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STUDY OF THE IR SPECTRA OF THE PRODUCTS OF THE ETHANOLYSIS OF OAK AND PINE LIGNINS

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In the study of lignin and other aromatic compounds in plants, wide use is made of ethanolysis [1–6], which gives both water-insoluble products (ethanol lignin) and water-soluble aromatic aldehydes, ketones, diketones, and ethoxy-esters generally called Hibbert ketones.

IR spectroscopy has been proposed to characterize a number of Hibbert ketones [7]. It is known that the lignin of coniferous species is characterized by the presence of guaiacyl structures and the lignin of foliate species by a mixture of syringyl and guaiacyl structures [1]. However, compounds of the syringyl series are scarcely considered by Hergert [7]. The authors of another paper [8], on studying samples of lignins of foliate and coniferous species record no differences whatever in the IR spectra. In view of this, we set ourselves the task of studying the IR spectra of the ethanolysis products of the lignins of foliate and coniferous species, including some not previously studied, and of attempting to find characteristic features enabling us to distinguish both the individual substances formed on ethanolysis and the lignins of different species.

We have also considered a number of individual compounds from the Hibbert ketones: vanillin R-CHO (V), guaicylacetone* $R-CH_2-CO-CH_3$ (GA), coniferyl aldehyde $R-CH=CH-CHO$ (CA), α-hydroxypropiovanillone $R-CO-CHOH-CH_3$ (α-HV), vanilloyl methyl ketone $R-CO-CO-CH_3$ (VMK), vanillic acid R–COOH (VA), syringic aldehyde R'–CHO (Syr), syringylactone $R'-CH_2-CO-CH_3$ (SA), sinapic aldehyde ($R'-CH=CH-CHO$) (Sin), α-ethoxypropiosyringone $R'-CO-CH(OC_2H_5)-CH_3$ (α-ES), and p-hydroxybenzaldehyde (PHB) (R represents a guaicyl and R' a syringyl radical).

Experimental

The IR spectra were taken on a UR-10 spectrophotometer in the 400–3700 cm^{-1} region. For spectroscopy, the substances were compressed with KBr under vacuum. Samples of 0.4–0.6 mg of the substance and 100 mg of KBr were used. The thickness of the plates was generally 0.4–0.6 mm. The methoxy groups in the lignin samples were determined by Vieböck and Schwappach's method and the molecular weights by precision ebullioscopy in ethanol [10].

The results of an investigation of the IR spectra of the Hibbert ketones with samples of oak and pine lignins are shown in Figs. 1 and 2. Since no characteristic absorption bands were found in the 400–700 cm^{-1} and 1800–2800 cm^{-1} regions, we do not give these regions. The spectra were interpreted in the light of papers [7, 8, 11–15] on the IR spectroscopy of lignin and compounds related to it and also from a number of general handbooks [16–18].

Figure 1 gives the IR spectra of some individual substances from the Hibbert ketones of foliate and coniferous species. The strong maximum at 3490–3510 cm^{-1} relate to the stretching vibrations of the O–H bonds of carboxy groups in aromatic compounds, and the broad band in the 3200–3450 cm^{-1} region to stretching vibrations of OH groups involved in hydrogen bonds. The weak absorption in the 3020–3040 cm^{-1} region is due to the stretching vibrations of CH groups in aromatic nuclei.

The well-defined maxima at 2970–2980 cm^{-1} and 2930–2950 cm^{-1} are due to the asymmetric stretching vibrations of C–H in methyl groups, and the maximum at 2850–2860 cm^{-1} (sometimes with splitting to form a second maximum at 2870–2880 cm^{-1}) are due to the symmetrical stretching vibrations of C–H in methyl groups. However, it must be borne in mind that C–H stretching vibrations in aromatic compounds may also appear at 2970 and 2880 cm^{-1}, and C–H vibrations in CHO groups of aromatic aldehydes at 2820 cm^{-1} [17]. All these maxima are seen fairly clearly in the case of p-hydroxybenzaldehyde. The maxima in the 1900 and 1770 cm^{-1} region are characteristic for para-substituted benzenes and we have observed them only for p-hydroxybenzaldehyde. The maxima in the 1670–1720 cm^{-1} region relate to the stretching vibrations of C=O groups. The maximum at 1720 cm^{-1} is characteristic for C=O groups not directly attached to aromatic nuclei (guaiacylacetone, syringylacetone, one keto group of vanilloyl methyl ketone). The maximum at 1670–1680 cm^{-1} is characteristic of a carbonyl group conjugated with a double bond, for example with a benzene nucleus or with a double bond in a side chain (coniferyl and sinapic aldehydes).

* The samples of syringic aldehyde and vanillic acid were kindly given to us by Prof. N. N. Shorygina, samples of vanilloyl methyl ketone and α-ethoxypropiosyringone by Dr. Gardner (Vancouver, Canada), the samples of α-hydroxypropiovanillone and guaiacylacetone by Dr. Adler (Göteborg, Sweden), and the sample of syringylacetone by Dr. Pepper (Saskatoon, Canada).

The strong bands at 1600–1620 and 1520 cm^{-1} are due to the skeletal vibrations (C=C) of the benzene nucleus.

The strong maximum at 1470 cm^{-1} (sometimes with splitting at 1480 and 1460 cm^{-1}) must be assigned to the asymmetric deformation vibrations of methyl groups. The strong bands at 1430–1450 cm^{-1} relate to the asymmetric vibrations of methyl groups and the skeletal vibrations of benzene nuclei, and the comparatively weak bands at 1370–1390 cm^{-1} to the symmetrical vibrations of methyl groups and to the skeletal vibrations of benzene nuclei.

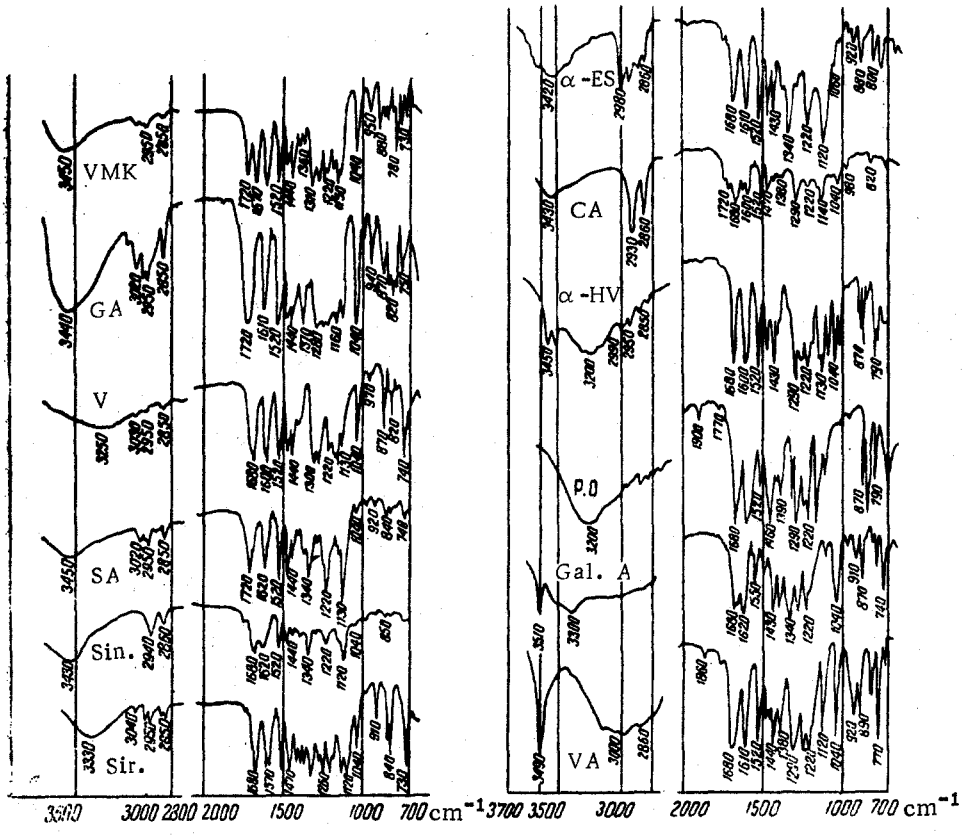

Fig. 1. IR spectra of the monomeric products of the ethanolysis of lignin.

The presence of a strong maximum at 1340 cm^{-1} is characteristic for all the compounds of the syringyl series that we have studied. This band does not appear with compounds of the guaiacyl series and with p-hydroxybenzaldehyde. Thus, the maximum at 1340 cm^{-1} must apparently be considered as characteristic for 1, 2, 3, 5-substitution of the benzene nucleus. In actual fact, gallic acid (Gal. A), with such substitution, also has this maximum, as can be seen in Fig. 1.

The maxima at 1270–1290 cm^{-1} relate to the vibrations of the =C–O– group and are therefore observed with substances containing methoxy or phenol groups.

The absorption at 1040–1050 cm^{-1} may relate to the vibrations of CH groups in aromatic nuclei located between two substituents [16], and therefore it appears in all the substances that we have investigated except p-hydroxybenzaldehyde, which has no such atom.

In contrast to the opinion of certain authors [7, 12] we have been unable to associate the maximum in the 1120–1190 cm^{-1} region with any definite groups or bonds. Thus, for example, the maximum at 1150 cm^{-1} which Hergert [7] assigns to the guaiacyl derivative has been observed in syringic aldehyde. The same must be said about the maxima at 1120–1130 cm^{-1} found both in guaiacyl and syringyl components. These maxima are apparently characteristic for the planar vibrations of CH groups in aromatic nuclei, and their intensity depends on the type of substitution of the benzene ring. We have also been unable to interpret the positions of the maxima in the region of the spectrum from 1000 to 700 cm^{-1}. Statements in the literature in this connection are again fairly contradictory [7, 11, 16, 17].

Figure 2 shows the IR spectra of samples of ethanol lignin from oak and pine and also of Brauns lignin from oak and oak lignin from brandy spirit. An interpretation of the IR spectra of the lignins shows that the broad band at 3430–3460 cm^{-1} is due to the stretching vibrations of OH groups involved in hydrogen bonds. The well-defined maximum at 2940–

2950 cm^{-1} is due to the asymmetric stretching vibrations of C–H in methyl groups, and the maximum at 2860 cm^{-1} is due to the symmetrical stretching vibrations of C–H in methyl groups. The maximum in the 1720–1730 cm^{-1} region is characteristic for the stretching vibrations of C=O groups not conjugated with a double bond. The maxima at 1610–1620 cm^{-1} and 1520 cm^{-1} relate to the vibration of benzene nuclei. The maximum at 1470 cm^{-1} is characteristic of the asymmetric deformation vibrations of methoxy groups.

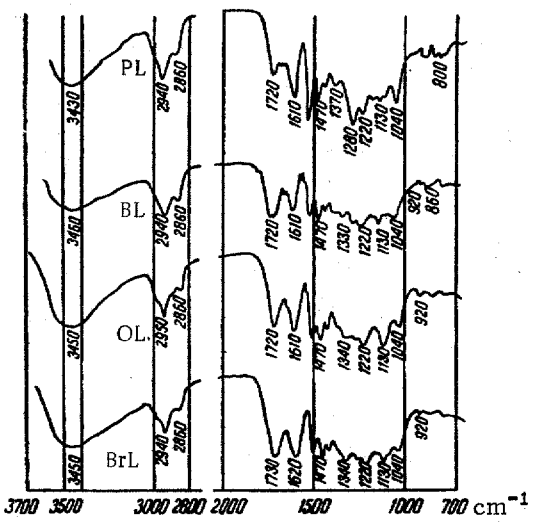

Fig. 2. IR spectra of samples of oak and pine lignins. PL– ethanol lignin from pine; BL– Brauns lignin from oak; OL– ethanol lignin from oak; BTL– oak lignin from 9-year brandy spirit.

In the 1430 cm^{-1} region appear both asymmetric deformation vibrations of methyl groups and skeletal vibrations of benzene nuclei. The maximum in the 1370–1380 cm^{-1} region relates to the symmetric vibrations of methyl groups and also to the skeletal vibrations of benzene nuclei. The maximum at 1330–1340 cm^{-1} as was shown in considering the IR spectra of the Hibbert ketones, is connected with the presence of 1, 2, 3, 5 substitution in benzene nuclei (in particular with the presence of syringyl structures) and is characteristic only for samples of oak lignin.

The maxima at 1270 and 1280 cm^{-1} and also at 1220 cm^{-1} relate to the vibrations of =C–O– groups and, possibly, to vibrations of the methoxy and phenyl groups. The maximum at 1040 cm^{-1} is characteristic for vibrations of CH groups in aromatic nuclei located between two substituents. Like other workers [8, 11], we have been unable to connect a number of maxima with any particular groups or bonds. This applies, in particular, to the peaks at 1160, 1130, and 860 cm^{-1}. Judging from published data [11, 17], the first two peaks may relate to the planar vibrations of aromatic C–H bonds for different types of substitution of the benzene nucleus, and the peak at 860 cm^{-1} to similar nonplanar vibrations. However, this question requires special experimental verification.

Our results on the IR spectroscopy of ethanol lignin from pine agree well with those of Hergert [7] and Reznikov [11] on the IR spectroscopy of lignins of coniferous species, and our results on the IR spectra of oak lignin with the results of Kudzin and Nord [8], who studied samples of oak lignin including Brauns lignin and lignin obtained after enzymatic liberation.

We studied three samples of oak lignin obtained by various methods: ethanol lignin, Brauns lignin, and brandy spirit lignin, which were characterized by molecular weights and contents of methoxy groups. As can be seen from the figures given below, the samples differed in chemical composition (particularly with respect to their contents of methoxy groups). However, their IR spectra (see Fig. 2) were practically identical:

Determination	Ethanol lignin	Brauns lignin	Brandy spirit lignin
Molecular weight	650	470	500
Methoxy groups, %	20.50	14.62	11.38

It is possible that the general appearance of the IR spectra of the lignins can give no information on small changes in the chemical composition of one and the same wood. Kratzl [19, 20] also found that hydrochloric acid lignins and

soluble natural lignins gave practically identical spectra, although, as is well known, such lignins differ considerably in chemical composition [1]. However, as can be seen from Fig. 2, lignins of foliate and coniferous species can be distinguished by their absorption in the 1330–1340 cm^{-1} region, coniferous species (pine) are characterized by the absence of an absorption maximum in this region, while foliate species (oak) have a very strong maximum.

Summary

The IR spectra of a number of compounds formed in the ethanolysis of the lignin of foliate and coniferous species have been studied using samples of ethanol lignin, vanillin, syringic aldehyde, p-hydroxybenzaldehyde, guaiacylacetone, coniferyl and sinapic aldehydes, vanilloyl methyl ketone, α-hydroxypropiovanillone, α-ethoxypropiosyringone, and vanillic and gallic acids. Differences in the absorption at 1330–1340 cm^{-1} have been found in the spectra of samples of ethanol lignin from oak and pine. Oak lignin has a strong maximum which is absent in pine lignin. Thus, the lignins of foliate and coniferous species can be distinguished by the absorption in the spectral region from 1330 to 1340 cm^{-1}.

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