lowered by increase in the dielectric constant of the medium.

2. The benzimidazoles studied are very reactive. The reactivity is apparently due to the benzimidazole grouping, being little affected by the alkyl groups attached to the carbon atom bearing the chlorine.

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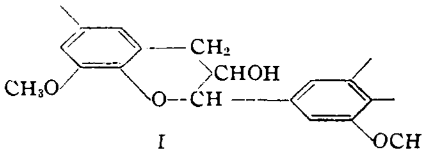
[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LXXII. The Ultraviolet Absorption Spectra of Compounds Related to Lignin

BY R. F. PATTERSON AND HAROLD HIBBERT

The use of ultraviolet absorption spectroscopy for the examination of lignins and related compounds is by no means a new approach to the study of lignin structure. Herzog and Hillmer[1] were the first investigators in this field. From the absorption spectra of a large number of lignins and simple compounds they concluded that lignin is derived from units consisting of partly or wholly etherified di- or trihydroxy phenols having side chains of about three carbon atoms containing neither carbonyl nor unsaturated linkages in conjugation with the benzene ring. They also noted a consistent difference in the position of the absorption maxima for lignins isolated from hardwoods and softwoods. Hägglund and Klingstedt[2] and Stamm, Semb and Harris[3] have also reported a difference between the curves of hardwood and softwood lignins, the latter workers placing the absorption maximum at 2740–2760 Å. for hardwoods and at 2800–2870 Å. for softwoods. Other absorption curves for lignins, reported by Goslawski and Marchlewski,[4] include those of methanol, ethanol, isobutylcarbinol and alkali lignins in ethanol and alkali solution. Maxima range from 2795 to 2835 Å. and the different curves have the same general shape in spite of the different extraction methods used. Glading[5] has recently determined the absorption spectra of spruce "native" lignin, lignins isolated by the use of phenol, glycol, thiophenol, alkali, etc., and various lignin derivatives, all of which show the same characteristic absorption band at approximately 2800 Å. This author also reports the absorption curves for benzalacetophenone, piperonalacetophenone, 2-hydroxychalcone, flavanone, quercetin, guaiacol and benzalacetone and by comparison with these known compounds he concludes that the spectrum of "native" lignin can be explained by the assumption that each building unit (mol. wt. 840) contains two pyran rings such as that present in I. The absorption spectrum of flavanone, on which this argument is largely based, has a maximum at 2530 Å. and it is assumed by Glading that polymerization to a compound having a molecular weight as great as that of lignin would produce a bathochromic shift of the absorption band to 2800 Å., this conception being based on the fact that a shift to longer wave lengths is observed when isoeugenol is polymerized to the dimer. This assumption does not seem to be justified by recent work on styrene[6] in which it was found that a shift of the absorption bands to *shorter* wave lengths occurred on polymerization.



I

All of these investigators used amorphous lignins—water-insoluble materials of relatively high molecular weight—and in most cases a direct comparison has been made with simple monomolecular model substances. Herzog and Hillmer[1] compared their lignin curves with those of such compounds as eugenol, isoeugenol and isosafrole which are compounds related to those isolated as degradation products of lignin. Glading has used a different approach by tentatively accepting one of Freudenberg's suggested lignin formulas and comparing it with the most closely related compounds available.

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(1) Herzog and Hillmer, *Z. physiol. Chem.*, **168**, 117 (1927).

(2) Hägglund and Klingstedt, *Svensk. Kem. Tid.*, **41**, 185 (1929); *Z. physik. Chem.*, **152**, 295 (1931).

(3) Stamm, Semb and Harris, *J. Phys. Chem.*, **36**, 1574 (1932).

(4) Goslawski and Marchlewski, *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, **1934A**, p. 261.

(5) Glading, *Paper Trade J.*, **111**, 288 (1940).

(6) Owens, *Ind. Eng. Chem.*, **11**, 643 (1939).

Recent investigations of Hibbert and co-workers have resulted in the isolation and positive identification of a substantial fraction of the water-soluble lignin products by the action of ethanolic hydrogen chloride on both hardwoods and softwoods. From maple wood meal it has been possible to obtain 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone,[7] 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione,[8] syringaldehyde,[9] 2-ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone,[10] 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone,[11] 1-(4-hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione[8] and more recently vanillin and 1-(4-hydroxy-3-methoxyphenyl)-2-propanone.[11] These substances are true progenitors of the isolated lignins and therefore furnish an excellent source of data for the interpretation of lignin absorption curves. That these phenylpropane derivatives are the precursors of amorphous lignins has received confirmation in the isolation of *n*-propylcyclohexane derivatives by hydrogenation of the lignins[12] and in their partial conversion to identifiable monomolecular compounds by re-ethanolysis.[13]

The present paper is concerned with the ultraviolet absorption spectra of a number of pure substances, including the water-soluble monomolecular ethanolysis products obtained from maple wood mentioned above and others closely related to them. Some of the substances investigated have been previously reported[14] but it was considered essential that their absorption curves be redetermined in the present work in view of the disagreement in the positions of absorption maxima to be found in the literature. An attempt has been made to relate the structure of the new compounds to their absorption spectra and so to pave the way for the interpretation of the lignin spectra which are described in the following communication.[15]

Experimental

In obtaining the absorption spectra a Hilger medium quartz spectrograph and a Hilger Spekker photometer were used. The light source consisted of a 15,000 volt condensed spark between steel alloy electrodes. The solution and solvent were contained in a matched pair of cylindrical quartz cuvettes each 1 cm. thick mounted on the photometer in the paths of two parallel rays of light from the source. By means of the mechanical diaphragm of the photometer the extinction was varied from 0.0 to 2.0 in successive intervals of 0.1 and an exposure made at each extinction value. The plates (Eastman "Process") were developed in Eastman D61A, fixed, washed and dried and the match points determined by visual inspection against an evenly lighted ground-glass field.

In each case a sample of the substance under investigation was weighed on a semi-micro balance and dissolved in 10 cc. of absolute ethanol (U. S. Industrial Chemicals, Inc., "Absolute Pure Ethyl Alcohol—100% U. S. P."). This solution was approximately ten times the concentration required and small samples from this reservoir were diluted to a concentration whereby the maximum of the principal absorption band was located between $E = 1.2$ and $E = 1.8$ on the plate.

The positions of the match points on the finished plates were read from a superimposed standard plate calibrated in millimicrons. Millimicrons were converted to fresnel units of frequency[16] and the curves plotted with these units as abscissas in order to facilitate the location of damped maxima by curve analysis (frequency is linearly related to energy, and absorption bands are symmetrical distribution curves when plotted on an energy base). Extinction values, read directly from the Spekker photometer and given by the equation $E = \log_{10} I_0/I$, were plotted as ordinates.

Where damped absorption bands were indicated by distinct inflections the position of the band maximum was determined by curve analysis. An example is given in Fig. 1 for 3-acetoxy-1-(3,4-dimethoxyphenyl)-1-propanone in which the solid line represents the absorption curve of the compound in ethanol solution (0.003 g. per 100 cc.) and the dotted line shows the reconstruction necessary to determine the position of the maximum at 983 f. The

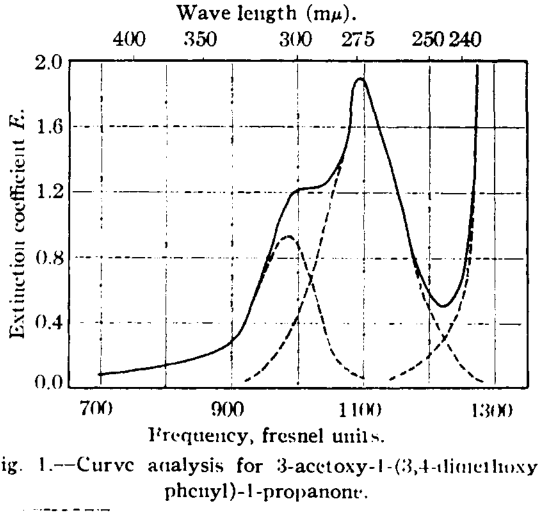

Fig. 1.—Curve analysis for 3-acetoxy-1-(3,4-dimethoxyphenyl)-1-propanone.

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[7] (a) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509 (1939); (b) MacInnes, West, McCarthy and Hibbert, *ibid.*, **62**, 2803 (1940).

[8] Kulka, Hawkins and Hibbert, *ibid.*, **63**, 2371 (1941).

[9] Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939).

[10] Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

[11] Kulka and Hibbert, *ibid.*, **65**, 1180 (1943).

[12] See review articles, Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941), and *Ann. Rev. Biochem.*, **11**, 183 (1942).

[13] Hewson and Hibbert, THIS JOURNAL, **65**, 1173 (1943).

[14] See, for example, Hillmer and Schorning, *Z. physik. Chem.*, **167A**, 407 (1933); **168A**, 81 (1934).

[15] Patterson and Hibbert, THIS JOURNAL, **65**, 1869 (1943).

[16] Fresnel units (f) = 3×10^5 divided by the wave length (λ) in millimicrons (mμ) = 0.03 multiplied by wave number (cm.$^{-1}$).

Table I. (Nuclear Type (A)—Fig. 2. (See Table II for footnotes.)

	Compound	Concn.[a]	Band A (Max.) f^b	λ^c	E^d	$\log_{10}K^e$	$\log_{10}\epsilon^g$	Band B (Max.) f	λ	E	$\log_{10}K$	$\log_{10}\epsilon$	Band C (Max.) f	λ	E	$\log_{10}K$	$\log_{10}\epsilon$
1	Vanillin	0.0020	975	3080	1.60	1.90	4.08	1080	2780	1.62	1.91	4.09	(1290)	(2320)			
2	2-Hydroxy-1- (4-hydroxy-	.0025	990	3030	1.45	1.76	4.05	1070	2800	1.60	1.81	4.10	(1294)	(2315)			
3	3-Hydroxy-1- 3-methoxy-	.0026	1005	2985	1.50	1.76	4.05	1081	2779	1.71	1.82	4.11	(1305)	(2300)	(2.3)	(1.94)	(4.23)
4	2-Ethoxy-1- phenyl)-1-	.0031	980	3060	1.20	1.59	3.94	1060	2830	1.50	1.68	4.03	1297	2315	2.15	1.84	4.19
5	2-Acetoxy-1- propanone	.0031	983	3050	1.56	1.70	4.08	1070	2800	1.80	1.76	4.14	(1297)	(2315)			
6	2-Acetoxy-1-(3-methoxy-4-acetoxyphenyl)-1-propanone	.0030	980	3030	0.57	1.28	3.73						1168	2570	1.52	1.71	4.16
7	1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione	.0029	914	3180	1.55	1.73	4.02	1052	2825	0.52	1.25	3.54	1277	2350	1.52	1.72	4.01
8	4-Hydroxy-3-methoxyphenylcarbinol	.0032						1075	2790	0.98	1.49	3.68	(1313)	(2282)	(2.26)	(1.85)	(4.04)
9	1-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone	.0051						1060	2830	1.65	1.51	3.86	Band indicated				
10	Methanol lignin from 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone	.0030						1069	2805	1.34	1.65		Band indicated				
11	Ethanol lignin from 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone	.0035	993	3020	1.52	1.64		1085	2765	1.72	1.69		Band indicated				
12	Eugenol	.0041						1068	2809	1.41	1.55	3.76	Band indicated				
13	Eugenol acetate oxide	.0102						1094	2740	1.40	1.14	3.49	Band indicated				
14	Isoeugenol	.0029	1000^f	3000	0.50	1.24	3.45	1140	2630	1.78	1.79	4.00	Band indicated				
15	4-Hydroxy-3-methoxyacetophenone	.0020	987	3040	1.26	1.80	4.02	1090	2753	1.52	1.88	4.10	(1308)	(2295)	(2.26)	(2.05)	(4.27)
16	2-Bromo-1-(4-hydroxy-3-methoxyphenyl)-1-propanone	.0030	950	3158	1.28	1.63	4.04	1063^f	2820	0.78	1.42	3.83	1283	2317	1.44	1.68	4.09
17	Coniferin	.0030	1015^f	2955	0.52	1.24	3.77	1160	2585	1.67	1.75	4.28	Band indicated				

Table II. Nuclear Type (B)—Fig. 2

	Compound	Concn.[a]	Band A (Max.) f^b	λ^c	E^d	$\log_{10}K^e$	$\log_{10}\epsilon^g$	Band B (Max.) f	λ	E	$\log_{10}K$	$\log_{10}\epsilon$	Band C (Max.) f	λ	E	$\log_{10}K$	$\log_{10}\epsilon$
1	Veratric aldehyde	0.0015	973^f	3080	0.78	1.69	3.91	1095	2737	1.45	1.99	4.21	(1310)	(2290)			
2	2-Hydroxy-1- (3,4-dimethoxy-	.0029	965^f	3110	0.64	1.34	3.66	1095	2737	1.60	1.74	4.06	(1310)	(2290)	(2.3)	(1.90)	(4.22)
3	2-Acetoxy-1- phenyl)-1-	.0030	962^f	3120	1.17	1.59	3.99	1087	2760	2.24	1.87	4.27	(1310)	(2290)			
4	3-Acetoxy-1- propanone	.0030	983^f	3050	0.93	1.49	3.89	1097	2733	1.90	1.80	4.20	(1314)	(2280)			
5	1-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone	.0058						1070	2800	1.48	1.41	3.73	Band indicated				
6	3,4-Dimethoxybenzoic acid	.0025	1043	2875	1.00	1.60	3.86	1163	2578	2.05	1.91	4.17					
7	3,4-Dimethoxy-ethylcinnamate	.0014	990	3030	1.53	2.04	4.41	1045	2870	0.72	1.71	4.08	1300	2305	1.06	1.88	4.25
8	2-Bromo-1-(3,4-dimethoxyphenyl)-1-propanone	.0031	962	3120	1.20	1.59	4.03	1048	2860	1.20	1.59	4.03	1297	2315	1.80	1.76	4.20
9	Piperonal	.0023	960	3125	1.90	1.92	4.10	1102	2723	1.73	1.88	4.06	Band or cut-off				
10	Isosafrole	.0019	1010	2972	0.84	1.65	3.86	1150	2605	1.60	1.93	4.14	Band or cut-off				
11	Safrole	.0051						1048	2860	1.26	1.39	3.60	1266	2370	1.48	1.46	3.69

[a] Grams solute/100 cc. solution. [b] Frequency in fresnel units. [c] Wave length in ångström units. [d] Extinction of band maximum. [e] Log$_{10}$ $E/(10 \times \text{concn.})$. [f] Band determined by curve analysis; band-head determined by extrapolation. [g] Logarithm of molecular extinction coefficient ($\epsilon = K \times$ molecular weight).

TABLE III

Nuclear Type (C)—Fig. 2

	Compound	Concn.[a]	Band A (Max.)					Band C (Max.)			
			f[b]	λ[c]	*E*[d]	$\log_{10}K$[e]	$\log_{10}\epsilon$[f]	*f*	λ	*E*	$\log_{10}K$
1	Syringaldehyde	0.0014	985	3045	1.07	1.88	4.14	1310	2290	1.40	2.00
2	1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanone	.0025	1013	2960	1.37	1.74	4.06	Band indicated			
3	2-Acetoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone	.0037	980	3060	1.97	1.73	4.16	Band indicated			
4	1-(4-Hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione	.0030	924	3250	1.55	1.71	4.06	Band indicated			
5	1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone	.0052	(1087)	(2760)	(0.43)	(0.92)	(3.24)	Band indicated			

[a] See Table II for footnotes.

TABLE IV

Nuclear Type (D)—Fig. 2

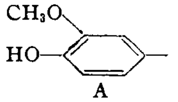
	Compound	Concn.[a]	Band A (Max.)				
			f[b]	λ[c]	*E*[d]	$\log_{10}K$[e]	$\log_{10}\epsilon$[g]
1	1-(3,4,5-Trimethoxyphenyl)-1-propanone	0.0029	1077	2785	1.60	1.74	4.09
2	2-Hydroxy-1-(3,4,5-trimethoxyphenyl)-1-propanone	.0030	1061	2825	0.91	1.48	3.86
3	2-Acetoxy-1-(3,4,5-trimethoxyphenyl)-1-propanone	.0033	1047	2865	1.41	1.63	4.08
4	2-Bromo-1-(3,4,5-trimethoxyphenyl)-1-propanone	.0034	1007	2980	1.28	1.58	4.06
5	Diethyl-3,4,5-trimethoxyphenyl carbinol	.0032	..	..	..	..	..

[a] See Table II for footnotes.

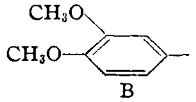
method of curve analysis recommended by Brode,[17] in which a constant frequency difference is assumed between bands, is more accurate than that used here but is inapplicable to simple curves in which only two clearly defined bands are apparent.

Discussion

Nuclear Types.—The data presented in Tables I to V represent an investigation of four main classes of aromatic nuclei and a few related compounds. In the following discussion substances will be designated as types A, B, C or D depending upon whether they are derivatives of guaiacol (A), veratrole (B), pyrogallol-1,3-dimethyl ether (C) or pyrogallol trimethyl ether (D) (see Fig. 2). In all cases the position of substitution in these nuclei has been that which gives rise to compounds such as vanillin, veratric aldehyde, syringaldehyde and 3,4,5-trimethoxybenzaldehyde.



A



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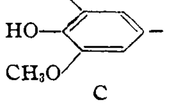

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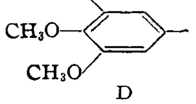

D

Examination of Tables I to IV and Diagrams I to IV reveals the following facts: Derivatives of types A and B in which a carbonyl group is adjacent to the benzene ring (as C_6H_5CO—) show three absorption bands which may be characterized as the 980 f, 1070 f and 1300 f maxima (Table I, nos. 1 to 7, 15 and 16; Diagram I; Table II, nos. 1, 2, 3, 4, 6 and 8; Diagram II). Similar compounds of type C (Table III, nos. 1, 2, 3 and 4; Diagram III) and of type D (Table IV, nos. 1, 2, 3 and 4; Diagram IV) show only two bands one of which is

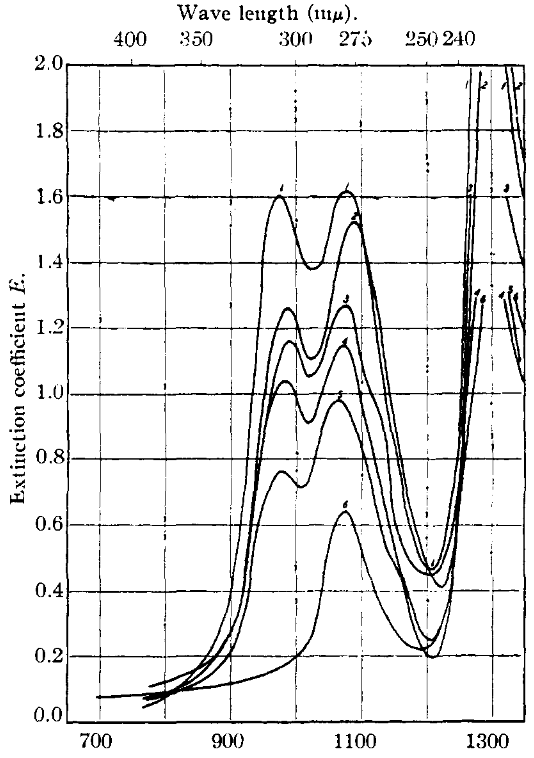

Fig. 2.—(1) Vanillin; (2) 4-hydroxy-3-methoxyacetophenone; (3) 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone; (4) 2-acetoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone; (5) 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone; (6) 4-hydroxy-3-methoxyphenylcarbinol; concentration, 0.002%; solvent, ethanol.

(17) Brode, *Proc. Roy. Soc.* (London), **118A**, 286 (1928).

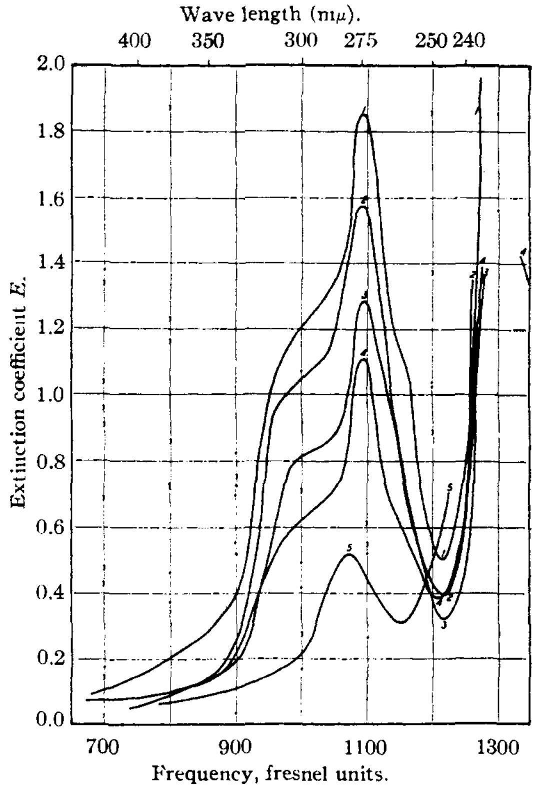

Fig. 3.—1, Veratric aldehyde; 2, 2-acetoxy-1-(3,4-dimethoxyphenyl)-1-propanone; 3, 3-acetoxy-1-(3,4-dimethoxyphenyl)-1-propanone; 4, 2-hydroxy-1-(3,4-dimethoxyphenyl)-1-propanone; 5, 1-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone; concentration, 0.002%; solvent, ethanol.

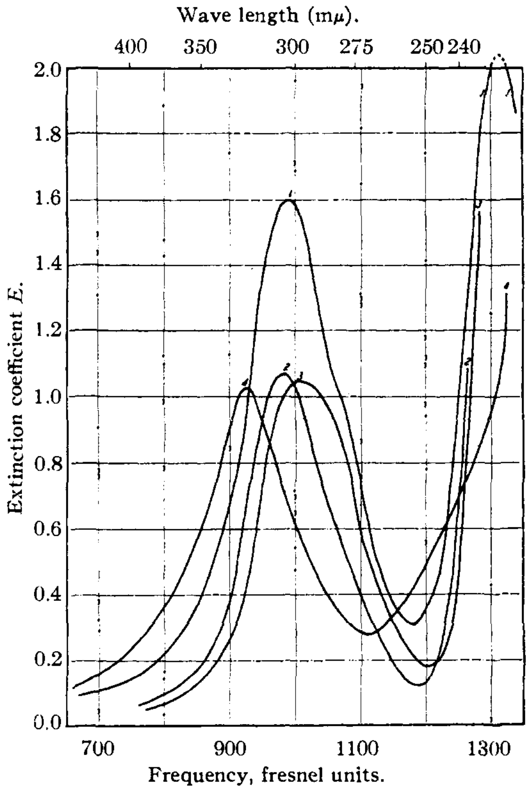

Fig. 4.—1, Syringaldehyde; 2, 2-acetoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone; 3, 1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone; 4, 1-(4-hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione; concentration, 0.002%; solvent, ethanol.

apparently the 1300 f band. From the structure of these compounds (Fig. 2) it will be seen that derivatives of A and B differ from those of C and D only in having the position meta to the side chain free. In the former category the hydrogen occupying this meta position is known to be very labile when the substituent para to the side chain is an ortho–para orienting group as is the case with both hydroxyl and methoxyl. In compounds of types C and D this active meta position is blocked and the electronic nature of the whole ring is thereby altered. The conclusion to be drawn is that one of the three bands of the A and B structural types should be assigned to the "meta-position freedom."

To determine which of the bands owes its origin to this "freedom," the other maxima of the absorption curves must be considered. The maximum in the extreme ultraviolet region (1300 f) may be ruled out since it is common to all of the four classes of nuclei (A, B, C and D). This particular band may be characteristic of the aromatic carbon–carbon linkage, a viewpoint supported by the absorption spectra of many organic compounds. The existence of this 1300 f maximum has only been demonstrated in a few cases with the products listed in Tables I–V but in other cases the ascending absorption curve at high frequency values and the fact that it has been possible to obtain the band head for very similar compounds are taken as indications of the existence of such a band.

Table V

Compound	Concn.[a]	f^b	λ^c	E^d	$\log_{10} K^e$	$\log_{10} \epsilon^f$
Pyrocatechol	0.0031	1180	2780	1.17	1.58	3.62
Guaiacol	.0032	1090	2750	1.22	1.58	3.67
Veratrole	.0060	1092	2748	1.10	1.26	3.40
Pyrogallol 1,3-dimethyl ether	.0085	1107	2710	0.96	1.05	3.24

[a] See Table II for footnotes.

In Diagram I it is seen that with curves 1–5 each exhibits the three typical absorption bands while curve 6 has clearly lost the one nearest the visible region. The first group of compounds (vanillin, 4-hydroxy-3-methoxyacetophenone, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, 2-acetoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone) contains the *vanilloyl* radical while curve 6 represents *vanillyl* alcohol. Furthermore, in Diagram II, veratric aldehyde, 2- and 3-acetoxy-1-(3,4-dimethoxyphenyl)-1-propanone and 2-hydroxy-1-(3,4-dimethoxyphenyl)-1-propanone show distinct inflections indicative of a band toward the visible from the principal (1070 f) maximum while 1-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone (curve 5, Diagram III) is completely lacking in such an inflection. Evidently this band at approximately 980 f must be due to the effect of the carbonyl group conjugated with the aromatic nucleus. The same band can also apparently originate from an ethylenic double bond in similar conjugation with the nucleus as shown by isoeugenol, coniferin and isosafrole (Table I, nos. 14 and 17, Table II, no. 10). Conversely, those compounds lacking a maximum in this region (980 f) have no side chain unsaturation in conjugation with the benzene ring. These findings are in agreement with the previously reported work of Hillmer and Schorning[14] and of Morton and Stubbs.[18] Comparisons of the absorption data for (a) eugenol and isoeugenol (Table I, nos. 12 and 14); (b) vanillyl alcohol and vanillin (Table I, nos. 8 and 1) and (c) 1-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone and 2-hydroxy-1-(3,4-dimethoxyphenyl)-1-propanone (Table II, nos. 5 and 2) demonstrate clearly this specific relationship between structure and absorption. Further confirmation is afforded by a comparison of the absorption spectra of the compounds in Table V with their corresponding aldehydes in Tables I-III. Thus, compared with guaiacol which gives a single band at 1090 f, vanillin, in which an aldehyde group is substituted para to the guaiacol hydroxyl group, has a second band at 975 f. Similarly, pyrocatechol exhibits a single maximum at 1080 f while protocatechuic aldehyde shows two bands at 1070 f and 960 f. Benzalacetophenone, a substance in which conjugation of a carbonyl and of an ethylenic double bond with aromatic nuclei is present, exhibits a strong band at 980 f (log K = 2.16) and a second weaker band at approximately 1315 f.

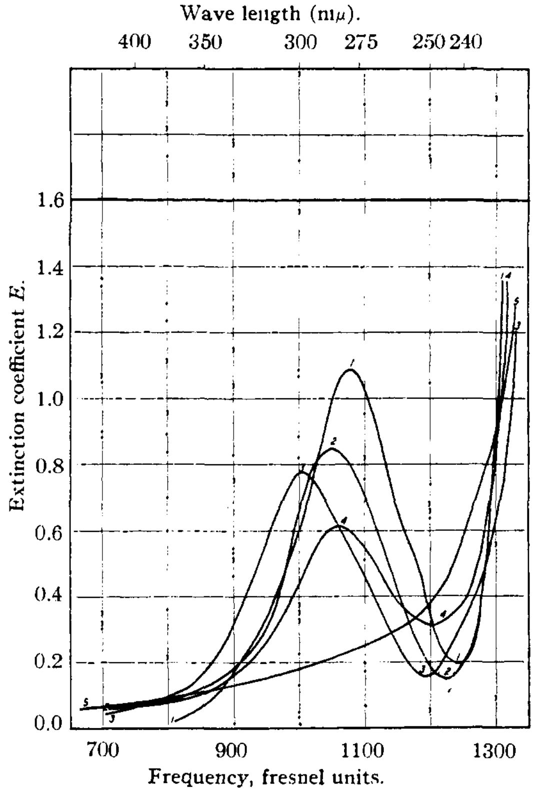

Fig. 5.—1, 1-(3,4,5-trimethoxyphenyl)-1-propanone; 2, 2-acetoxy-1-(3,4,5-trimethoxyphenyl)-1-propanone; 3, 2-bromo-1-(3,4,5-trimethoxyphenyl)-1-propanone; 4, 2-hydroxy-1-(3,4,5-trimethoxyphenyl)-1-propanone; 5, diethyl-(3,4,5-trimethoxyphenyl)-carbinol; concentration, 0.002%; solvent, ethanol.

Summarizing, derivatives of types A and B (and closely related substances) in which the ring is conjugated with the side chain will have absorption spectra consisting of three bands in the ultraviolet region in the neighborhood of 980 f, 1070 f, and 1300 f, these being due, respectively, to the presence of a side chain chromophore in conjugation with the benzene ring; to freedom of the position meta to the point of attachment of the side chain, and to some unexplained characteristic of the aromatic nucleus. There appears to be one exception to this generalization, namely, in the case of 2-acetoxy-1-(3-methoxy-4-acetoxyphenyl)-1-propanone (Table I, no. 6) but here the acetoxy group attached to the benzene ring is strongly meta directing (73% in the case of nitration). In consequence the position meta to the side chain is rendered relatively stable and the electron concentration shifted to the ortho position so that in this instance a closer comparison is found with type structures C and D than

[18] Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

A and B. The loss of activation at the meta position has thus resulted in elimination of the 1070 f band.

With substances of the C and D types (Tables III and IV, Diagrams III and IV) only two bands are formed, one of which has already been indicated as characteristic of the aromatic nucleus. The other must be assigned to the conjugated carbonyl group. In the case of the 4-hydroxy-3,5-dimethoxyphenyl derivatives (C) this assumption seems amply justified by the agreement found in the position and strength of the 980 f and 1300 f bands with similar structures of type A. With derivatives of type D, on the other hand, the best agreement is found with the above mentioned typical 1070 f band. This latter can only originate from the presence of the carbonyl group adjacent to the ring (as evidenced by the absence of this band in the spectrum of diethyl-(3,4,5-trimethoxyphenyl)-carbinol, curve 5, Diagram IV) and it would seem that some peculiarity of the trimethoxyphenyl nucleus has brought about an 80–90 f shift of what has been termed the 980 f band. With type D derivatives the band in the extreme ultraviolet also appears to have undergone a hypsochromic shift and this same effect seems to be present, though to a much smaller extent, in the transition from derivatives of type A to type B.

The relationship between aromatic nuclear chemical structure and absorption in the ultraviolet is not confined merely to the general *shape* of the curves, for in spite of inaccuracies introduced by the visual spotting of match points and the assumption of the validity of Beer's law some conclusions may be drawn regarding the *intensity* of absorption. Thus, methylation of the phenolic hydroxyl group decreases the maximum extinction value of the 980 f band in passing from both vanilloyl (A) to veratroyl (B) and from syringoyl (C) to trimethoxybenzoyl (D) in those cases where the side chains are the same. In addition the 1070 f band undergoes a hyperchromic shift as a consequence of the conversion of the nuclear structure A into B on methylation. From the limited amount of data available the 1300 f band does not appear to be appreciably affected by this change.

Side Chain Substitution.—The marked effect which the side chain may exert on the shape of the absorption curves has been indicated previously in the case of eugenol and isoeugenol and analogous pairs. In these an unsaturation in conjugation with the ring was shown to be responsible for a definite band in the ultraviolet region while the same type of unsaturation, when not conjugated, does not produce resonance in this region (980 f).[14] It is thus possible, on this basis, to distinguish clearly between compounds having isomeric side chains such as —CH=CH—CH$_3$ and —CH$_2$—CH=CH$_2$; —CO—CHOH—CH$_3$ and —CHOH—CO—CH$_3$; and —CHO and —CH$_2$OH. The carbonyl group, ordinarily considered as a resonator in the photographically available ultraviolet, only gives rise to an absorption band in the series under consideration when it is conjugated with the aromatic nucleus. 1-Hydroxy - 1 - (3,4 - dimethoxyphenyl) - 2 - propanone (Diagram II, curve 5), for example, shows a single maximum at 1070 f and the close similarity between its absorption curve and that of vanillyl alcohol (Diagram I, curve 6) clearly indicates that this band cannot be due to the carbonyl group.

A second effect of side chain substitution is to be seen in the persistent decrease in the extent of absorption when the aldehydic hydrogen is replaced by a substituted ethyl group. Vanillin, veratric aldehyde and syringaldehyde are stronger absorbers than any of their derivatives investigated. The results of substitution in the α or β position to a conjugated carbonyl group in a three carbon side chain are seen to vary greatly with the nature of the substituent but it is impossible to formulate any definite rules in this connection. The statement seems justified, however, that the replacement of the aldehydic hydrogen by bromoethyl or acetyl groups will produce strong hypochromic and bathochromic shifts of the principal maxima.

The conclusions drawn in the above discussion are applicable only to compounds of the four structural types considered (A, B, C and D, Fig. 2). An attempt was made to correlate the present data with still simpler substances such as benzaldehyde, *p*-hydroxybenzaldehyde, protocatechuic aldehyde and resorcinol in order to permit of wider generalizations but due to the necessity for preparing and investigating a much larger number of derivatives this broader aspect of the subject was abandoned.

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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.

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[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).