INVESTIGATION OF THE LIGNINS OF PHRAGMITES COMMUNUS TRIN.

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In the production of cellulose, annual plants, reeds and cereal straw, are used as well as wood. Reeds are widespread in the deltas of the southern rivers. There they are renewed annually.

We have investigated Phragmites communus Trin. (common reed) growing in the delta of the Amu-Darya, where it occupies an area of about 400,000 hectares. This type of reed is of industrial importance [1].

The chemical composition of the different parts of this plant gathered in 1964 can be seen from the data of Table 1. The table shows that the reed lignin is similar in respect of the number of methoxy groups to conifer lignin, as has been shown by Rumanian scientists studying Danubian reed [2], while in its amount the lignin resembles that of broad-leaved trees.

Table 1

Chemical Composition of Various Parts of the Reed Plant (% of absolutely dry starting material)

Component	Stem	Sheath	Leaves	Panicle
Cellulose	50.48	38.15	—	—
Lignin	20.12	16.13	15.65	15.81
Pentosans	22.80	25.31	—	—
Ash	3.36	11.05	—	—
Substances extractable with a mixture of alcohol and benzene	3.84	4.91	—	—
Methoxy groups	5.07	3.06	2.39	2.51

The cellulose content of the reeds was determined by Kürschner's method and that of lignin by König's method as modified by Komarov [3].

We studied the chemical composition and structure of the reed lignins isolated by various methods. There is no information in the literature on the composition of the lignin of this plant.

To isolate the lignin, we took the comminuted stems of the reed plant ground in a coffee mill, passed through a sieve with a 0.5-mm diameter apertures and extracted with a mixture of alcohol and benzene. The lignin was isolated by two methods: by Willstötter's hydrochloric acid method [5] and by Freudenberg's copper-ammonia method [5]. The hydrochloric acid lignin had a light brown color and the copper-ammonia lignin a brown color.

Before analysis the lignin was dried over P_2O_5 in a desiccator and then in a vacuum pistol at the boiling point of acetone. The data of Table 2 show that the yield obtained by the hydrochloric acid method was four times greater than that by the copper-ammonia method. The number of methoxy and hydroxy (total) groups and the elementary composition with respect to C, H, and O of the two lignins almost coincided. The ash content of the lignins was considerably higher (9.02% in the hydrochloric acid sample and 9.35% in the copper-ammonia sample) than in the reed itself (3.36%). Carbohydrates (by Bertrand's method, after hydrolysis of the lignin with 5% sulfuric acid) and nitrogen were found only in traces in the hydrochloric-acid and the copper-ammonia lignins. The total content of hydroxy groups was determined by Verley's method [6].

Table 2

Elementary Composition and Functional Groups of Reed Stem Lignins (figures, corrected for ash content, % of the absolutely dry starting material)

Method of isolation	Yield	Content			Elementary composition			Ash content
		OCH_3	OH	Total				
Hydrochloric acid	21.43	16.36		10.38	61.14	5.86	33.0	9.02
Copper-ammonia	5.16*	14.96		9.68	63.98	6.12	29.9	9.35

*The low yield is due partly to high losses in the isolation of the lignin.

The mean composition of the C_6-C_3 structural unit was calculated on the basis of the results obtained: for the hydrochloric-acid lignin it was $C_9H_{7.23}O_{1.81}(OCH_3)_{1.02}(OH)_{1.20}$, and for the copper-ammonia lignin

$C_9H_{7.66}O_{1.52}(OCH_3)_{0.89}(OH)_{1.02}$.

As is well known, the oxidation of lignin with nitrobenzene in the presence of alkali gives aromatic aldehydes. In this process, lignins from angiosperm (leafy) plants give vanillin and syringaldehyde, gymnosperms give vanillin and a small amount of p-hydroxybenzaldehyde, and annual plants give all three aldehydes [7].

To elucidate the structure of the lignin of reed stems, we oxidized the lignin with nitrobenzene in the presence of alkali at 180°C for 2 hr. This reaction gave syringaldehyde, vanillin, and p-hydroxybenzaldehyde. The total yield of aldehydes amounted to 3.5% of the Komarov lignin. The qualitative separation was carried out by paper chromatography. The aldehydes were separated quantitatively in a thin layer of silica gel. The ratio of syringaldehyde to vanillin and p-hydroxybenzaldehyde in the mixture of aldehydes obtained was about 1:9:14.5; and the content of methoxy groups in the mixture of aldehydes was 12.35%.

Experimental

Oxidation of the reed stems with nitrobenzene. Finely comminuted reed stems (25 g) that had been extracted with a mixture of alcohol and benzene were mixed with 275 ml of 2 N caustic soda solution and 28 ml of nitrobenzene. The mixture was heated at 180°C for 2 hours in a 0.5-l rotating autoclave. The reduction products were distilled off with live steam until a red-yellow oil ceased to pass over, the residue was filtered, and the filtrate was acidified to pH 1 with concentrated sulfuric acid. A brown precipitate was deposited. The solution and the precipitate were extracted with trichloroethylene (900 ml). The extract was treated with a 5% solution of caustic soda (600 ml). A current of carbon dioxide was passed into the alkaline solution to pH 7. The solution was shaken with ether (1000 ml). The ethereal solution was treated with 7% sodium bisulfite solution (600 ml) and the bisulfite solution was decomposed with concentrated sulfuric acid (30 ml). A current of carbon dioxide was passed through the hot solution (in a water bath) to eliminate the sulfur dioxide. Then the solution was treated with ether (1000 ml), the extract was dried over calcined sodium sulfate, and the solvent was distilled off. The residue amounted to 0.1527 g (3.05% of the Komarov lignin).

The mixture of aldehydes obtained was chromatographed on paper ("crab" paper) and in a thin layer of silica gel. The solvent used for the paper chromatography was a mixture of hydrocarbons [octane, heptane, nonane (1 : 1 : 1)] – butyl ether–water (1:0.2:0.2), and the solvent for the thin layer of silica gel was butyl ether–butan-1-ol (2:1). The chromatogram was developed for 3 hours after which it was dried and was developed once more for three hours with the same mixture of solvents. The aldehydes on the paper were revealed with a 0.2% solution of 2, 4-dinitrophenylhydrazine in 2 N hydrochloric acid. The R_f values of the aldehydes were: syringaldehyde 0.16, p-hydroxybenzaldehyde 0.35, vanillin 0.44.

For quantitative separation in a thin layer of silica gel the aldehydes obtained were extracted with alcohol. The ratio of syringaldehyde to vanillin to p-hydroxybenzaldehyde was 1:9:14.5.

Summary

1. Lignin has been isolated from the stems of Phragmites communus Trin. by the hydrochloric acid and the copper-ammonia methods. Its elementary composition and functional groups have been determined. The mean composition of the C_6-C_3 structural unit has been determined.

2. The oxidation of comminuted reed stems with nitrobenzene in the presence of alkali has given a mixture of aldehydes: syringaldehyde, vanillin, and p-hydroxybenzaldehyde. Their yield was 3-4 times less than from wood.

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