25° and 100 at 35°, from which the values for $CF_3CH_2CH_2CO_2H$ are computed as 381 at 25° and 439 at 35°. From these figures, the values in Table IV were computed.

TABLE IV

WEAK ACIDS

V	$\alpha_{25°}$	$K_{25°}$	$\alpha_{35°}$	$K_{35°}$
		$CF_3CH_2CO_2H$		
9.91	0.0926	9.54×10^{-4}	0.0884	8.64×10^{-4}
19.8	.129	9.64×10^{-4}	.123	8.75×10^{-4}
39.6	.177	9.56×10^{-4}	.168	8.50×10^{-4}
49.6	.195	9.53×10^{-4}	.187	8.72×10^{-4}
99.1	.262	9.35×10^{-4}	.253	8.66×10^{-4}
Average selected: $K_{25} = 9.52 \times 10^{-4}$ and $K_{35} = 8.65 \times 10^{-4}$				
		$CF_3CH_2CH_2CO_2H$		
10.0	0.0263	6.93×10^{-5}	0.0257	6.78×10^{-5}
20.0	.0366	6.91×10^{-5}	.3058	6.61×10^{-5}
40.1	.0515	6.95×10^{-5}	.0513	6.89×10^{-5}
80.2	.0727	7.10×10^{-5}	.0711	6.78×10^{-5}
100	.0811	7.14×10^{-5}	.0808	7.08×10^{-5}
201	.1108	6.88×10^{-5}	.8907	6.69×10^{-5}
Average selected: $K_{25} = 6.98 \times 10^{-5}$ and $K_{35} = 6.80 \times 10^{-5}$				

Equivalent Points.—Using a MacBeth *p*H meter, curves were obtained for *p*H *versus* ml. of 0.1 N sodium hydroxide added, and they were used for the selection of the indicators in the preparation of the salts needed for conductance measurements. At the half-neutralization point the *p*H of $CF_3CH_2CO_2H$ and $CF_3CH_2CH_2CO_2H$ solutions were read as 2.90 and 3.95, which correspond to K values of 1.2×10^{-3} and 1.0×10^{-4}, respectively, on the basis of $pH = pK$; this equality should however be restricted to the range of *p*H between 4 and 10,[10] yet when k values were computed from other points of the *p*H curves, practically the same values were obtained for K.

Heat of Dissociation.—The conductances of the acids were measured at 35° as well as 25° in order to obtain values for the heats of dissociation or heats of activation of the acids in solution. By means of a form of the Arrhenius equation,[11] $d \ln K/dT = \Delta H/RT^2$ the values for $-\Delta H$ listed in Table I were calculated from the ionization constants of the acids. The values of K for CF_3CO_2H and $CF_3CF_2CF_2CO_2H$ were calculated from the conductance ratio for a 0.1 N solution, and since they are not representative of true ionization constants, a direct comparison with the weak acids is impossible. Although the ΔH value for CF_3CO_2H is more negative than for $CF_3CF_2CF_2CO_2H$, indicating a greater tendency for CF_3CO_2H to dissociate in solution, the magnitudes are approximately the same. This serves to substantiate the claim, based on the conductance ratio, that the acidity of CF_3CO_2H is approximately the same as that of $CF_3CF_2CF_2CO_2H$. A direct comparison of the ΔH values calculated for $CF_3CH_2CO_2H$ and $CF_3CH_2CH_2CO_2H$ should be valid. The more negative value for the stronger acid, $CF_3CH_2CO_2H$, indicates a greater tendency for the acid to dissociate and this is in accord with what is expected.

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[10] Bennet, Brooks and Glasstone, *J. Chem. Soc.*, 57, 1821 (1935).

[11] F. Daniels, "Outlines of Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 375.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON]

Ultraviolet Absorption Spectra of Chromatographic Fractions of Lignins

BY A. BAILEY

Chromatographic fractions of two softwood lignins have been examined with the aid of ultraviolet absorption spectroscopy.

The recent separation of lignin preparations into chromatographically heterogeneous fractions[1] posed the problem of ascertaining the validity of fluorescence phenomena as evidence of chemical difference and of establishing whether chemical differences actually existed in the fractions.

Curves of the ultraviolet absorption of lignin preparations and related compounds have been presented and their significance discussed by Aulin-Erdtman,[2] Glading,[3] Jones[4] and Patterson and Hibbert.[5] Patterson and Hibbert[6] employed ultraviolet absorption to determine the effects of the solvent precipitation of lignin.

Butanol lignins from different genera, fir and spruce, selected because of close similarity in fluorescence behavior,[1] were separated into four zones by adsorption on cellulose sheets. The zones were cut apart, each extracted separately by the capillary action of dioxane, and the ultraviolet absorption of the dioxane solutions of the lignin components was measured.

The ultraviolet absorptions of these materials are shown in Figs. 1 and 2. The primary purpose of this study was to investigate identity or non-identity. The non-identity was so distinctive that any of the ten materials examined could be easily identified by its absorption curve alone. In view of the fact that the complete curve is an unique property of a particular compound, the conclusion that the lignins studied contained components of different chemical species appears to rest on a solid foundation.

The curves of the fractions of fir lignin had absorption maxima at 280 mμ and in the 220–240 mμ region, although the curves varied somewhat in shape and the corresponding values of specific extinction varied several-fold. The curves suggest that similar chromophoric groupings are responsible for these maxima and that perhaps the fractions stand in near chemical relationship. These curves, of course, reflect principally the effect of those structures capable of resonance between several configurations and are not an accurate index of the minor and other architecture of the molecule which do not give rise to strong chromophoric effects.

The curves of the fractions of spruce lignin showed inflection points but no true absorption maxima at 280 mμ with the exception of Zone I. Curiously, the parent lignin material showed two definite maxima at 281 and 277 mμ. The difference in the absorption curves of the individual zones of spruce was generally comparable to that existing in the absorption curves of fir lignin. The

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[1] A. Bailey, *Paper Ind. and Paper World*, **32**, 395 (1950).

[2] G. Aulin-Erdtman, *Tappi*, **32**, 160 (1949).

[3] R. E. Glading, *Pap. Trade J.*, **111**, TS 288 (1940).

[4] E. J. Jones, Jr., *Tappi*, **32**, 311 (1949).

[5] R. F. Patterson and H. Hibbert, THIS JOURNAL, **65**, 1862 (1943).

[6] R. F. Patterson and H. Hibbert, *ibid.*, **65**, 1869 (1943).

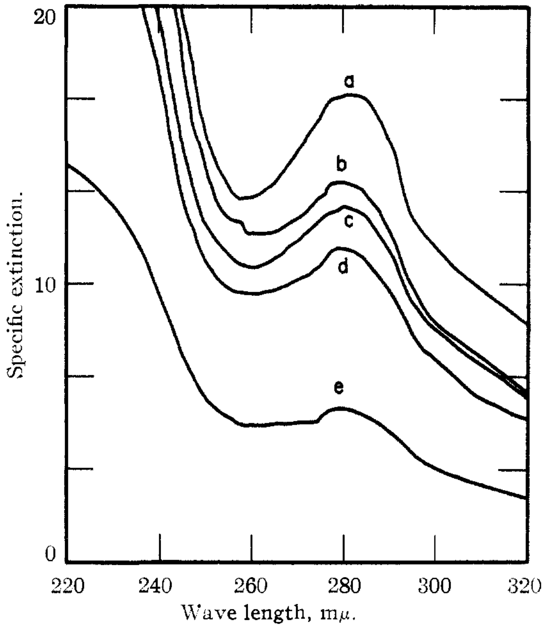

Fig. 1.—Ultraviolet absorption spectra of fir lignin: a, entire lignin preparation; b, Zone II; c, Zone III; d, Zone IV; e, Zone I. Zones were numbered outward on paper chromatogram. For illustrations of chromatograms see reference (1).

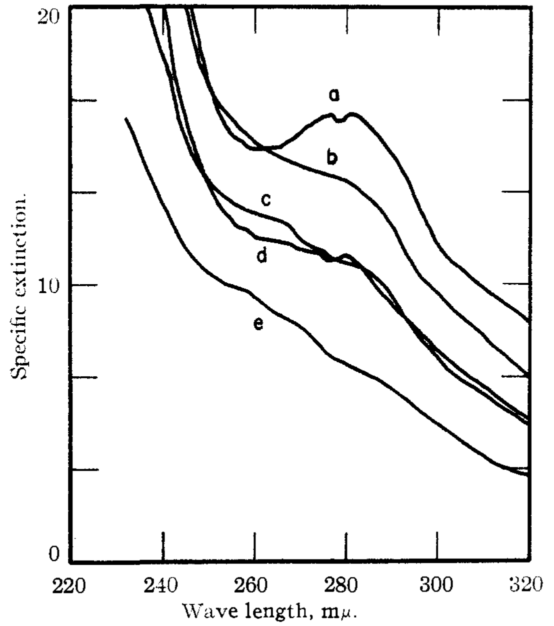

Fig. 2.—Ultraviolet absorption spectra of spruce lignin: a, entire lignin preparation; b, Zone II; c, Zone III; d, Zone I; e, Zone IV.

curves of fir lignin were notably different from spruce in possessing distinct maxima. From these results, it seems probable that the lignins of different genera will generally be found to contain components of different chemical species.

The absorption maxima or inflections at 280 mμ and maxima in the 220 to 240 mμ region are similar to those found in most lignin preparations, and although these are the most specific data which can be derived from the curves, the present level of ultraviolet absorption spectroscopy is not adequate to permit prediction of specific structures responsible for the effects found.

Spectroscopic evidence thus far obtained supports the validity of fluorescence observations as indications of chemical differences in the lignins studied, as widely used in the general field of chromatography and proposed by Gilman[7] to assist in the identification of pure organic compounds.

No claim is made that the fractions were homogeneous.

Experimental

Lignin preparations were isolated from balsam fir (*Abies balsamea*, Mill.), and white spruce (*Picea glauca*, Voss) by digestion of cold-water-extracted wood meal samples in equal volumes of *n*-butanol and water at 160° for one hour. The wood–liquor ratio was 1 to 15. The two-phase digestion liquor was filtered and made alkaline (*p*H 9), the butanol distilled off and the lignin precipitated by dilute hydrochloric acid. The precipitated lignin was filtered, washed thoroughly with distilled water, and air-dried. Yields (oven-dry basis) were 45 and 58% of the total lignin for fir and spruce, respectively.

The chromatography was effected on cellulose sheets using butyl acetate as the eluant, illustrated and described more fully elsewhere.[1]

The ultraviolet absorption spectra of these materials were determined in dioxane. The original dioxane was Eastman Kodak Company practical grade. It was distilled in a column packed with $^1/_8$ inch glass helices, having a packed section 14 mm. by 200 cm. and having an efficiency equivalent to 30 theoretical plates. The fraction boiling between 101.0 and 102.0° was collected and redistilled in the same column; the fraction boiling between 101.2 and 101.7 was collected and redistilled, retaining the fraction boiling at 101.4°. A final distillation yielded a central fraction having a threshold transmittance of 215 mμ. Klevens and Platt[8] found a value of 203 mμ as the minimum wave length transmitted. The threshold transmittance was the minimum wave length at which a perceptible reading on a Beckman model DU quartz spectrophotometer could be obtained, with the sensitivity knob at the left and the slit at 2.0 mm. This threshold transmittance was used as a reference standard to check the performance of the instrument and the purity of the dioxane, as well as to follow the deterioration in dioxane. Reference standards were also established by comparing the transmittance of the dioxane samples referred to distilled water as a standard. These reference values as well as the threshold transmittance were obviously characteristic of the particular instrument, varying with hydrogen arc output, phototube sensitivity, and other factors, but were decidedly useful as sensitive criteria of purity. Spectroscopic clarity of such samples deteriorated in a week or two at room temperature so that repurification was necessary. All spectroscopic measurements of the transmittance of lignin solutions were made at minimum slit width using quartz cells of 1 cm. thickness.

The quantity of material actually extracted from the chromatograms was in the following ratios: fir, Zones I, II, III and IV, respectively, 32, 21, 21 and 26%; spruce, 30, 34, 27 and 9%. A small quantity of the lignin adsorbed in Zones I and II of spruce was not dissolved by dioxane, pyridine or glacial acetic acid, and an even smaller quantity of the lignin of Zones I and II of fir behaved similarly. These were removed by dilute alkali and precipitated by acid. As the quantity was very small, further examination was not conducted. It is possible that these portions are of a different chemical species than those of the soluble portions and may warrant later investigation. The zones of spruce lignin showed increasing solubility in dioxane solution, Zone IV (outer) being greatest; fir lignin was similar but to a lesser degree. The absorption curves of these materials suggest differences in molecular weight as one possible cause.

SEATTLE, WASH. RECEIVED AUGUST 21, 1950

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(7) A. F. Gilman, Jr., *Chem. Anal.*, **36**, 38–9 (1947)

(8) H. B. Klevens and J. R. Platt, THIS JOURNAL, **69**, 3055 (1947).