IR SPECTROSCOPY OF WOOD AND ITS MAIN COMPONENTS. XVIII. IR SPECTRA OF PREPARATIONS OF LIGNOSULFONIC ACIDS FROM THE WOOD OF CONIFEROUS AND BROAD-LEAVED SPECIES

V. B. Karklin'

UDC 547.992.3:543.422.4

General features characterizing the IR spectra of lignosulfonic acids obtained from the wood of coniferous and broad-leaved species have been established the use of which together with quantitative spectral and chemical characteristics of preparations of lignosulfonic acids from spruce- and birchwoods will permit, in spectrochemical investigations, the characteristics of analogous preparations obtained from the wood of coniferous and broad-leaved species to be given.

The IR spectrum is an individual characteristic of a polymer, because of which the method of IR spectroscopy is widely used for identifying the most diverse preparations of lignin [1, 2], but no unit classification of IR spectra of lignin exists at the present time. Consequently, the task of performing a systematic investigation of the IR spectra of lignin preparations obtained by various methods from various types of tree is an urgent one. The investigation of lignins performed by the quantitative analysis of the intensities of the absorption bands of the IR spectra will form the basis for the creation of spectral-mathematical complex (combination of IR spectrometry with computers) for the recognition and characterization of high-molecular-weight substances obtained from wood in various methods for its processing [3]. The investigation of technical lignin preparations is of particular importance.

The present paper gives the IR spectra of preparations of lignosulfonic acids (LSAs) obtained from the wood of spruce, pine, birch, and aspen (Fig. 1). For a clear characterization of the differences, differential IR spectra taken directly (Fig. 2) were studied, and these confirmed the results of the quantitative analysis of the intensities of the absorption bands of the corresponding IR spectra performed by the base-line and internal standard methods (Table 1). A chemical analysis of the main functional groups of the lignosulfonic acids was made (Table 2).

The absorption in the 3600-3100 cm^{-1} region the maximum of which is found at about 3400 cm^{-1} in the IR spectra of the lignosulfonic acid preparations is characterized by a marked asymmetry on the side of smaller wave numbers, a fairly distinct change in the slope of the spectral curve being observed at about 3300 cm^{-1}. It is important to note that the slopes of the spectral curve in the 3400-3000 and 2800-2400 cm^{-1} regions are the same. This shows that the absorption due to the hydroxy groups of the lignosulfonic acids included in hydrogen bonds is distributed over the whole range from 3400 to 2400 cm^{-1}. On the background of this "diffuse" absorption of hydroxy groups, in the 3000-2800 cm^{-1} region absorption appears with two distinct maxima at 2940 and 2840 cm^{-1} which is due to the stretching vibrations of CH groups of various types. Another characteristic feature of the IR spectra of the lignosulfonic acids is the fact that the background absorption in the 3800-3600 cm^{-1} region is smaller than in the 2400-2200 cm^{-1} region. All these specific features of the IR spectra of lignosulfonic acids in the quantitative analysis of changes, particularly those connected with the absorption of CH groups, require a special substantiation of the method of drawing the base lines in each individual case according to the particular problem being studied. The differential IR spectra between preparations of lignosulfonic acids in the 3600-2200 cm^{-1} region show some differences in the intensities of the absorption bands connected with hydroxy groups.

Siberian Scientific-Research Institute of Pulp and Board, Bratsk. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 774-779, November-December, 1981. Original article submitted July 28, 1981.

 0009-3130/81/1706-0566$07.50

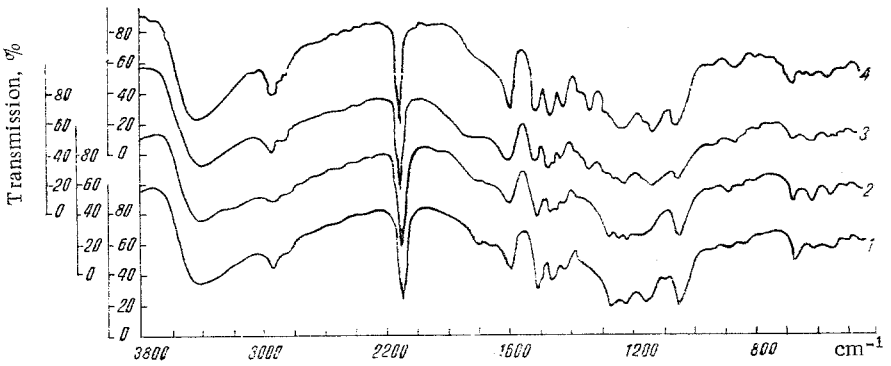

Fig. 1. IR spectra of preparations of lignosulfonic acid obtained from the wood of: spruce (1), pine (2), birch (3), aspen (4).

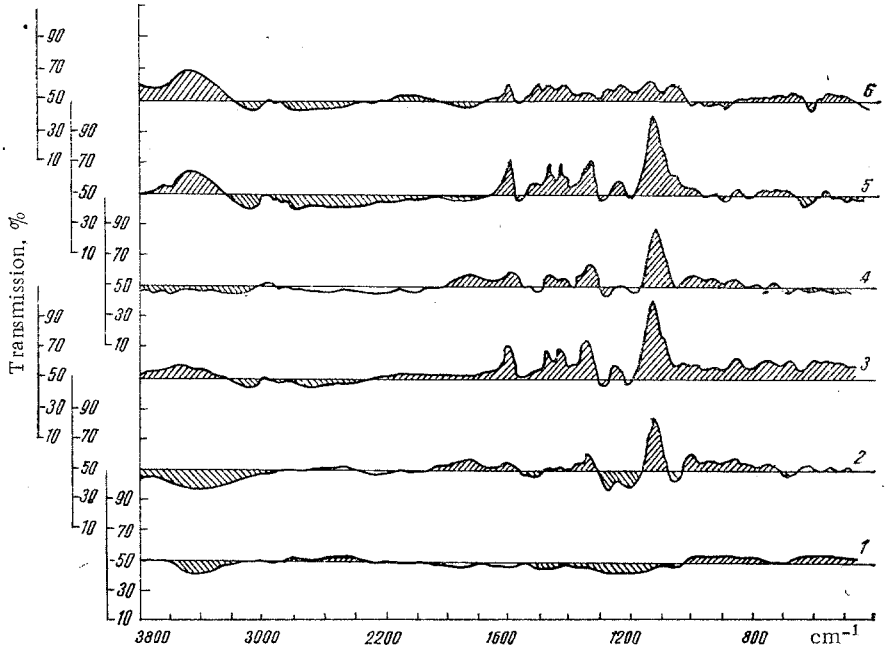

Fig. 2. Differential IR spectra of preparations of lignosulfonic acids (LSAs) taken relative to various LSAs of coniferous and broad-leaved species: 1) pine/spruce; 2) birch/spruce; 3) aspen/spruce; 4) birch/pine; 5) aspen/pine; 6) aspen/birch.

The nature of the spectral curve of the lignosulfonic acid preparations in 2200-1800 cm^{-1} region permits the absorption band of potassium hexacyanoferrate at 2100 cm^{-1} to be used for standardizing the intensities of the absorption bands of the IR spectra of these preparations.

In the 1800-1600 cm^{-1} region of the IR spectra no particularly well-defined maxima are observed in spite of the always considerable general absorption in this region, while, with the exception of the birchwood lignosulfonic acids, the absorption at 1710 cm^{-1} is smaller than that at 1660 cm^{-1}. A fine structure in the form of weak shoulder-like inflections in the spectral curve in the 1800-1600 cm^{-1} is observed for all the lignosulfonic acids.

The absorption band at 1600 cm^{-1} in the IR spectra of the lignosulfonic acids is characterized by high asymmetry on the side of large wave numbers. The absorption band at 1510 cm^{-1} consists of three absorption bands at 1515, 1505, and 1495 cm^{-1} fused together, the absorption at 1505 and 1515 cm^{-1} in the birch and aspen lignosulfonic acid preparations being the same, while for the pine- and sprucewood lignosulfonic acid preparations the absorption at 1515 is greater than that at 1505 cm^{-1}.

TABLE 1. Relative Optical Densities of the Absorption Bands of the IR Spectra of the Lignosulfonic Acids of Spruce (1) and Birch (2). 2110 cm^{-1} is the Band of the Internal Standard. Ratio of Experimental and Standard Substances 4:2.5. Number of Samples Prepared in Parallel — 4

Frequency, cm^{-1}	1	2	Frequency, cm^{-1}	1	2
3420±10	0,80±0,03	0,68±0,02	1380±3	0,34±0,02	0,38±0,01
3240±10	0,60±0,02	0,48±0,01	1330±3	0,38±0,01	0,55±0,03
2945±3	0,48±0,02	0,50±0,01	1270±3	0,95±0,03	0,64±0,01
2845±3	0,35±0,01	0,36±0,01	1215±3	0,99±0,03	0,82±0,03
1760±5	0,09±0,01	0,10±0,01	1150±3	0,87±0,02	0,73±0,02
1710±5	0,20±0,01	0,26±0,01	1030±3	0,50±0,02	0,68±0,03
1660±3	0,24±0,01	0,24±0,01	1010±5	0,93±0,03	0,71±0,01
1597±3	0,43±0,01	0,40±0,01	870±5	0,19±0,01	0,15±0,03
1515±3	0,67±0,02	0,47±0,01	820±5	0,12±0,01	0,16±0,01
1505±3	0,61±0,02	0,47±0,02	650±5	0,28±0,02	0,14±0,02
1460±3	0,56±0,02	0,58±0,01	590±5	0,19±0,01	0,14±0,01
1450±3	0,53±0,02	0,51±0,02	520±5	0,15±0,01	0,13±0,02
1422±3	0,45±0,02	0,47±0,02			

TABLE 2. Chemical Characterization of the Lignosulfonic Acids Obtained from the Wood of Spruce (1), Pine (2), Birch (3), Aspen (4), %

Sample	OCH_3	$-OH_{tot}$	$-OH_{phen}$	$-OH_{str.acid}$	$-OH_{alip}$	CO	C	H	O	S
1	11,29	7,11	1,82	3,05	5,29	6,88	52,93	4,93	33,05	9,09
2	10,21	6,27	2,09	3,83	4,18	7,37	50,00	4,33	36,31	9,36
3	15,76	9,00	3,14	4,04	5,86	6,34	51,45	4,79	37,61	6,15
4	18,04	9,28	1,93	1,88	7,35	4,18	51,50	4,52	39,02	4,96

The absorptions at 1465 and 1455 cm^{-1} in the IR spectra of the pine- and sprucewood lignosulfonic acids have approximately the same intensities, while for the aspen- and birchwood lignosulfonic acids that at 1465 cm^{-1} is greater than that at 1455 cm^{-1}. An absorption band at 1422 cm^{-1} with a small shoulder at 1410 cm^{-1} is better-defined in the lignosulfonic acids of the wood of the broad-leaved species than in that of the conifers.

Absorption bands in the 1520-1400 cm^{-1} region form a characteristic triplet, while in the lignosulfonic acids of the wood of coniferous species their intensities decrease successively and in the lignosulfonic acids of the wood of broad-leaved species the absorption bands at 1510 and 1422 cm^{-1} have approximately equal intensities and the absorption band at 1465 cm^{-1} a higher intensity.

In the 1400-1300 cm^{-1} region of the IR spectra of preparations of lignosulfonic acids of the wood of the broad-leaved species there is absorption at 1330 cm^{-1} with a slight shoulder at 1380 cm^{-1}, while for the lignosulfonic acids of the wood of the coniferous species there is no pronounced absorption in this region although the spectral curve bends sharply downwards.

The IR spectra of the lignosulfonic acids of coniferous species show pronounced absorption in the 1300-1100 cm^{-1} region which consists of a combination of three fused absorption bands with maxima at 1285, 1220, and 1160 cm^{-1} and a shoulder at 1105 cm^{-1}. The positions of the maxima of these bands and their intensities differ somewhat for the lignosulfonic acids of spruce and pine. In this region the IR spectra of the lignosulfonic acids of aspen- and birchwoods have an absorption band at 1230 cm^{-1}, with shoulders at 1280, 1260, and 1205 cm^{-1}, and also an absorption band at 1140 cm^{-1} with shoulder at 1170 and 1105 cm^{-1}. The ratios of the intensities of these bands for the lignosulfonic acids of aspen- and birchwoods are different.

For all the lignosulfonic acids a single absorption band at 1060 cm^{-1} is observed in the 1100-1000 cm^{-1} region of the IR spectrum, but it is more pronounced for the lignosulfonic acids of coniferous species than for those of broad-leaved species.

In the 1000-800 cm^{-1} region the IR spectra of preparations of lignosulfonic acids of coniferous species are very similar to one another and have small absorption bands at 950, 895, 850, and 800 cm^{-1} while for the lignosulfonic acids of the wood of the broad-leaved species small absorption bands are observed at 950 and 870 cm^{-1} the latter being more pronounced in the aspenwood lignosulfonic acids.

The 700-500 cm^{-1} region is the most characteristic for the lignosulfonic acids, since it contains the absorption bands characteristic of sulfo group which are not masked by other absorption bands. In the main, three bands are observed in this region — at 780, 710, and 660 cm^{-1}. However, the ratios of their intensities are different for different lignosulfonic acids. If these ratios of the intensities of the given absorption bands are due in the first place to the type of wood and show stability in the preparation of the lignosulfonic acids, they can be used to identify lignosulfonic acids obtained from different species of tree. However, this requires further special investigation. The differences in the intensities of these absorption bands for different lignosulfonic acids can serve as an indication of different structural environments of the sulfo groups in the lignosulfonic acids which to some extent agrees with the differences in the 1300-1000 cm^{-1} region.

The differential IR spectra of the lignosulfonic acids of the wood of the coniferous species differ only slightly from one another, while the differences between the IR spectra of the lignosulfonic acids of the wood of the broad-leaved species are pronounced and are due mainly to the amounts of sulfo groups in these samples of lignosulfonic acids. (For the lignosulfonic acids of aspenwood there are fewer of them and therefore as a basis for comparison of the quality of the lignosulfonic acids of the wood of broad-leaved trees a preparation of the lignosulfonic acids of birchwood has been selected, and the values of the relative optical densities of the absorption bands of the IR spectrum have been calculated for it.) The main differences in the 1800-1000 cm^{-1} region between the IR spectra of the lignosulfonic acids of the woods broad-leaved and of coniferous species resemble in their general outlines the differences between the corresponding IR spectra of the dioxane lignins. The differences in the absorption at 800-500 cm^{-1} are due to features of the position of the sulfo groups in the various lignosulfonic acids.

Thus, the investigation performed has permitted characteristic features of the IR spectra of lignosulfonic acid preparations obtained from the woods coniferous and broad-leaved species of trees to be established on the basis of which it has been shown that, in spite of some differences in the IR spectra of all the lignosulfonic acid preparation studied, definite characteristic features exist which permit the IR spectra of the lignosulfonic acids to be distinguished from the IR spectra of other types of lignin [4]. The absorption band at 2845 cm^{-1} can be used as an internal standard for comparing the IR spectra of different lignosulfonic acids, since it has the same intensity for all the lignosulfonic acid preparations studied. For the same reason the absorption band at 1595 cm^{-1} can be used to compare the IR spectra of lignosulfonic acids within the group of coniferous or within the group of broad-leaved trees. As has been established by Tupureine et al. [5], the absorption band at 1040 cm^{-1} can be used as an internal standard in the study of the IR spectra of lignosulfonic acids that have been highly modified, for example, by ozonization. However, to obtain correct IR-spectral information it is always necessary to bear in mind the preliminary index of the validity of the use of an internal standard for the given investigation, i.e., the previous finding of an internal spectrochemical correlation, ISC-III, as described by Tupureine et al. [5].

EXPERIMENTAL

The lignosulfonic acids were isolated by precipitation with hexamethylenecobaltichloride from the lyes of laboratory cooks of extracted sawdust which were made with the cooking acid of the Sloka pulp and paper combine under conditions analogous to those used in the combine [6]. The composition of the cooking liquid: total SO_2 5.6-5.7%, free SO_2 4.6%, bound SO_2 1.0-1.1%, CaO + Na_2O content not less than 1.1% (CaO:Na_2O = 2:1), liquor ratio 1:6. Time of cooking for spruce- and pinewoods 6.5 h (rise in temperature to 105°C — 1 h; impregnation at 105°C — 1 h; rise in temperature to 140°C — 1 h; cooking at 140°C — 3.5 h). The time of cooking for the birch- and aspenwoods was 6 h (rise in temperature to 105°C — 1 h; impregnation at 105°C — 1 h; rise in temperature to 135°C — 1 h; cooking at 355°C — 3 h).

The following amounts of lignosulfonic acids were obtained from 400 g of sawdust: 77.9 g (yield (15.6%) and for pine, 12.1 g (yield 2.4%); from 500 g of sawdust: for birch, 19.2 g (yield 3.9%), and for aspen 125.4 g (yield 25.1%).

The chemical analysis of the lignosulfonic acid preparations isolated was carried out in accordance with methods described in a handbook [7]. The results of the analysis were obtained as the arithmetic mean of three parallel determinations. The values of the mean square deviations of the methods for determining functional groups that were used correspond to those given by Tupureine et al. [5].

The samples of lignosulfonic acids investigated were ground with carbon tetrachloride in a vibromill for 5 min. After grinding, the samples were dried under an infrared lamp at 60-80°C. Then 4.00 mg of a sample, 2.50 mg of potassium hexacyanoferrate, and 0.8 g of potassium bromide (grade OSCh 6-4) were mixed in a vibromill for 1 min, after which tablets were molded under a pressure of about 4500 kgf/cm^2. Pressing was carried out in a vacuum mold of standard type.

IR spectra were taken on a UR-20 double-beam spectrophotometer. The 400-700 cm^{-1} interval was recorded with a potassium bromide prism, the 700-2300 cm^{-1} interval with a sodium chloride prism, and the 2300-3800 cm^{-1} interval with a lithium fluoride prism, using the following main parameter: split width program 4; rate of recording 64 cm^{-1}/min; time of recording for full amplitude 16 sec; recording scale 10-20 mm/100 cm^{-1}; time constant 2; signal amplification 9.1 with delay element switched on.

The method of analyzing the intensities of the absorption bands of the IR spectra with respect to an internal standard has been described elsewhere [8]. As internal standard we used the absorption band at 2100 cm^{-1} of potassium hexacyanoferrate. The relative optical densities of the absorption bands were obtained as the arithmetic means of four IR spectra of samples prepared in parallel, with a statement of an estimate of the mean square error. The accuracy of the given positions of the maxima of the absorption bands is 4-6 cm^{-1}.

The present investigation was carried out at the experimental base of the Institute of Wood Chemistry of the Academy of Sciences of the Latvian SSR. The samples of lignosulfonic acid analyzed were obtained by A. S. Ludzishaya who, together with L. N. Mozheiko, provided assistance in the performance of this investigation.

SUMMARY

1. General features characteristic of the IR spectra of lignosulfonic acids obtained from the woods coniferous and broad-leaved species of trees have been established.

2. The quantitative IR-spectral and chemical characteristics of preparations of lignosulfonic acids (from spruce- and birchwoods) that have been obtained can be used for comparison in the spectrochemical investigation of analogous preparations obtained from the woods of coniferous and broad-leaved species of trees.

LITERATURE CITED

1. V. B. Karklin', in: Abstracts of Lectures at an All-Union Seminar on the IR and UV Spectroscopy of Wood and Lignin [in Russian], Riga (1977), p. 10.
2. O. P. Grushnikov and V. V. Elkin, Advances and Problems in Lignin Chemistry [in Russian], Moscow (1973).
3. M. A. Zil'bertleit and V. M. Reznikov, Khim. Drevesiny, No. 6, 99 (1979).
4. V. B. Karklin', A. S. Ludzisha, and L. N. Mozheiko, in: Abstracts of Lectures at an All-Union Seminar on IR and UV Spectroscopy of Wood and Lignin [in Russian], Riga (1977), p. 88.
5. A. D. Tupureine, V. B. Karklin', and R. E. Reizin'sh, Khim. Drevesiny, No. 6, 31 (1976).
6. M. N. Tsypkina and I. M. Balashova, Zh. Prikl. Khim., 32, No. 1, 166 (1959).
7. G. F. Zakis. L. N. Mozheva, and G. M. Telysheva, in: Methods of Determining the Functional Groups of Lignin [in Russian], Riga (1975).
8. V. B. Karklin', Khim. Drevesiny, No. 1, 56 (1975).