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SYNTHETIC LIGNIN

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In 1931 Hawley and Wiertelak (1) reported the chemical analysis of wood that had been subjected to a temperature of 135° C. for several periods of time up to 8 days. The analysis showed a partial decomposition of carbohydrates in the wood and the formation of a material (roughly equivalent in amount) that was isolated along with the lignin. In order to investigate this lignin-like material farther, it was prepared from Cross and Bevan cellulose and was thus obtained unmixed with the lignin of the original wood. The results of that investigation, confirming and extending the previous work, were presented at the spring, 1931, meeting of the American Chemical Society, but they were not published because meanwhile Sherrard and Harris (5) and Ritter, Seborg, and Mitchell (3) had shown the possibility of serious error in the standard method used for lignin determination. Instead of publishing, the researchers decided to repeat the experimental work, using the improved method for determining lignin. Only the parts of the data from the first experiments that are required for comparison will be presented here.

Heat Treatment of Cellulose

In the present experiments large quantities of Cross and Bevan cellulose were prepared from white spruce and sugar maple by the method used in isolating the cellulose for its quantitative determination. Fifteen-gram samples were sealed in glass tubes and heated in a pressure-steam retort for 1, 2, and 8 days at 135° C. Duplicate runs were made, and, except in the few instances where a tube was broken accidentally, the figures in the table are the averages of two closely agreeing determinations, one from each duplicate tube. The slight gas pressure remaining in the tubes after cooling was relieved by breaking an end of each tube under water, and an approximate determination of the gas evolved was made. This gas was largely carbon dioxide, but under the conditions of the experiment no significant quantitative figure could be obtained. The amount of water formed during the heating can be calculated approximately from the difference in moisture content of the samples before and after heating.

The data in Table 1, when considered alone, indicate that the rate of the reaction with the spruce was much faster than with the maple celluloses. This difference, however, is probably caused by something else than inherent differences between the species. In the previous work a maple cellulose, prepared and treated in as nearly as possible the same way, gave 18.8 per cent lignin in 8 days, while the softwood cellulose (loblolly pine in this case) gave only 11.2 per cent. With any one lot of cellulose the rate seems to be the same in all runs, as is shown by the relation between period of heating and extent of reaction, and the close checks in duplicate runs; but with different lots of cellulose the rates may be very different. Small amounts of impurities probably exert a considerable catalytic effect.

The later work has confirmed the general conclusions of Hawley and Wiertelak in regard to the decomposition of the carbohydrates in wood. The carbohydrates are decomposed with the formation of water-soluble and alcohol-benzene soluble substances that apparently are intermediate products in the formation of lignins. In the treatment of the hardwood cellulose, the pentosans were the first constituent to decompose, but the reaction was not carried far enough to determine whether ultimately other carbohydrates would be attacked. In the softwood cellulose, hexosans were decomposed even in the earlier stages of reaction.

Comparison of Synthetic and Natural Lignin

The additional information obtained in this work with wood carbohydrates essentially free from lignin is based on examinations of the lignin isolated from the heated cellulose by comparison with the lignin similarly isolated from wood. As already reported (6), the lignin produced by the heat treatment of maple cellulose had an ultra-violet absorption spectrum typical of the hardwood lignins. The particular sample examined for this purpose was one of the first lot not described in detail here for reasons previously given. The lignin formed amounted to about 18 per cent of the treated material and, from the analyses, appeared to be derived largely from the pentosans in the cellulose.

All these lignin samples, as shown by the method of their isolation and determination, are similar to lignin in wood in their resistance to 72 per cent sulfuric acid. Furthermore, the isolated lignins dissolve readily in sulfite solutions after chlorination in the same way as lignin which is isolated directly from wood.

Ritter, Mitchell, and Seborg (2) have recently shown that spruce lignin, put into solution by chlorination and sulfites, has a reducing value which is 29.5 per cent of that of an equal amount of glucose, and that maple lignin had a reducing value of 34.5 per cent. The lignin isolated

Table 1.--Chemical composition of wood cellulose heated for 0, 1, 2, and 8 days, calculated in per cent of weight oven-dry

Composition	White spruce Cross and Bevan cellulose				Sugar maple Cross and Bevan cellulose			
	Days heated --				Days heated --			
	None	1	2	8	None	1	2	8
Moisture.....	6.2	7.8	12.2	35.3	6.1	5.9	6.5	8.7
Hot-water soluble.....	0.0	15.4	17.8	21.7	0.0	4.3	4.8	3.0
Reducing sugar in hot-water soluble.....	0.0	0.17	0.24	0.0	0.0	0.19	0.14	0.06
1 per cent alkali soluble: corrected for hot water	19.5	20.0	17.0	1.0	19.8	27.5	28.8	23.5
Alcohol-benzene soluble..	0.0	11.8	15.5	19.2	0.0	2.4	2.8	2.2
Cross and Bevan cellulose:.....	71.6	63.2	8.0	91.4	90.6	86.4
Lignin.....	0.3	8.5	15.5	70.3	0.3	1.5	2.9	6.9
Pentosan.....	9.3	4.2	2.3	0.0	20.5	11.3	9.5	6.0

from the 8-day treatment of spruce cellulose, when treated in the same manner, had a glucose equivalent, in reducing value, of 26 per cent; the 8-day maple lignin had an equivalent of 31.0 per cent.

The material prepared as described contains no methoxyl but it can be methylated. Two methylations at 50° C. for 2 hours each gave a product having 7.0 per cent of methoxyl, which is far below the value of 32.5 per cent that has been obtained with natural lignin (5). Attempts will be made to obtain a higher degree of methylation.

By four diverse methods of characterization, the main product obtained in these experiments has shown a close similarity to the lignin obtained directly from wood, and the authors believe they are justified in calling it "synthetic lignin." At least they have prepared a product that, in its basic chemical characteristics, corresponds to lignin. In certain quantitative respects the correspondence may not be complete, but this should be expected, not only from the variability of natural lignins but also on account of probable impurities, such as intermediate or by-products, in the synthetic product.

By-Products and Intermediate Products

It is interesting to note how closely these experimental results correspond to the hypothesis of Shrauth (4) on the constitution of lignin. He assumed a hypothetical intermediate product between glucose and lignin similar to 5-hydroxymethyl furfural, 3 molecules of which condense with elimination of 6 molecules of water to form a compound of 5- and 6-atomed rings. This compound contains three hydroxyl groups in the central six-carbon ring that require hydrogenation for their removal and thus for the completion of the formation of a compound that accounts for the chemical characteristics of lignin. The water-soluble and alcohol-benzene soluble material, formed by the heat decomposition of the cellulose, corresponds to Schrauth's hypothetical intermediate product, and the amount of water formed corresponds roughly to the 6 molecules required. There is no indication in the present experiments of reduction of the hydroxyl groups except that carbon dioxide may be formed by the oxygen given off. The amount of carbon dioxide, however, is sufficient to account for only a small part of this oxygen.

Although the water-soluble material, containing as it does intermediate products between cellulose and lignin, is of great interest, it has been given only a cursory examination. It has only a trace of reducing value even after hydrolysis with dilute acid. On acidification with mineral acids, a partial precipitation takes place and a part of the precipitate is resistant to chlorination and subsequent treatment with sulfites. The material resistant to chlorination may then be completely

dissolved in 72 per cent sulfuric acid. No conclusions are drawn from such fragmentary data, but it is merely suggested that further study of this water-soluble material seems to offer an important new field for research in the chemistry of both cellulose and lignin.

Hardwood and Softwood Lignins

Although there are many slight qualitative differences to be noted between hardwood and softwood lignins, there are few well-defined quantitative differences. Perhaps the most characteristic are in the ultra-violet absorption spectra and in the reducing number. It has already been shown that the synthetic lignin made from hardwood cellulose, and evidently formed largely by the decomposition of pentosan units, has an absorption spectrum and a reducing value that correspond closely to a typical hardwood lignin, while the synthetic lignin made from a softwood cellulose, and evidently formed largely from hexosan units, has a reducing value corresponding closely to a typical softwood lignin. (The authors have not yet had opportunity to measure the absorption spectrum of such a sample.) This information leads directly to the hypothesis that the differences between natural hardwood and softwood lignins are due to the relative proportions of hexose and pentose units that have entered into their formation. This hypothesis will be developed further as the next step in the research on synthetic lignins. It should be readily possible to prepare lignins from pure pentosans, pure hexosans, and known varying proportions of the two, and thus to establish the relation between the source and the characteristics of the product.

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