Chemistry of Natural Compounds, Vol. 34, No. 4, 1998

SORPTION PROPERTIES OF TECHNICAL LIGNINS.
III. IR-SPECTRAL INVESTIGATION OF THE SORPTION CAPACITY OF TECHNICAL LIGNINS AND THEIR DERIVATIVES IN RELATION TO BILE ACIDS

G. N. Dalimova and É. L Kristallovich

UDC 547.99.992

It has been established by IR-spectral investigations that the sorption of bile acids by technical lignins takes place through the formation of hydrogen bonds between the functional groups of the lignins and the bile acids, the form of these bonds being determined by nature of the lignins and acids concerned.

It has been shown previously [1-5] that the IR-spectral characteristics and, namely, the frequency of the absorbed radiation, is extremely sensitive to structural changes in the lignin on the sorption of heavy metals. In view of this, we have used the IR-spectral method in a study of the sorption of bile acids by technical lignins and their derivatives (hydrolysis lignin from cottonseed husks — HLCSH-, sulfolignin — SL-, and nitrolignin — NL).

The characteristic frequencies of the stretching vibrations of the CO, COOH, and OH groups of the lignins investigated are given in Table 1.

The high frequencies (1751 and 3408 cm^{-1}, respectively) of the stretching vibrations of the carbonyl and hydroxy groups of nitrolignin (NL, sample 3) relative to the analogous frequencies for HLCSH and SL (samples 1 and 2) probably show the presence of free ester CO groups in NL. We must mention the high level of carbonyl groups in NL as compared with HLCSH and SL (7.6, 7.1, and 6.0%, respectively) which correlates with the results of IR-spectral analysis.

The low frequency of the stretching vibrations of the COOH groups [sic] of taurocholic acid (1651 cm^{-1}) and the presence of an absorption band in the 2200-2500 cm^{-1} region, in contrast to the analogous frequencies of the stretching vibrations of the COOH groups of cholic acid (1716 cm^{-1}) indicate the existence of strong dimeric associations of taurocholic acid formed through a hydroxy group.

An analysis of the frequencies of the stretching vibrations of the CO groups of the samples investigated (see Table 1) after the sorption of cholic acid by the lignins (samples 6-8) shows a retention of the frequencies of the C=O stretching vibrations for samples (6) and (7) and a shift of the C=O absorption bands by 43 cm^{-1} in the low-frequency direction on the absorption of cholic acid by NL (sample 8) in comparison with the corresponding frequencies of the initial components (samples 1-4).

In the region of the stretching vibrations of the OH groups of the lignins, the sorption of cholic acid led to a lowering of the OH frequency by 70-80 cm^{-1} in the case of samples (6) and (8) and by more than 200 cm^{-1} for sample (7).

The changes in the frequencies of the stretching vibrations of functional groups (CO, COOH, OH) of HLCSH, SL, and NL and also of the stretching vibrations of the COOH and OH groups of cholic acid adsorbed by the lignins are obviously explained by the formation of a hydrogen bond (HB) between the proton-donating phenolic OH groups of HLCSH and SL and the alcoholic OH groups of cholic acid in samples (6) and (7), while in sample (8) in addition to OH···OH HBs, an HB is also formed between a proton-accepting CO substituent of NL and an OH group of cholic acid.

The results presented give grounds for assuming that NL sorbs cholic most effectively (as compared with HLCSH and SL).

The sorption of taurocholic acid by the lignins under investigation (samples 1-3) led to the appearance, in the region of the stretching vibrations of carbonyl groups, of absorption bands at 1600 cm^{-1} (in samples 9 and 11) and 1597 cm^{-1} in the IR spectrum of sample (10).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (371) 240 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 545-547, July-August, 1998. Original article submitted December 29, 1997.

0009-3130/98/3404-0499$20.00

TABLE 1. Characteristic IR Frequencies of the Stretching Vibrations of CO, COOH, and OH Groups of Technical Lignins and Their Derivatives before and after the Sorption of Bile Acids

Specimen No.	Stretching vibrations of the groups, cm^{-1}	
	CO, COOH	OH
1. HLCSH	1703	3357
2. SL	1702	3397
3. NL	1751, 1700	3400
4. Cholic acid	1716	3473, 3345
5. Taurocholic acid	1651	3391
	After the sorption of cholic acid	
6. HLCSH	1710	3622, 3272
7. SL	1708	3631, 3125
8. NL	1708	3622, 3266
	After the sorption of taurocholic acid	
9. HLCSH	1708	3651 (inflection), 3294 or infl.
10. SL	1708, 1579	3652, 3082
11. NL	1719, 1608	3622, 3266

The absence of a maximum at 1651 cm^{-1} for the lignin samples after the absorption of taurocholic acid permits the absorption maxima at 1608 and 1579 cm^{-1} to be ascribed with the highest degree of probability to the absorption of the COOH substituent of taurocholic acid.

As in the case of the sorption of cholic acid by the lignins, in the field of absorption of active hydrogen at 3000-3600 cm^{-1} in the IR spectra of samples (9-11) there was an appreciable shift of the frequencies of the stretching vibrations of OH groups in the direction of low frequencies by more than 200 cm^{-1} in samples (10 and 11) and by almost 100 cm^{-1} in the case of sample (9) relative to the stretching vibrations of the OH groups of the initial components (samples 1-5).

Thus, to all appearance, the sorption of taurocholic acid by the lignins under investigation takes place through the formation of HBs between the COOH group of taurocholic acid and a phenolic OH group of HLCSH, SL, and NL. However, the absence from the IR spectrum of an absorption band at 1751 cm^{-1} in the case of the sorption of taurocholic acid by NL (sample 11) does not exclude the manifestation of a proton-acceptor function of the carbonyl groups of NL, as has been shown previously for the sorption of cholic acid by NL (sample 8).

On the basis of what has been said above, it may be concluded that the sorption of bile acids by the lignins investigated — HLCSH, SL, and NL — takes place through HBs the nature of which is determined by the type of lignin and of the corresponding bile acids. The results obtained presuppose the highest sorption activity of NL in the sorption of cholic and taurocholic acids as compared with HLCDSH and SL.

EXPERIMENTAL

The hydrolysis lignin (HL) was freed from traces of sulfuric acid by washing with distilled water until the wash-waters were neutral and was then extracted with ethyl alcohol to eliminate carbohydrates and resinous substances. The dried lignin was used for the subsequent investigations.

Nitrolignin was obtained by treating the HL with a mixture of 10% HNO_3 and 28% H_2SO_4 (1.5:1.0) at room temperature for 2 h. After the lapse of this time the product was washed with water to neutrality and dried at 100°C; yield 75%.

Sulfolignin was obtained by treating the HL with concentrated sulfuric acid at a ratio of the reactants of 1.0:2.5 at 160°C for an hour. After this time, the product was washed with water to neutrality. Yield 84%.

The IR spectra of the samples were taken on a Perkin-Elmer (Sweden) system 2000 Fourier IR spectrometer with a resolution of 4 cm^{-1} at a rate of scanning of 0.2 cm^{-1}/sec. The samples were prepared in the form of tablets by molding on a KBr support.

REFERENCES

1. N. V. Gaivoronskaya, G. M. Vasil'eva, and T. P. Grigor'ev, Zh. Prikl. Khim., **43**, No. 10, 2369 (1970).

2. N. V. Gaivoronskaya, G. M. Vasil'eva, and T. P. Grigor'ev, Zh. Prikl. Khim., **47**, No. 3, 667 (1974).
3. S. N. Bhattacharya and M. Khurana, Indian J. Chem., **A16**, No. 11, 988 (1978).
4. D. A. Armitage, Organomet. Chem., **8**, 160 (1980).
5. Yu. M. Chernoberezhskii and A. B. Dyagileva, Kolloidn. Zh., **52**, No. 6, 1213 (1990).