P.) and also the Spruce Falls Power and Paper Company for their kind financial assistance. They are indebted also to the Massachusetts Institute of Technology for the use of the spectroscopic equipment and to Dr. G. R. Harrison and Mr. A. Knudsen of the Physics Department of that institution for their helpful coöperation.

Summary

The ultraviolet absorption spectra of pyrocatechol and pyrogallol-1,3-dimethyl ether, their methyl ethers and various derivatives in which a carbon side chain is substituted para to the phenolic hydroxyl have been determined. Compounds containing the vanilloyl or veratroyl group have three absorption bands in the ultraviolet region at approximately 980 f, 1070 f and 1300 f, syringoyl derivatives have bands at 980 f and 1300 f and trimethoxybenzoyl derivatives at 1070 f and 1300 f.

The effect of side chain substitution is discussed briefly.

MONTREAL, CANADA RECEIVED MARCH 11, 1943

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LXXIII. The Ultraviolet Absorption Spectra of Ethanol Lignins

BY R. F. PATTERSON AND HAROLD HIBBERT

In the previous communication[1] the ultraviolet absorption spectra of a large group of substances closely related to lignin, or actual lignin progenitors, were discussed. In the present article this work has been extended to an investigation of a series of ethanol lignins obtained by the ethanolysis of spruce and maple woods. Based on these results an attempt has been made to correlate structure and absorption and in this way to provide more definite evidence from the physicochemical standpoint concerning the structure of lignin.

Experimental

The products investigated comprised four groups of ethanol lignins obtained by the ethanolysis of spruce and maple wood meals employing 2% ethanolic hydrogen chloride as extractant.[2]

A detailed description of the separation and isolation as ether insoluble, ether soluble and water soluble lignins and also as ethanolysis low-boiling oils has already been given.[2] The degree of molecular complexity has been shown to decrease in the order named.[2]

The absorption curves were obtained in exactly the same manner as described previously for the pure compounds.[1] Ethanol was used as solvent except in the case of the ether insoluble lignins where it was necessary to employ chloroform.

Discussion

Spruce Lignins.—The absorption curves for spruce and maple lignins are given in Diagrams 1 and 2, respectively. In the case of spruce the low-boiling oils (comprising the monomolecular entities) and the water soluble lignin group each show three absorption bands in the ultraviolet region and these may be classified as of the 980 f, 1070 f, and 1300 f types typified in the vanilloyl and veratroyl compounds.[1] The closest agreement between the absorption curve of the low-boiling oils and the monomolecular materials previously investigated[1] is obtained with 2-acetoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone in which the acetoxy group (a two carbon side chain without new resonators) has been attached to the three carbon side chain of a phenylpropane unit. Compounds of this type (*e. g.*, the ethyl ether of 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone) have been isolated from the spruce ethanolysis low-boiling oils in fair yields and it would appear, on the basis of the present spectroscopic evidence, that the remainder of the members comprising this lignin group do not differ markedly in structure from the 2-acetoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone type. If, as previously indicated, the 980 f band is to be assigned to a carbonyl group in conjugation with the aromatic nucleus and the 1070 f band to "meta position freedom" it is to be expected from curve 1, Diagram 1, that not all of the components present in the spruce low-boiling oils con-

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[1] Patterson and Hibbert, THIS JOURNAL, **65**, 1862 (1943).

[2] Patterson, West, Lovell, Hawkins and Hibbert, *ibid.*, **63**, 2065 (1941).

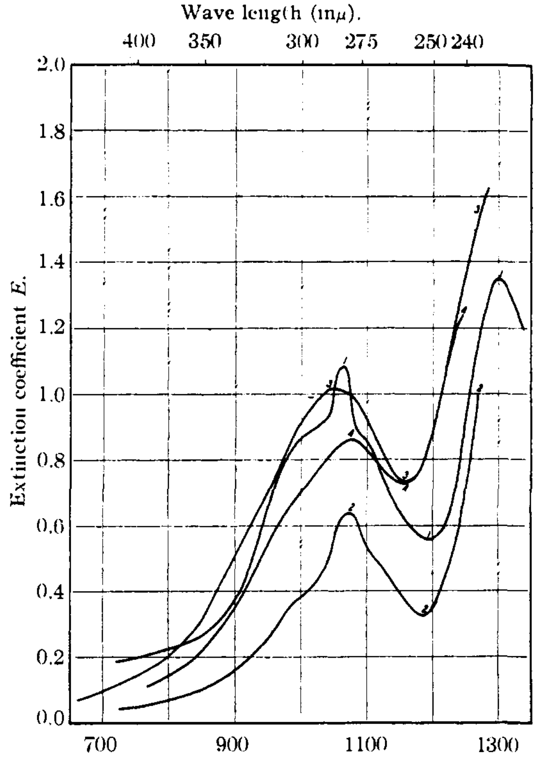

Fig. 1.—Spruce lignins: 1, low-boiling oils; 2, water-soluble lignin; 3, ether-soluble lignin; 4, ether-insoluble lignin; concentration, 0.003%; solvent, ethanol for 1, 2 and 3, chloroform for 4.

tain a conjugated carbonyl group since the 980 f band is weaker than in the case of the vanilloyl compounds. The parallelism of the curves is evidently closer with the veratroyl than with the vanilloyl series but there is no experimental evidence warranting this comparison since neither veratroyl nor veratryl derivatives have been isolated, as yet, from wood. The recently isolated lignin progenitors or degradation products in which the carbonyl group is in the 2 position in the side chain and thus not conjugated with the nucleus (*e. g.*, 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone)[3] would account for the decreased absorption in the 980 f region.

The point to be emphasized in connection with the absorption spectrum of the low-boiling oils (curve 1, Diagram 1) is that only in this group is a fairly complete picture provided of the actual chemical nature of the mixture (about 30% of the spruce lignin oils having already been isolated as crystalline compounds). In extracted lignins, or their precursors, from spruce and other soft woods there is present only the 4-hydroxy-3-methoxyphenyl nucleus so that in each case the position meta to the side chain is unsubstituted, at least in the monomolecular distillable oils. This position may not be free in the more complex condensation polymers. In spite of the fact that the spruce low-boiling ethanolysis oils consist of a mixture of at least five different phenylpropane derivatives, it is possible to predict from a consideration of the spectra of pure compounds already discussed[1] that the mixture should show absorption at about 1070 f and examination of curve 1, Diagram 1 shows that this does actually occur, a result in complete harmony with conclusions drawn from the spectra of the pure compounds.

In the case of the spruce water-soluble lignin group very little is known of the chemical nature of the constituents but a comparison of the absorption curve 2 (Diagram 1) with that of the low-boiling monomolecular oils points to a decided similarity between the two groups. Water soluble lignins are known to have higher molecular weights than the low-boiling oils and it seems likely that the former are derived from one or more of the simple monomolecular units by condensation reactions. With both spruce and maple there is a definite decrease in the intensity of absorption on passing from the low-boiling ethanolysis oils to the water soluble lignin and, if the assumption of the origin of the latter as condensation products is correct, this decrease is suggestive of a non-resonance-transmitting linkage between building units. One such type of linkage which could originate from a monomer such as 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone is an ether linkage formed through elimination of water from an aliphatic and a phenolic hydroxyl. It must be emphasized that absorption spectra furnish no proof of such a linkage and that an oxygen union is merely *one* satisfactory way of explaining the decrease in intensity of absorption.

From the ether soluble and ether insoluble spruce lignin groups it is possible to obtain vanillin by oxidation,[1] *n*-propylcyclohexane derivatives by hydrogenation,[5] and 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione and 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone by retreatment with ethanolic hydrogen chloride.[6] Although the yields are relatively small in each case

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(3) Kulka and Hibbert, This Journal, **65**, 1180 (1943).

(4) Creighton, McCarthy and Hibbert, *ibid.*, **63**, 312 (1941).

(5) Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941).

(6) Hewson and Hibbert, This Journal, **65**, 1173 (1943).

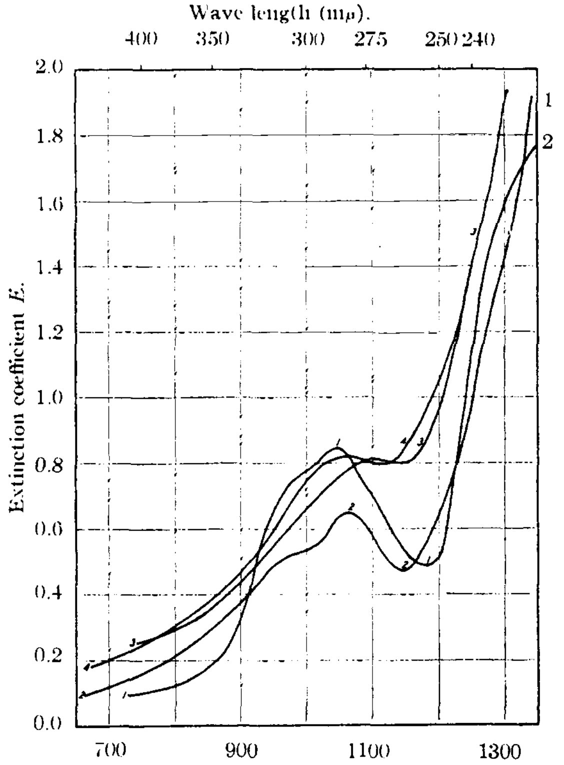

Fig. 2.—Maple lignins: 1, phenol fraction of the low-boiling oils; 2, water-soluble lignin; 3, ether-soluble lignin; 4, ether-insoluble lignin; concentration, 0.003%; solvent, ethanol for 1, 2 and 3, chloroform for 4.

it is probable that these complex lignin groups are formed from phenylpropane derivatives similar to those under discussion and on this basis a theoretical interpretation of the absorption curves 3 and 4 in Diagram 1 can be attempted. They show a very broad absorption band with maxima at 1050 f and 1075 f, respectively. The single maximum in this region led Herzog and Hillmer[7] to conclude that extracted lignins, in general, were lacking in carbonyl groups conjugated with the aromatic nuclei, a conclusion not necessarily true since the common broad absorption band may be indicative of two maxima of nearly the same extent of absorption. In Diagram 3 a curve analysis is given for curve 3 of Diagram 1 and serves to illustrate the possible presence of either carbonyl groups or ethylenic double bonds in conjugation with the benzene ring even in those instances where only a single maximum is observable. It seems highly probable that these water insoluble, amorphous lignins consist of more than one type of polymer in which both conjugation of the aromatic nucleus with the side chain and also "meta position freedom" are present to varying extents. This is confirmed by variations in the width of the absorption bands and the location of maxima for the curves of different lignins. It is regrettable that lignins are, in general, insoluble in the non-polar solvents most suitable for ultraviolet absorption spectroscopy since otherwise it might be possible to obtain resolution of the 980 f and 1070 f bands.

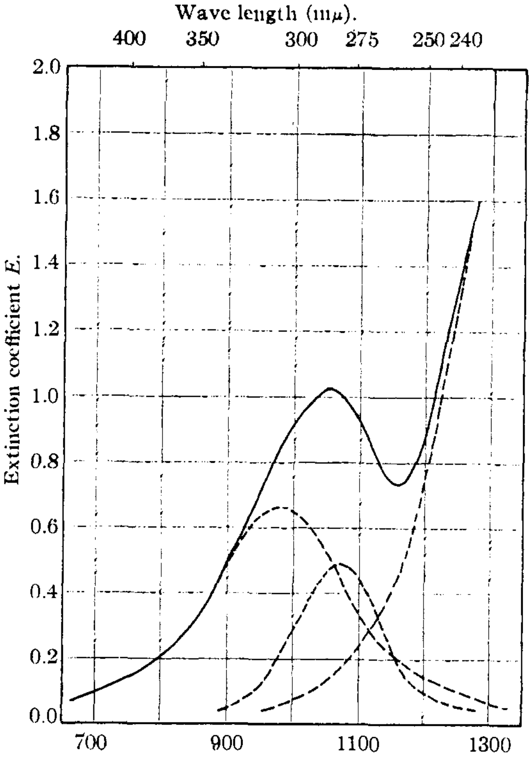

Fig. 3.—Curve analysis for ether-soluble spruce lignin: solid line, absorption spectrum; broken line, possible configuration of component bands.

Maple Lignins.—In Diagram 2 the absorption curves of representative *maple* ethanol lignins similar to those discussed above (Diagram 1) are given. In place of the total low-boiling ethanolysis oil group the "phenol fraction" isolated from it by extraction with 5% sodium hydroxide solution[8] has been substituted (curve 1).

The above comments on spruce lignins apply here with equal force and a comparison of Diagrams 1 and 2 will show that there is a close similarity between curve 1, Diagram 1 and curve 1, Diagram 2 and between curves 2 in the two diagrams, the difference between these and

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[7] Herzog and Hillmer, *Ber.*, **64**, 1288 (1931).

[8] Pyle, Brickman and Hibbert, THIS JOURNAL, **61**, 2198 (1939).

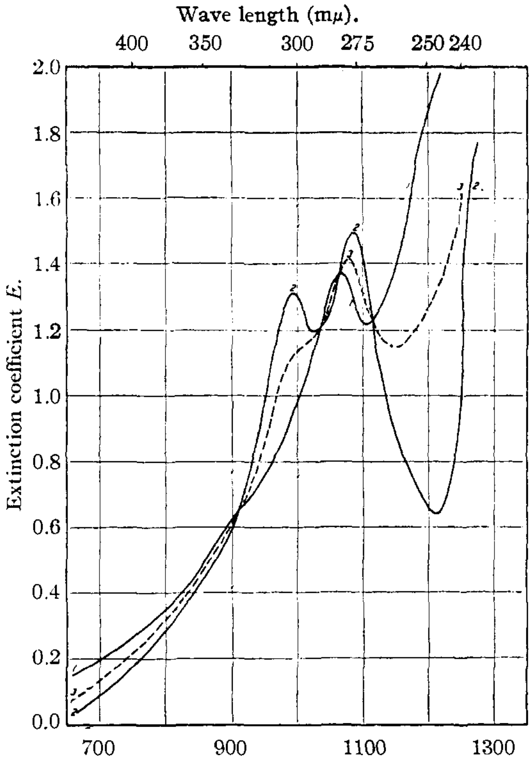

Fig. 4.—1, ethanolysis product from 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone; 2, ethanolysis product from 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone; 3, average of curves 1 and 2; concentration, 0.003%; solvent, ethanol.

curves 3 and 4 being readily apparent. It is evident that in the extreme ultraviolet region (above 1200 f) the curves of the water soluble (curves 1 and 2) and water insoluble (curves 3 and 4) materials form two distinct types, the former occurring at higher frequency values and being in better agreement with those of the monomolecular units within the same frequency range. Polymerization is thus apparently accompanied by a bathochromic shift of this band.

Maple water-soluble lignins and low-boiling oils show a relatively greater absorption in the 980 f as compared with the 1070 f region than do the corresponding spruce lignin groups. This finds a ready explanation in that the maple lignins contain both the 4-hydroxy-3,5-dimethoxyphenyl and the 4-hydroxy-3-methoxyphenyl nuclei and the 1070 f band has been shown to be absent in the former.

The absorption bands of maple water-insoluble lignins (curves 3 and 4, Diagram 2) are not as distinct as the corresponding bands of spruce lignins due, probably, to the increased complexity resulting from a polymerization involving two types of compounds. The chemical nature of such a complex material cannot be predicted from absorption spectra and indeed attempts to do so may lead to erroneous conclusions. If attention is confined to the lignins isolated by the use of ethanolic hydrogen chloride, however, a few broad conclusions seem justified: (a) Ultraviolet absorption spectra confirm chemical evidence that lignin is built up of compounds of the types exemplified by the hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanones and the hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanones. (b) The general banded structure of the lignin absorption curves is indicative of the aromatic nature of the material, particularly the absorption in the extreme ultraviolet (1300 f region). (c) The width of the absorption bands for the amorphous lignins, *i. e.*, the shape of the curves between 800 f and 1000 f, suggests that a carbonyl group or an ethylenic double bond in conjugation with the benzene ring is present *to some extent*.

As a check on the validity of these conclusions the absorption spectra of two synthetic, amorphous, lignin-like materials prepared by ethanolysis of 2- and 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone were determined. These polymers were formed by treatment of the pure compounds with 2% ethanolic hydrogen chloride at reflux temperatures under conditions identical with those used in the ethanolysis of wood. The curves are given in Diagram 4 and show that both substances exhibit an absorption band in the typical "meta-free" 1070 f region. The ethanolysis product from 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone has an additional band head at 990 f (curve 2) and hence the ultraviolet absorption spectra of lignins in this region could be accounted for by the presence of this type of polymer. A mixture of equal quantities of the two polymers would presumably give rise to the absorption curve 3 in Diagram 4 (obtained by averaging curves 1 and 2) and the similarity between the shape of this curve and those of the water soluble lignins is apparent.

Acknowledgment.—The authors wish to thank the National Research Council of Canada for the award of a Fellowship to one of them (R. F. P.) and also the Spruce Falls Power and Paper Company for their kind financial assistance. They are indebted also to the Massachusetts Institute of Technology for the use of the spectroscopic equipment and to Dr. G. R. Harrison and Mr. A. Knudsen of the Physics Department of that institution for their kind and helpful coöperation.

Summary

The behavior of lignins as absorbers of energy in the ultraviolet region has been compared with that of known compounds in the same region and certain conclusions drawn from such comparison. These have been enumerated above and may be briefly summarized as follows:

1. The spectra of amorphous lignins can be explained satisfactorily on the assumption that they are derived from lignin precursors of the types exemplified by hydroxy derivatives of 1-(4-hydroxy-3-methoxyphenyl)-1-propanone and 1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone.
2. The absorption curves indicate that lignin is aromatic in nature.
3. The evidence suggests that a carbonyl group or an ethylenic double bond is present in conjugation with the aromatic nucleus to some at present unknown extent.

MONTREAL, CANADA RECEIVED MARCH 11, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

X-Ray Diffraction of Sodium Laurate, Palmitate and Stearate at Room Temperature

BY JAMES W. MCBAIN, O. E. A. BOLDUAN AND SYDNEY ROSS

In a previous communication[1] the characterization of different phases of sodium stearate was made on the basis of X-ray powder diffraction photographs. In the present paper fiber photographs of sodium laurate, sodium palmitate and sodium stearate are interpreted, yielding further information with regard to different soap phases.

Materials.—The soaps used throughout the present investigation were prepared from the corresponding fatty acids of the greatest purity supplied by Kahlbaum. Dr. R. D. Vold had prepared fibers of sodium palmitate by sealing a mixture of 25% water, 75% soap in an Erlenmeyer flask in an oven at 90° for a few weeks. It was found that soap fibers could be more easily prepared by placing a mixture of 25% water and 75% soap in an open beaker, under a bell jar without seal, in an oven at 90°. After about twelve hours it was observed that inside the porous mass of soap there were fine bundles of fibers about 3 mm. long and about 0.1-0.2 mm. in diameter. The sodium laurate fibers were much better formed than those of the sodium palmitate and stearate.

Mounting of Soap Fibers.—Fine glass capillary tubing, with an outer diameter of 1.5 mm. and an inner diameter of about 0.1-0.2 mm., is used. A small bundle of fibers, three or four millimeters long, having a diameter slightly greater than the internal diameter of the capillary and with a pointed end, is placed in the capillary and gently forced into it for a distance of about 1 mm. until it is firm. The fiber bundle is examined under a lens and all fibers not in line with the main bundle are carefully removed. Examination with a telescope having a cross-hair is made to ascertain that the fiber is aligned along the axis of the capillary. The capillary, with the fiber, is mounted at the end of a steel shaft which fits into the camera and is rotated at a speed of one revolution per minute by a Telechron motor.

Method.—The radiation used was Cu $K\alpha$ ($\lambda = 1.537$ Å.), filtered through nickel foil. All the data were examined for possible Cu $K\beta$ lines and also for lines due to the L radiation of tungsten from the filament ($\lambda = 1.675$ Å.).

1. **Results with Sodium Laurate.**—Sodium laurate fibers, prepared and mounted as previously described, were photographed in a cylindrical camera with a radius of 50 mm. The photograph obtained is shown in Fig. 1a and Fig. 1b. Using a different fiber and the cylindrical camera designed for high temperature,[2] with a radius of 57.3 mm., the photograph shown in Fig. 2 was obtained. Powder photographs taken with the flat casette camera and high temperature camera are reproduced in Figs. 3 and 4, respectively. With the casette camera the soap was pressed into a hole in a brass washer 1.0 mm. thick which was mounted on the end of the collimating tube. The soap sample for the cylindrical camera was "cast" in the form of a stick which was mounted on the end of a rotating shaft. This method uses the same technique as de Bretteville.[3] The powder photographs obtained by these two methods are identical.

Previous investigations have shown that soaps crystallized from water are monoclinic and that in soap fibers and crystals the *b* axis of the unit cell

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[1] J. W. McBain, A. de Bretteville and S. Ross, *J. Chem. Phys.*, 11, 179 (1943).

[2] A. de Bretteville, *Rev. Sci. Instruments*, 13, 481 (1942).

[3] A. de Bretteville, Ph.D. Dissertation, Stanford University, 1941. May be ordered copied in bibliofilm or photoprint form by the Bibliofilm Service, United States Department of Agriculture Library, Washington, D. C.