoxyl, 6.6 per cent pentosan, and 69.7 per cent alpha cellulose. By the same procedure, Heiduschka and Chang obtained 36.4 per cent cellulose from paper mulberry bark and 54.6 per cent cellulose from the corresponding bast (26). The nitric acid method is more drastic than the chlorination method. Hence the yields of cellulose and alpha cellulose are lower than those obtained by chlorination. Both procedures give arbitrary values.

CORK

Related to the cork in bark is the suberin content. Ordinary cork from the bark of the oak tree *Quercus suber* contains 35 to 40 per cent of suberin (17). Because of its cork content the bark of this tree holds first position in commerce. The suberin content of some trees grown in Russia was determined by Sharkov and coworkers (66). Bark from pines, fir, aspen, oak, and plane trees contained 2.0–8.3 per cent of suberin. Sequoia trees of the Socha region contained 8.1 per cent of suberin. Various kinds of birch barks are relatively high in suberin—19.7 to 38.8 per cent. The thick bark of the Douglas fir, *Pseudotsuga taxifolia*, is a rich source of cork, which can be recovered in the form of granules of fairly large dimensions by proper grinding procedures (24). Shakov holds that the transformation of living bark to the dead bark is accompanied by the development of suberin (61).

The exact composition and nature of cork is still unknown. Although cork is one of the most familiar objects in daily use by chemists, it is a substance concerning which relatively little is known chemically. Suberin, which appears to be the major constituent, is very stable chemically. It requires very drastic treatment with acids, alkalies, or oxidizing agents before it is decomposed (17). Suberin yields suberic acid (1,6-hexanedicarboxylic acid) when oxidized by nitric acid. On the other hand, Pope believes that cutose constitutes the greater part of cork. Cutose is insoluble in cold sulfuric acid of specific gravity 1.78 and in the cuprammonium solution that dissolves cellulose; it appears to be composed of stearocutic acid, $C_{28}H_{48}O_4$, with five equivalents of oleocutic acid, $C_{14}H_{20}O_4$ (53). Among the most important properties of cork is its resistance to moisture and to penetration by liquids.

EXTRACTIVES

Early investigations of bark were often directed to the study of new extractive compounds and their possible usefulness in medicinals. As a result a more extensive literature exists on the extraneous substances from barks than on other bark components. Barks of *Angostura, Cascarilla, Condurango,* and *Cinchona* have long been of interest for their production and storage of drugs. Some American medicinal barks have been described by Henkel (27).

Bark extractives contain all the types of compounds present in wood extractives. It is claimed by Richter that the chemical composition of the extractives from the outer and inner barks varies considerably, depending upon the species (58). There is greater solubility in ethyl ether than in petroleum ether. Hence the ethyl ether extracts are conveniently separated into petroleum-soluble and petroleum-insoluble fractions. Of the compounds included in table 2 those most abundant in the ether extractive are higher alcohols, fats and fatty acids, resins, hydrocarbons, and waxes. Phytosterol and ceryl alcohol are commonly present. Palmitic, stearic, oleic, and linoleic acids are the most common fatty acids found. Direct extraction of waste barks is not feasible for the production of fats and fatty acids, because the concentration is too low. The above, along with many other substances, such as coloring matters, tannins, phlobaphenes, and alkaloids, are likewise extracted with alcohol. In the aqueous extract tannins, starch, pectins, sugars, and glucosides predominate. Among the hexoses, fructose, glucose, galactose, and mannose have been reported. The pentoses include arabinose and xylose. Certain of the glucosides have fluorescent properties (43).

It must be realized that the lines of separation in the above extractives are not sharp and there is bound to be some overlapping of components. There is generally some water-soluble material in the alcohol extract. Acidulated aqueous solutions, as well as alcohol, are good solvents for the basic alkaloids.

Probably the most widely distributed compound in a genus is betulinol. This is the white pigment, "birch camphor," of birch trees. It is found in the barks of all white birches, hornbeam (7), and in other Betulaceae (63, 75). A yield of 35 per cent has been obtained from paper birch, *Betula papyrifera*, and 42.7 per cent from the white birch of Europe and Asia, *Betula alba* L. (63). Besides betulinol, the bark of *Betula alba* contains betulol, $C_{15}H_{24}O$, a sesquiterpene boiling at 255–256°C., and a hydrocarbon melting at 49–50°C. A glucoside, m.p. 190°C., is extracted with water. From sweet birch, *Betula lenta* L., is obtained oil of wintergreen (methyl salicylate) and a paraffin, $C_{30}H_{62}$ (78).

PECTIN

The uronic acid substances extracted from barks are heterogeneous compositions. Balsam, *Abies balsamae*, which is the source of the Canada balsam of commerce, is extracted with difficulty for its tannin, because of a highly gelatinous pectin-like material (23). Crude pectins of various properties are obtained from pines and firs. According to Sharkov, Girchits, and Sartaniya, pine bast contains approximately 11 per cent of pectin substances soluble in hot 96 per cent alcohol, 8 per cent of pectin substances insoluble in alcohol and soluble in water at 10–80°C., and 15 per cent of pectin substances which hydrolyze slowly in boiling water (65). Paper mulberry bark contains 9.1 per cent of pectin (26).

The pectin extracted from pine bark with ammonium oxalate solution gave upon analysis 57.5 per cent polyuronides, 12.6 per cent pentosans, 2.0 per cent methoxides, 4.2 per cent lignin, 1.6 per cent cork, and about 3 per cent volatile acids (68). A birch pectin contained 71 per cent of uronic acids and resembled the pectin from pine (68). According to Sharkov and Girchits (64), pectins from barks possess no jellying properties, although the degree of methylation may not be lower than that of pectins from beet and citrus fruit skins. Ash bark, *Fraxinus excelsior*, contains approximately 7 per cent of pectin substances together with 20 per cent of hemicelluloses (9).

A crude pectin substance containing 58.3 per cent uronic acid anhydride, 12 per cent pentosan, 11.2 per cent lignin, and 6.2 per cent ash is extracted with hot water from redwood bark. Mannan is also present as an impurity. Purification of the crude pectin with bromine water gave a pectic acid with 76 per cent uronic acid, 25.9 per cent pentosan, and 0.53 per cent methoxyl; these results indicate that it is similar to pectins isolated from other natural sources (42).

The mucilage from the bark of slippery elm, *Ulmus fulva,* is a mixture of polyuronides. Hydrolysis products are galacturonic acid, *l*-rhamnose, and *d*-galactose (1). The methyl ester of a galacturonidorhamnopyranoside has been isolated from this mucilage (22).

TANNINS

Some barks are potential sources of commercial tannin extracts, where the economic obstacles involved in collecting and transporting are not insuperable and the physicochemical properties (color, purity, astringency, degree of fixation by hides) of the extracts prepared from them are satisfactory. Among the domestic sources of tannin currently considered is the bark of western hemlock (*T. suga heterophylla*), oak, and second-growth Douglas fir. Tannin analyses of the barks of some American softwood and hardwood species were made by Levi and Manuel in 1909 (41). Their findings showed that (*1*) maple, birch, and black ash had low or negligible tannin content, (*2*) oaks, hickory, sweetgum, and yellow pine had relatively high tannin (5–11 per cent), and (*3*) white ash showed a higher tannin content than black ash. The tannin content of the barks of several eastern Canadian conifers was determined by Graham and Rose (23). Russell has made a comprehensive survey of the tannin contents of tree species of the Southeastern United States. The bark of the willow oak, *Quercus phellos,* contains over 10 per cent of tannin, and both the wood and the bark of *Castanea ashei* contain 12 per cent of tannin (59a).

The barks of Australian trees have liberal supplies of tannin unequalled in any other part of the world. Mimosa or wattle bark (*Acacia* species) has up to 40 per cent of tannin (78). Mallet bark, *Eucalyptus occidentalis,* has a tannin content of 35–52 per cent (78). The tannins from *Calletris* bark are similar to that from hemlock and their action on hide is said to be rapid and complete (72); the per cent of tannin from the different species varies from 10.7 to 30.9 (13). Another high-tannin bark is mangrove (17–48 per cent).

According to Kubelka and coworkers, the yield of tannin from pine bark can be increased by 45–75 per cent by the use of 1.35 per cent of a 1:1 mixture of sodium sulfite and bisulfite in the leach water (34). Sulfiting the tannin extract decreases the insolubles and is held to give a softer, more elastic leather. Sharkov, Tyayunova, and Kalnina obtained the best results by using 40 per cent of a 1:1 sulfite–bisulfite mixture, based on insolubles, and heating for 9 hr. at 95–98°C. (68).

In this country a vast untapped reservoir of tannin is the bark of the western hemlock, *T. suga heterophylla.* This tree is one of the principal pulpwoods in the Pacific Northwest, and its bark has long been known as a source of tanning material. Hemlock wood itself has little or no tannin. According to Pittam, who describes a pilot-plant operation (52), about 1 ton of dry bark with an average tannin content of 6.15 per cent is produced per 6 tons of pulp. Smoot and Frey obtained an average value of 15.5 per cent tannin in moisture-free bark (71). The difference is attributed to the leaching action while the logs lay in the boom. An improved process for the preparation of the tannin from hemlock bark with sodium bisulfite is described by Potter and coworkers (54).

NITROGEN COMPOUNDS

On the whole, the investigations on the nitrogen compounds in barks have not been sufficiently comprehensive to permit general conclusions.

Quinine, strychnine, and brucine are the best known of the alkaloids that occur in certain barks. The barks of certain *Strychnos* species, *S. nux vomica* and *S. ligustrina,* may contain over 7.0 per cent of strychnine and brucine (78). The early natives in South America, Guiana, and Java are said to have made an exceedingly poisonous extract from the bark of various *Strychnos* trees, which they used as an arrow poison. The poisonous properties of the extract were particularly manifested when brought in contact with a cut or scratch.

The barks of various species of *Cinchona* long were known for their antifebrile properties. These properties are chiefly due to the presence of quinine and of closely analogous alkaloids. The bark richest in alkaloids (8–12 per cent), of which 3–8 per cent is quinine, is *Cinchona ledgeriana* (10). Besides the alkaloids, the *Cinchona* barks contain fiber, starch, gum, mineral matters, coloring matters, wax, fat, traces of volatile oil, and oxalic and quinic acids (78).

Several barks of lesser known species are used in their respective countries of origin for various purposes. The barks of *Alstonia* trees occuring in India, Java, Australia, and the Philippine Islands are used as bitter tonics and for the treatment of malaria. These barks all contain alkaloid mixtures. The *Kurchi* bark of India, used as a remedy for dysentery, contains the alkaloids conessine and holarrhenine (69). The Yohimba bark of commerce contains alkaloids with physiological action resembling cocaine (69). The bark of *Aspidosperma quebracho blanco,* which grows in South America, is used as a febrifuge; it contains at least three alkaloids of similar physiological action (18). Other barks which contain more or less mixtures of alkaloids are *Aspidosperma quirandy* (19), *Lunasia costulata* Miq. (16), and the *Remijia* species (10). The absence of yohimbine and the presence of corynanthine in *P. africana* and *P. mayumbensis* support the classification of these species in the genus *Pseudocinchona* (56).

A surprisingly large quantity of a poisonous protein (12.9–27.9 per cent) is present in the bark of the common black locust tree, *Robinia pseudacacia* (30). According to Jones and Phillips, this protein was found to consist chiefly of a globulin, albumin, and a proteose. Studies on the isolated proteins found them similar in properties and composition to most vegetable and animal proteins; practically the same assortment and proportions of amino acids are present (30).

Lemesle reported that a complex protein–tannin–resin substance, which is insoluble in alcohol, water, or alkali (40), is present in the bark of *Drings winteri.*

MINERAL CONSTITUENTS

The subject of ash in barks has been reviewed by Czapek (14). The ash content and composition may vary within relatively broad limits for different trees. Often the mineral content of the bark may exceed ten times that of the wood. Manaresi and Tonegutti (45) found the ash content of the bark of the pear tree to be only about three times that of the wood.

About two-thirds to three-fourths of the ash is lime; potash may account for 10–30 per cent; sodium 0.5–2.0 per cent; magnesium 2–5 per cent; iron 0.5–3 per cent; and manganese under 1 per cent. Of the acid constituents, silica is present in largest amount; yields of 20–30 per cent of the total ash are not uncommon. A high silica content is accompanied by a low calcium content. Phosphoric acid may range from 1.5 to 4 per cent. Sulfur and chlorine usually occur only in traces. Fraymouth (20) has described a process for the recovery of oxalates from barks.

TABLE 4

Heating value of typical barks (59)

Based on oven-dry weight of bark

SPECIES	PER CENT ASH	B. T. U. PER LB.
Hardwood		9,410
Lodgepole pine		9,386
Douglas fir	0.95	10,820
Western yellow pine	1.30	9,275
Jack pine	1.51	9,870
Balsam fir	5.19	8,970
Spruce	2.53	9,590
Spruce	2.48	9,395
Hemlock	1.57	9,680

USES OF BARK

It is said that to the lumber and pulp industries bark is a necessary evil which must be disposed of in the easiest and most economical way possible. In the majority of the cases this is accomplished by burning to produce power and steam or by just burning in a waste burner. The possibility of utilizing this bark in other ways than as a fuel has been studied to a limited extent. A few special uses have been found and have been applied in isolated cases. Inasmuch as power and steam are always in demand, this was believed by Rue and Gleason to be the best use in pulp and paper mills (59). The extreme wetness of the bark (35–85 per cent) constitutes one of the chief obstacles to its utilization as a fuel.

The heating value of bark can be considered equal to or higher than that of wood. To illustrate, the heat value of Douglas fir bark, heartwood, and sapwood is respectively 10,100, 9,000, and 8,500 B.T.U. per pound of oven-dry material (79). The heating value of dry non-resinous woods is generally from 7560 to 9000 B.T.U. per pound; whereas the heat value of barks as given in table 4 normally exceeds 9000 B.T.U. The comparative fuel value of some European woods and their barks was investigated by Klein (31).

The heat value of bark and wood is affected by the extraneous materials. Mineral matters contribute little to the heating value, while rosin has about twice the heating value of wood, so that resinous woods and barks have a somewhat higher heating value depending upon the resin content.

Reduction of bark by standard chemical pulping methods ordinarily gives a low yield of pulp, accompanied by a very heavy consumption of chemicals. An exception appears to be the barks of *Crotalaria juncea* and *Sesbania sesbans.* When cooked with 20 per cent of soda they are said to give 40–44 per cent yields of pulps with high tensile strength and good alpha-cellulose content (47). Disintegration of linden bark is effected by leaching with hot lime water and shredding the product into strips (44). Spinnable fibers are claimed to be obtained from willow bark by boiling the raw bark for ½-1 hr. in a 1 per cent alkaline liquor (2). Paper mulberry bark has been used by the Chinese as a paper material for over a thousand years, and a bleached pulp comparable in quality to rag stock is described by Uchastikina and Matveer (76).

Mechanical fibers from long-fibered barks, such as redwood, are used for insulation, furniture upholstery, etc.; the bark dust is suitable for insecticide extenders. Other proposed uses for disintegrated barks are as (*a*) impregnation material for tars, asphalt, etc. (55), (*b*) wall papers, (*c*) insulating board, and (*d*) sheathing, bottle wrappers, deadening felts, chipboard, and box board (32).

Carbonization of barks gives low yields of volatile products. Comparative experiments with spruce, fir, pine, and birch gave a somewhat higher output of charcoal and tar, and less pyroligneous acid and methanol for bark than for the corresponding wood (3). Barks have practically no fertilizer value.

Long roads of research and practice must be travelled before the maximum or optimum utilization of barks can be attained. On the other hand, the complex and varied components of barks do hold possibilities. Some barks which today serve only a limited purpose will be in time explored for a much wider field of utilization.

REFERENCES

(1) ANDERSON, E.: J. Biol. Chem. **104,** 163 (1934).
(2) BECHTOLD, A.: Belgian patent 444,878 (April 20, 1942).
(3) BERGSTROEM, H.: Jernkontorets Ann. **109,** 157 (1925).
(4) BISKO, J., AND ZELLNER, J.: Monatsh. **64,** 12 (1934).
(5) BRIDEL, M., AND CHARAUX, C.: Bull. soc. chim. biol. **17,** 780–92 (1935); **15,** 642 (1933).
(6) BRIDEL, M., AND RABATE, J.: Bull. soc. chim. biol. **12,** 332–41 (1930).
(7) BRUNNER, D., AND WIEDMANN, G.: Monatsh. **63,** 368–73 (1933).
(8) BRUNNER, D., AND WÖHRE, R.: Monatsh. **64,** 21 (1934).
(9) BUSTON, H. W., AND HOPF, H. S.: Biochem. J. **32,** 44–6 (1938).
(10) CHICK, O.: In Allen's *Commercial Organic Analysis,* 5th edition, Vol. VII. P. Blakiston's Son and Company, Inc., Philadelphia (1929).
(11) CLOTOFSKI, E., AND JUNGE, W.: Ber. **74B,** 1415–19 (1941).
(12) CLOTOFSKI, E., WEIKERT, H., AND NICK, H.: Ber. **74B,** 299–307 (1941).
(13) COOMBS, F. A., AND DETTMAN, A. H.: J. Soc. Chem. Ind. **33,** 232 (1941).
(14) CZAPEK, F.: *Biochemie der Pflanzen,* Vol. 2, pp. 414–20. G. Fischer, Jena (1920).

(15) Danoff, C. G., and Zellner, J.: Monatsh. **59,** 307–13 (1932).

(16) Dieterle, H., and Beyl, H.: Arch. Pharm. **275,** 174–91 (1937).

(17) Druce, J. G.: Pharm. J. **130,** 552 (1933).

(18) Field, E.: J. Chem. Soc. **125,** 1444–50 (1924).

(19) Floriani, H. L.: Rev. centro estud, farm. bioquím. **25,** 373–94, 423–47 (1925).

(20) Fraymouth, W. A.: U. S. patent 1,525,806 (February 10, 1925).

(21) Froeschl, N., Zellner, J., and Zikmunda, E.: Monatsh. **56,** 204–11 (1930).

(22) Gill, R. E., Hirst, E. L., and Jones, J.: J. Chem. Soc. **1939,** 1469.

(23) Graham, W. E., and Rose, A.: Can. J. Research **16B,** 369–79 (1938).

(24) Grondal, B. L.: West Coast Lumberman, (October, 1942.)

(25) Hay, K., and Lewis, H. F.: Paper Trade J. **111,** No. 25, 39–43 (1940).

(26) Heiduschka, A., and Chang, Y.: Cellulosechem. **17,** 77–80 (1936).

(27) Henkel, Alice: "American Medicinal Barks," U. S. Dept. Agr. Bull. **No. 139** (1909).

(28) Hilpert, R. S., and Knackstedt, W.: Ber. **72B,** 1582–8 (1939).

(29) Jaeger, P.: Bull. soc. botan. France **87,** 130 (1940).

(30) Jones, D. B., and Phillips, S.: J. Am. Chem. Soc. **59,** 595–6 (1937).

(31) Klein, A. S.: Zellstoff u. Papier **12,** 326–8 (1932).

(32) Kress, O.: J. Ind. Eng. Chem. **8,** 883–6 (1916).

(33) Krug, W. H.: *Yearbook of the Department of Agriculture,* p. 321, Washington, D. C. (1902).

(34) Kubelka, V., Mosner, L., Micek, K., and Dusanek, V.: Collegium **1943,** 35–59.

(35) Kuntara, W., and Grassmann, W.: Collegium **1943,** 79–86; Chem. Abstracts **38,** 2519.

(36) Kürschner, K., and Hoffer, A.: Tech. u. Chem. Papier. u. Zellstoff-Fabr. **26,** 125–39 (1929).

(37) Larsen, E. E., and Lynn, E. V.: J. Am. Pharm. Assoc. **26,** 288–90 (1937).

(38) Lehman, E., and Eisenhuth, F.: Ber. **72,** 1657 (1939).

(39) Lehman, E., and Wilke, G.: Cellulosechem. **20,** 73–86 (1942).

(40) Lemesle, R.: Compt. rend. **214,** 237–8 (1942).

(41) Levi, L. E., and Manuel, E. V.: Hide and Leather (January 2, 1909).

(42) Lewis, H. F., Brauns, F. E., Buchanan, M. A., and Kurth, E. F.: Ind. Eng. Chem. **36,** 759 (1944); Paper Trade J. **119,** No. 22, 34–8 (November 30, 1944).

(43) Lingelsheim, A.: Ber. botan. Ges. **37,** 73 (1919).

(44) Lynbarskiĭ, E., Menshutkin, V., and Prikhozhim, N.: Russian patent 44,633 (October 31, 1935).

(45) Manaresi, A., and Tonegutti, M.: Staz. sper. agrar. ital. **43,** 714–17.

(46) Murti, P., and Seshadri, T. R.: Proc. Indian Acad. Sci. **21A,** 8–18, 147–54 (1945).

(47) Nakamura, Y., and Minia, Y.: Rept. Govt. Sugar Expt. Sta., Tainan, Formosa, **No. 7,** 219–30 (1940).

(48) Oku, M.: J. Agr. Chem. Soc. Japan **12,** 555 (1936); Chem. Abstracts **30,** 6786.

(49) Pajari, K.: Ann. Acad. Soc. Fennicae **59A,** No. 6, 7–160 (1942); Chem. Abstracts **38,** 4648.

(50) Perrot, E., Millat, L., and Colas, R.: Bull. sci. pharmacol. **44,** 325–8 (1937).

(51) Phillips, M.: *Wood Chemistry,* L. E. Wise (*Editor*). Reinhold Publishing Corporation, New York (1944).

(52) Pittam, W.: Paper Trade J. **120,** No. 24, 40–4 (1945).

(53) Pope, T. H.: In Allen's *Commercial Organic Analysis,* Vol. I, p. 550. P. Blakiston's Son and Company, Inc., Philadelphia (1929).

(54) Potter, E., Williams, K., Swenson, T., and Feustel, I.: Ind. Eng. Chem. **36,** 1146–9 (1944).

(55) Quinn, R. G.: U. S. patent 2,035,921 (March 31, 1936).

(56) Raymond-Hamet: Compt. rend. **212,** 305–6 (1941).

(57) Rogerson, H.: Proc. Chem. Soc. **28,** 138; J. Chem. Soc. **101,** 1040–52 (1912).

(58) Richter, G. A.: Ind. Eng. Chem. **33,** 75–81 (1941).

(59) Rue, J. D., and Gleason, E. P.: Paper Trade J. **78,** No. 16, 14–50 (1924).

(59a) Russel, A.: J. Am. Leather Chem. Assoc. **37,** 340–56 (1942); **38,** 144–8; 235–8 (1943); **39,** 173–8 (1944); **40,** 422–6 (1945).
(60) Sharkov, V. I.: Lesokhim. Prom. **1938,** No. 3–4, 16–17.
(61) Sharkov, V. I.: Bumazhnaya Prom. **16,** No. 8, 32–6 (1938).
(62) Sharkov, V. I.: Lesokhim. Prom. **2,** No. 8, 11 (1939).
(63) Sharkov, V. I., and Belyaevskii, I.: Lesokhim. Prom. **1,** No. 3–4, 30–3 (1932).
(64) Sharkov, V. I., and Girchits, A.: Lesokhim. Prom. **1939,** No. 2, 9–12; **1940,** No. 1, 14–23.
(65) Sharkov, V. I., Girchits, A., and Sartaniya, F. A.: Lesokhim. Prom. **1939,** No. 3, 40–6.
(66) Sharkov, V. I., Kalnina, V. N., and Sobetskiĭ, S. V.: Lesokhim. Prom. **1939,** No. 5, 8–12.
(67) Sharkov, V. I., and Kalnina, V. N.: Lesokhim. Prom. **2,** No. 9, 25–31 (1939).
(68) Sharkov, V. I., Tyagunova, Z. A., and Kalnina, V. M.: Lesokhim. Prom. **6,** No. 2, 9–10 (1938).
(69) Sharpe, T. M.: In Allen's *Commercial Organic Analysis*, 5th edition, Vol. VII. P. Blakiston's Son and Company, Inc., Philadelphia (1929).
(70) Smoot, C. C.: J. Am. Leather Chem. Assoc. **8,** 107–9 (1913).
(71) Smoot, C. C., and Frey, R. W.: U. S. Dept. Agr. Tech. Bull. **No. 566** (1937), U. S. Government Printing Office, Washington, D. C.
(72) Smith, H. G.: J. Soc. Chem. Ind. **30,** 1358 (1911).
(73) Sosa, A.: Rev. acad. cienc. Madrid **31,** 81–100 (1934).
(74) Stather, F., Herfeld, H., and Schöpel, H.: Collegium **1939,** 561–81.
(75) Steiner, M.: Mikrochemie, Festschrift von Hans Molisch **1936,** 405–17.
(76) Uchastkina, Z. V., and Matveer, V. Y.: Tsentral. Nauch.-Issledovatel. Inst. Bumazhnai Prom., Materialy **1934,** No. 4, 100–7.
(77) Wacek, A. V., and Schön, A.: Holz Roh-u. Werkstoff **4,** 18–26 (1941).
(78) Wehmer, C.: *Die Pflanzenstoffe.* G. Fischer, Jena (1929).
(79) Willey, E. C.: Oregon State College, Eng. Expt. Sta., Circular **No. 7,** September, 1942.
(80) Wilson, S. A.: Mimeographed Report, January 31, 1946, "Sawmill Waste Developed, Used, and Not Used in Oregon and Washington in 1944," Pacific Northwest Forest and Range Experiment Station, Portland, Oregon.
(81) Zellner, J.: Monatsh. **47,** 151–76 (1926).
(82) Zellner, J.: Monatsh. **46,** 309–31, 611–30 (1926).
(83) Zellner, J.: Monatsh. **47,** 659–79 (1926).