

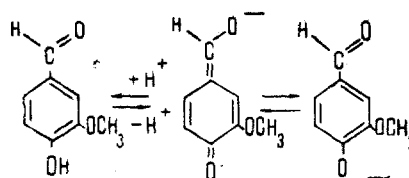
# ULTRAVIOLET AND DIFFERENTIAL ABSORPTION SPECTRA OF OAK AND PINE LIGNIN ETHANOLYSIS PRODUCTS

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The most characteristic reaction of lignin, enabling it to be distinguished from other components of wood, is ethanolysis (Brauns [1]), which leads to the formation of various aromatic ketones, aldehydes, and ethers generally called "Hibbert ketones" and to water-insoluble products, ethanol lignin. It has been found that the ethanolysis of coniferous species forms compounds of the guaiacyl series, while deciduous species give a mixture of substances of the guaiacyl and syringyl series. Paper chromatography with the use of color reagents has been used for the identification of the Hibbert ketones [1-3]. Hibbert and Patterson [4] have studied the UV spectra of a number of Hibbert ketones and have found that the guaiacyl derivatives have absorption maxima at about 230, 280, and 300 m $\mu$ , while the compounds of the syringyl series have only two maxima, at 230 and 300 m $\mu$ .

It has been shown that substances with similar structures to the Hibbert ketones, i.e., having a phenolic hydroxy group in the position para to a carbonyl group, undergo a displacement of the absorption maximum in the long-wave direction in an alkaline medium (bathochromic effect) with a simultaneous increase in the intensity of absorption [5, 6]. This shift is explained by the ionization of the phenolic hydroxy group. Thus, for example, it has been suggested that in an alkaline medium a resonance hybrid containing a quinoid structure is formed with vanillin [7].



Aulin-Erdtman [8, 9], by deducting the absorption of a substance in a neutral medium from the corresponding absorption in an alkaline medium, obtained a so-called "differential" curve ( $\Delta\epsilon$  curve or  $\Delta\epsilon$  spectrum). Deduction excluded the absorption by nonionized groups which is the same in neutral and in alkaline solutions. Consequently, the new curve ( $\Delta\epsilon$  spectrum) depended only on the ionizable chromophores. In a study of model compounds it was established that the presence of maxima in the  $\Delta\epsilon$  spectra in the 250 and 300 m $\mu$  regions is characteristic for nonconjugated guaiacols [10, 11]. Maxima in the 250 and 350-420 m $\mu$  regions appear in the case of aromatic compounds in which a phenolic group is conjugated through the ring with a carbonyl group or with a double bond in a side chain [5, 10, 11].

In spite of the importance of the study of the UV spectra of Hibbert ketones, many of these substances have not been investigated, while in some cases contradictory results have been obtained [2-4];  $\Delta\epsilon$  spectra have been studied to an even smaller extent [2]. In view of this, we decided to study the UV and  $\Delta\epsilon$  spectra of the main Hibbert ketones obtained by the ethanolysis of deciduous and coniferous species, and also samples of ethanol lignins.

## Experimental

The investigation was carried out with substances composing the Hibbert ketones of deciduous and coniferous species: vanillin (V), syringaldehyde (Syr), guaiacylacetone (GA), syringylacetone (SA), vanilloyl methyl ketone (VMK),  $\alpha$ -hydroxypropiovanillone ( $\alpha$ -HV),  $\alpha$ -ethoxypropiovanillone ( $\alpha$ -EV) (we synthesized from  $\alpha$ -hydroxypropiovanillone by Cramer and Hibbert's method [14]),  $\alpha$ -ethoxypropiosyringone ( $\alpha$ -ES), p-hydroxybenzaldehyde (PHB), sinapic aldehyde (Sin), and coniferyl aldehyde (CA). In addition, by a published method [16] we obtained samples of the ethanol lignin of oak as a representative of deciduous species and of the ethanol lignin of pine as a representative of coniferous species.

The absorption measurements were carried out on a SF-4 spectrophotometer (1-cm quartz cell). Weighed samples of the substances under investigation were dissolved in 96 vol. % ethanol in concentrations of 10-40 mg/l for the Hibbert ketones and 7-15 mg/l for the samples of ethanol lignin. To obtain the spectra in an alkaline medium, 0.05 ml of 1 N caustic soda was added to 3 ml of the solution of the substance.

The results of a study of the UV spectra in neutral and alkaline media and of the  $\Delta\epsilon$  spectra of the Hibbert ketones (Figs. 1 and 2) show that the compounds of the guaiacyl series investigated, apart from coniferyl alcohol, have three maxima in a neutral medium (one at 225-240 m $\mu$ , the second at 278-290 m $\mu$ , and the third at 305-320 m $\mu$ ), and also two absorption minima, at 250-265 m $\mu$  and at 295 m $\mu$ . The compounds of the syringyl series possess only two maxima,

at 200–230  $m\mu$  and at 300–310  $m\mu$ , and one minimum at 250–260  $m\mu$ . In an alkaline medium, all the compounds mentioned showed two maxima, one nonspecific one at 245–260  $m\mu$  and a second in the 340–420  $m\mu$  region which is characteristic for the individual compounds of the guaiacyl and syringyl series. However, differences between the UV spectra in a neutral medium as compared with the UV spectra in an alkaline medium cannot reliably distinguish compounds of the guaiacyl series from those of the syringyl series.

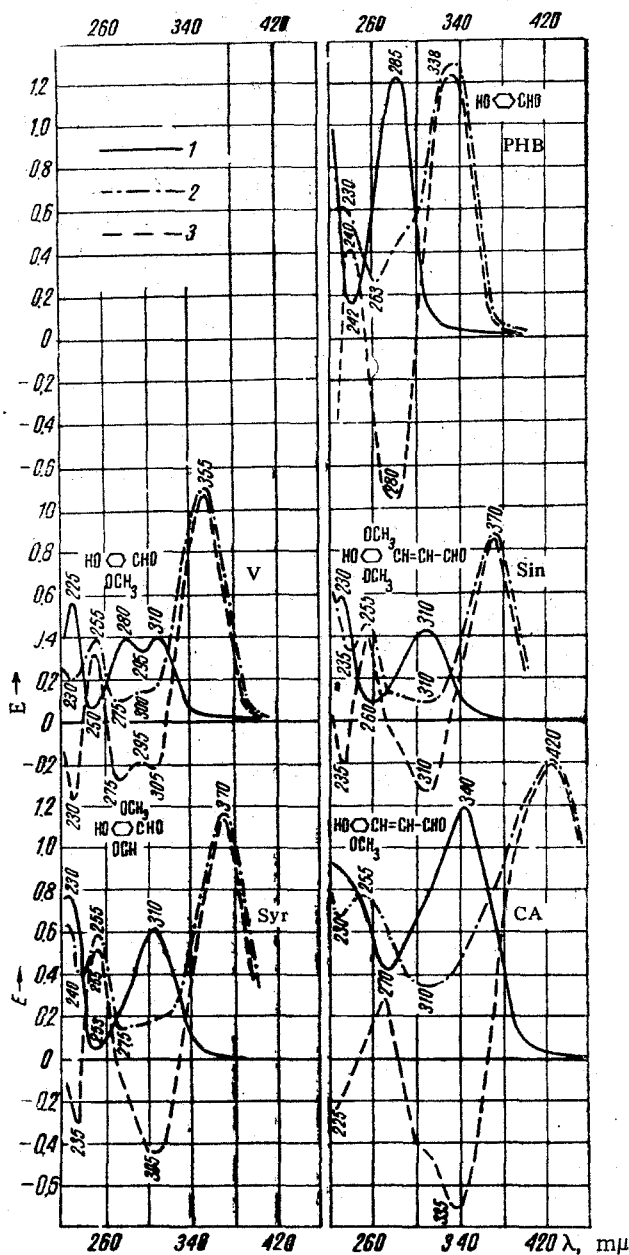


Fig. 1. UV absorption spectra in neutral (1) and alkaline (2) media; and  $\Delta\epsilon$  spectra (3) of Hibbert ketones.

The  $\Delta\epsilon$  spectra proved to be the most indicative for characterizing the Hibbert ketones. For the compounds considered, apart from coniferyl aldehyde, the  $\Delta\epsilon$  spectra have a common maximum in the 250–260  $m\mu$  region. In the compounds of the guaiacyl series a maximum (or a plateau) appears in the 295–320  $m\mu$  region but is absent in the compounds of the syringyl series. In the 350–375  $m\mu$  region there is a maximum characteristic of the individual compounds of the guaiacyl and syringyl series.

The position of the minima of the  $\Delta\epsilon$  spectra is characteristic for assigning a compound to one series or the other. Thus, the compounds of the guaiacyl series are characterized by two minima (or breaks) at 275–280 and 300–320  $m\mu$ , while substances of the syringyl series have only one minimum at 305–310  $m\mu$ . Thus, the  $\Delta\epsilon$  spectra include the most

valuable features of the spectra in neutral and alkaline media and can be used both to decide to which series a compound belongs and to characterize individual substances.

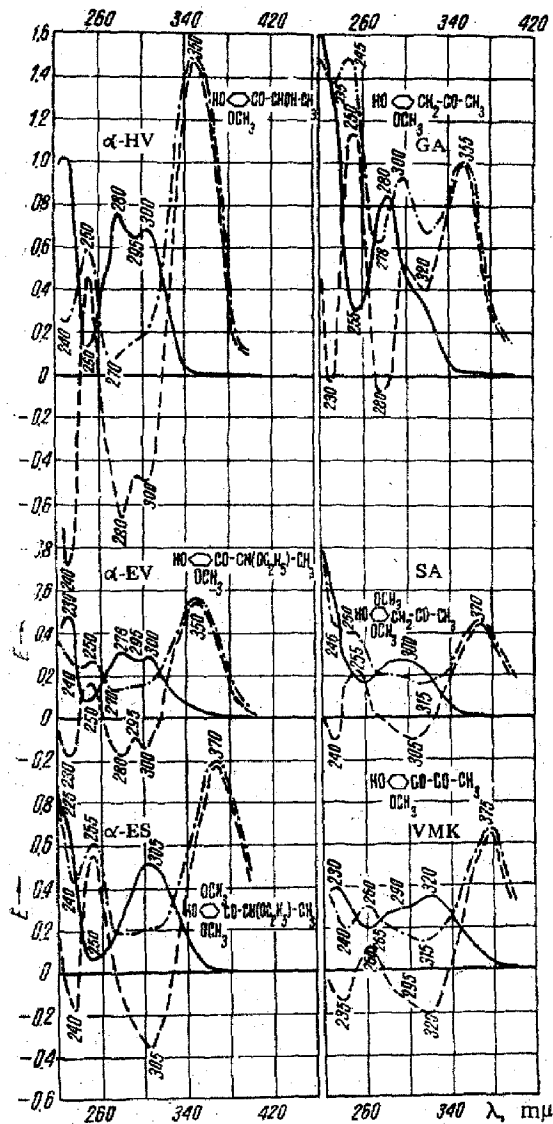


Fig. 2. UV absorption spectra in neutral (1) and alkaline (2) media; and  $\Delta\epsilon$  spectra (3) of Hibbert ketones.

The spectra of coniferyl aldehyde are peculiar, possessing one maximum in a neutral medium at 340 mμ, which agrees with literature data [15], and one maximum in an alkaline medium at 420 mμ. The  $\Delta\epsilon$  spectrum also differs from those of the other compounds (maxima at 270 and 420 mμ and minimum at 335 mμ). We have not elucidated the causes of the anomalous behavior of coniferyl aldehyde.

Figure 3, which gives the UV spectra of lignin samples, shows that oak ethanol lignin in a neutral medium has a maximum at 273 and a minimum at 240 mμ, while pine ethanol lignin has a maximum at 285 and a minimum at 260 mμ. Differences between the spectra of the oak and pine lignins are also found in an alkaline medium: oak lignin has a maximum at 265 and a minimum at 235 mμ, while pine has a maximum at 300 and a minimum at 280 mμ. A considerable difference is observed in the nature of the  $\Delta\epsilon$  spectra of the samples, oak ethanol lignin having maxima at 255 and 300 mμ, while pine ethanol lignin has maxima at 250 and 360 mμ with a plateau at 300 mμ. It is known [6-13] that a maximum in the  $\Delta\epsilon$  spectra at 300 mμ is characteristic of phenolic groups in simple aromatic compounds while that at 350-420 mμ is characteristic of phenolic compounds conjugated with a carbonyl group, which is also confirmed by the data of Figs. 1 and 2.

Thus, it can be seen from Fig. 3 that oak lignin possesses nonconjugated phenolic chromophores, while pine lignin has conjugated chromophores.

The sample of syringaldehyde was provided by N. N. Shorygina, the vanilloyl methyl ketone and the  $\alpha$ -ethoxypropiosyringone by Dr. Gardner (Vancouver, Canada), the  $\alpha$ -hydroxypropiovanillone and guaiacylacetone by Dr. Adler (Göteborg, Sweden), and the syringylacetone by Dr. Pepper (Saskatoon, Canada). The samples of oak and pine ethanol lignin were obtained by us together with B. N. Efimov.

### Summary

The UV spectra in a neutral and an alkaline medium and the  $\Delta\epsilon$  spectra have been obtained for a number of Hibbert ketones: vanillin, guaiacylacetone, vanilloyl methyl ketone,  $\alpha$ -hydroxypropiovanillone,  $\alpha$ -ethoxypropiovanillone,  $\alpha$ -ethoxypropiosyringone, syringylacetone, coniferyl, syringyl, and sinapic aldehydes, and p-hydroxybenzaldehyde, and also for samples of oak and pine ethanol lignins. Characteristic minima and maxima that can be used for identification have been found in the above-mentioned spectra.

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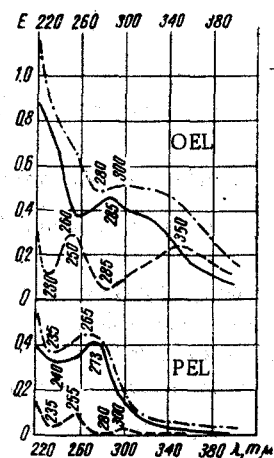


Fig. 3. UV absorption spectra in neutral (1) and alkaline (2) media and  $\Delta\epsilon$  spectra (3) of oak ethanol lignin (OEL) and pine ethanol lignin (PEL).