Lignin preparations with very low carbohydrate content

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SUMMARY: Lignin preparations having a very low carbohydrate content were obtained from milled spruce wood lignin after treatment in an acetic acid-water-pyridine-chloroform system. Besides the purified lignin, fractions containing lignin-carbohydrate compounds were obtained.

☐ Ligninpreparat med mycket lågt kolhydratinnehåll har framställts ur malvedslignin från gran med användning av ett ättiksyra-vatten-pyridin-kloroformsystem, varvid fraktioner, anrikade på kolhydrater och innehållande ligninkolhydratföreningar, även erhölls.

Milled wood lignin (MWL) prepared according to Björkman contains small amounts of carbohydrates (1), the content usually being a few per cent. The nature of the carbohydrate portion is of interest in connection with questions concerning lignin-carbohydrate bonds. In analytical and spectral studies of lignin, the presence of carbohydrates is a disadvantage.

It has been reported (2) that the carbohydrate content in MWL can be decreased to less than 0.2 % by the addition of aluminium oxide and benzene to a dioxane-water solution of the lignin. However, the calculated value of the carbohydrate content in a lignin-rich material is strongly affected by the analytical procedure adapted and, usually, the values obtained are too low due to degradation of carbohydrates and incomplete hydrolysis of lignin-carbohydrate bonds (3).

In the present work, products obtained from spruce wood by milling and subsequent extraction with dioxane-water according to Björkman (1 a) were dissolved in dioxane-water (20:1). Water was added to give a dioxane-water ratio of 5:2 and the mixture was then extracted with chloroform (the volume of chloroform was one half the volume of the dioxane-water solution). The organic layer contained low molecular weight lignin and related materials and the aqueous layer contained sugars and, according to tentative examinations, lignin-carbohydrate compounds.

A lignin precipitate was present in the aqueous layer. The precipitate, which was filtered off, washed with water, and dried, constituted one half of the material originally extracted. The carbohydrate content was 1.0 %. The product was dissolved in pyridine-acetic acid-water (9:1:4) and extracted with chloroform. It was found that in this solvent system the lignin had a very strong tendency to remain dissolved in the organic layer even when the ratio chloroform/pyridine was high. By increasing the amount of chloroform, it was gradually possible to diminish the carbohydrate content in the organic layer. Thus, when the chloroform-pyridine ratio was 6:1, work-up of the organic layer gave a lignin preparation (yield 52 %) containing as little as 0.05 % carbohydrates. The relative carbohydrate contents of the original precipitate and the purified lignin, respectively, are given in *table 1*. Except for the significant increase in the arabinose content and the decrease in the mannose content the values found for the samples are rather similar. For comparison, the relative carbohydrate content of an LCC preparation (lignin content 42 %) is also given.

Table 1. Relative carbohydrate composition

Sample	Relative carbohydrate composition, %				
	Arabinose	Xylose	Mannose	Galactose	Glucose
Original precipitate	19.1	25.1	26.8	19.2	9.7
Purified lignin	28.7	20.4	17.8	20.4	12.7
LCC[1]	10.8	31.9	31.3	14.2	11.8

[1] Prepared according to Björkman (4).

A procedure for the preparation of milled wood lignin with a very low carbohydrate content has been developed (5) on the basis of results obtained after treatment in the pyridine-acetic acid-water-chloroform system. So far, investigation of the aqueous layers strongly indicates the presence of lignin-carbohydrate compounds, a considerable part of which has a low molecular weight.

Literature

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