INVESTIGATION OF THE LIGNIN ISOLATED FROM PHRAGMITES COMMUNIS BY THE METHOD OF MECHANICAL MILLING

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In a previous paper an account was given of the isolation of lignins from the stems of Phragmites communis Trin. (reed) by the hydrochloric acid and cuprammine methods. The elementary composition and functional groups were determined, and the mean composition for the C_6-C_3 structural unit of the lignins isolated was calculated [1]. Since the methods mentioned involve a change in the structure of the lignins, we decided to use the method of mechanical milling (Bjorkman [2]) to isolate them from reed stems.

A sample of the powdered stems of reeds cut in 1964, ground in a mill (coffee-mill type) and passed through a sieve with apertures of diameter 0.5 mm, was extracted for 18 hr with dichloroethane and for 24 hr with a mixture of alcohol and benzene (1:1) and was then dried for 3 days in a vacuum desiccator over P_2O_5. The powder contained 20.12% of lignin (by Komarov's method), 5.07% of OCH_3, and 3.36% of ash. The milling was carried out in absolute toluene in a VNIINSM [All-Union Scientific Research Institute for Building Materials] model vibratory ball mill with a vibrational amplitude of 4 mm at 3000 rpm in an atmosphere of nitrogen. The yield of lignin was 11.12% (taking the ash into account) of Komarov lignin. The lignin obtained was subjected to further purification by Freudenberg's method [3]. The fraction soluble in cold butanol amounted to 1.78% of the lignin taken for purification.

Bjorkman lignin	Elementary composition			Content of functional groups		
	%					
	C	H	O	OCH_3	Total OH	CO
From reed stems	61.01	6.23	32.76	17.59	10.39	2.92
From cotton stems	61.15	6.22	32.63	18.12	11.55	2.27

The purified lignin was first dried in a vacuum desiccator over P_2O_5 and then in a vacuum gun at the boiling point of carbon tetrachloride for 30 hr. The carbohydrate content of the resulting faintly colored sample (Bertrand's method, hydrolysis with 5% sulfuric acid) was 1.04%. The elementary analysis and functional group analysis of the Bjorkman lignin [4] from reed stems, in comparison with lignin from cotton stems, are shown in the table (figures given with correction for the carbohydrate content).

The OCH_3 content was determined by Zeisel's method, the total OH by Verley's method [5], and the CO groups by Gierer and Söderberg's method [6], applying the correction proposed by Adler, Marton, and Persson [7].

The benzyl alcohol groups were determined together with the benzl ether groups by methylation with absolute methanol containing 0.5% of hydrochloric acid by Adler and Gierer's method [8]. The methylated lignin contained 20.08% of OCH_3 groups. The ratio of OCH_3 groups introduced to those present in the initial lignin was calculated by Adler and Gierer's method as 0.19.

However, the amount of OCH_3 and OH groups in reed lignin is somewhat lower than in cotton lignin, and that of CO groups is higher. It was shown previously that in contrast to cotton lignin (Malvaceae group) reed lignin (Gramineae group) contains p-hydroxycinnamyl alcohol structures [1].

From the figures obtained, the mean composition for the C_6-C_3 structural unit was found: $C_9H_{9.03}O_{2.94}(OCH_3)_{1.11}$ or, in the form proposed by Freudenberg [9], $C_9H_{7.15}O_2(H_2O)_{0.94}(OCH_3)_{1.11}$.

When a molar amount of functional groups is isolated, the formula acquires the following form: $C_9H_{7.82}O_{1.52}(OCH_3)_{1.11}(OH)_{1.21}(O_{carbonyl})_{0.21}$. Mol. wt. of a unit = 198.48.

The lignin isolated was readily soluble in polar organic solvents (dioxane, pyridine, acetone, benzene, phenol, and alcohol), in acetic acid and acetic anhydride, and in dilute alkalis.

Experimental

Production of Bjorkman lignin. Each of the four 100-ml stainless-steel cylinders of the vibratory ball mill was two-thirds filled with steel balls (diameter of 4–5 mm) and with 7 g of powdered reed stems that had been ground and passed through a sieve with apertures having a diameter of 0.5 mm, extracted, and dried in vacuum over P_2O_5. Then the cylinders were filled with absolute toluene. Milling was carried out for 15 hr, after which the milled mass was centrifuged, and the lignin was extracted from the residue with 85% aqueous acetone for 6 days (on a shaker) the solvent being changed twice. The residue after the elimination of the acetone was dissolved in 90% acetic acid (25 ml for 1 g of lignin) and, with stirring (by means of a magnetic stirrer) was poured into water (1 g of lignin to 300 ml of water). The precipitated lignin was centrifuged off, and the subsequent treatment was identical with that described by Bjorkman [2]. The powder (28 g) gave 0.64 g of lignin. The product (a total of 5.71 g) was treated as described by Freudenberg [3]. This gave 4.95 g of a light cream-colored material.

Determination of carbonyl groups. The CO groups were determined by Gierer and Söderberg's method [6]. The volume of unconsumed hydrogen was measured in a gas buret over mercury.

1st determination: weight of lignin 0.1236 g, volume of hydrogen consumed 2.99 ml,
CO groups 3.02%

2nd determination: weight of lignin 0.1127 g, volume of hydrogen consumed 2.54 ml,
CO groups 2.82%
Mean for CO groups 2.92%.

Summary

Lignin has been isolated from the stems of the reed Phragmites communis Trin. by the mechanical milling method. The elementary composition and functional groups have been determined. The mean composition for the $C_6 - C_3$ structural unit has been calculated.

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