Studies on nitration of bamboo protolignin

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SUMMARY

Extractive-free bamboo dust was nitrated both in aqueous and non-aqueous media with nitric acid. The yields of nitrolignins were higher in non-aqueous medium. The yield increases with the increase of time and temperature. The nitrolignins were examined for their elemental composition, methoxyl content and nitric content. From the investigation it was concluded that nitration was accompanied by the substitution of nitrogen and loss of methoxyl content in protolignin. The loss of methoxyl is higher in aqueous medium than in non-aqueous medium, indicating the lesser drastic action of nitric acid in non-aqueous medium.

INTRODUCTION

Dendrocalamus strictus is a commonly available species of bamboo and is an important raw material of paper mills of India. Nitration is amongst the most widely studied of all lignin reactions. Lignin being phenolic in nature readily undergoes nitration. The present investigation deals with the nitration of bamboo protolignin under different conditions.

EXPERIMENTAL

(i) Raw Material

The bamoo used in the present investigation was **Dendrocalamus strictus**. The bamboo culms were chipped on a pilot plant chipper. These chips were then converted into dust (60.80 mesh). The dust was exhaustively extracted with alcohol benzene (1:2) for 6 hours. The extractive-free dust was washed with hot water and dried.

(ii) Nitration of Protolignin in Aqueous Medium

The pre-extracted bamboo dust (50 g.) was taken in a 1 litre Erlenmeyer flask. Nitric acid (300 ml., sq.gr. 1.30) and sodium nitrite (2.5%) were added, keeping the material: liquor ratio 1:6. The flask was refluxed in a thermostat at 65°C and 85°C for 2 to 3 hours. The solution was filtered, and the hot filtrate was cooled in ice cold water, when an amorphous yellow coloured precipitate of nitro lignin (A) was obatined. The residue was washed thoroughly with hot distilled water and then extracted with 10 percent sodium hydroxide for 2 hours at 85°C keeping the material to liquor ratio as 1 : 6. Alkaline black liquor obtained after extraction was precipitated with hydrochloric acid, when a brown flocky precipitate of nitrolignin (B) was obtained. The nitrolignins were analysed for carbon, hydrogen, nitrogen, methoxyl content and nitro content. The yields and chemical composition of nitrolignins are recorded in Table I and II.

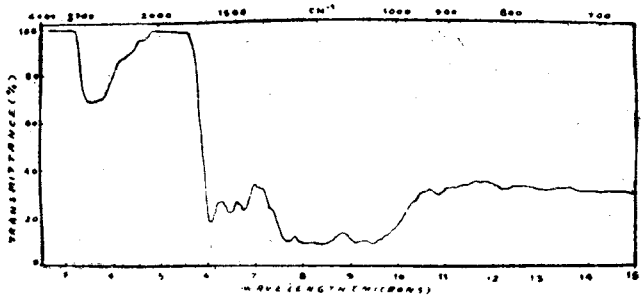

Fig. I. Infrared spectrum of proto nitrolignin (carbon-tetra-chloride-medium)

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TABLE—I YIELD & ANALYSES OF PROTO-NITROLIGNINS IN AQUEOUS MEDIUM AT 65°C

Sl. No.	Amount of sodium nitrite %	Cooking period Hours	Fraction of proto nitro-lignin	Yield* %	Carbon %	Hydrogen %	Nitrogen %	Nitro %	Methoxyl %
1.	0.0	2	A	0.28	—	—	1.98	—	7.7
			B	6.98	48.4	6.4	1.64	6.3	8 5
2.	1.0	2	A	0.33	—	—	2.11	—	7.4
			B	7.55	48.0	6.1	1.66	6.5	8.2
3.	1.5	2	A	0.36	—	—	2.18	—	7.1
			B	8.05	47.2	5.7	1.75	7.2	7.9
4.	2.0	2	A	0.41	—	—	2.25	—	6.8
			B	8.60	46.8	5.3	2 09	7.8	8.4
5.	2.5	2	A	0.37	—	—	2.05	—	0.6
			B	7.90	47.6	6.2	1.96	7.5	7.9
6.	0.0	3	A	0.32	—	—	2.03	—	7.5
			B	7.44	47.9	6.4	1.83	6.8	8.8
7.	1.0	3	A	0.38	—	—	2.14	7.2	8.4
			B	7.95	54 2	6.0	1.85	7.2	8.4
8.	2.0	3	A	0.42	—	—	2.18	—	5.2
			B	8.70	43.0	5.5	2.11	7.6	8.2

*expressed on the basis of oven-dry bamboo.

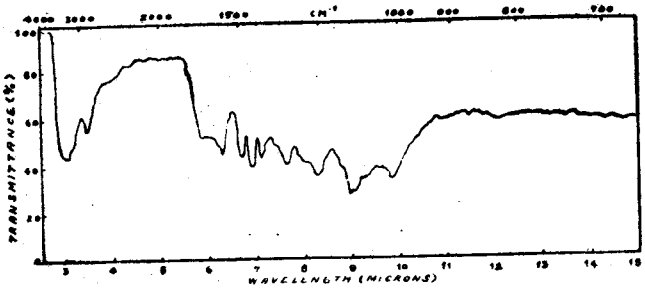
TABLE—II YIELD & ANALYSIS OF PROTO-NITROLIGNIS PREPARED ON AQUEOUS MEDIUM AT 85°C

Sl. No.	Amount of Sodium Nitrite %	Cooking period Hours	Fraction of proto-nitrolignin	Yield* %	Carbon %	Hydrogen %	Nitrogen %	Nitro %	Methoxyl %
1.	0.0	2	A	0.35	—	—	2.13	—	7 6
			B	7.52	48.3	6.5	1.82	5.7	9·0
2.	1.0	2	A	0.38	—	—	2 24	—	7.1
			B	8.40	47.5	5.4	1.94	8.1	8.5
3.	2.0	2	A	0.43	—	—	2.28	—	6.5
			B	9.10	44.6	5.2	2.03	8.7	8.4
4.	0.0	3	A	0.41	—	—	2.15	—	7.3
			B	8.20	47.8	5.8	1.96	7.4	8.2
5.	1.0	3	A	0.44	—	—	2.20	—	7.5
			B	8.65	46.1	6.1	1.98	7.7	8.0
6.	2.0	3	A	0.48	—	—	2.30	—	6.2
			B	8.93	45.8	5 7	2.19	8.1	7.7

(iii) Nitration of Protolignin in Non-Aqueous Medium

Pre-extracted dust (20 g.) was nitrated with a freshly prepared mixture of nitric acid (50 ml.) and carbontetrachloride (200 ml.) at room temperature by varying time of nitration (1-3 hours). After the reaction period, the dust was filtered off and washed with carbon tetrachloride. The nitrated dust was dried and extracted with 10% sodium hydroxide at 40°C for 2 hours. The alkaline extract was poured into ice-cold water to precipitate nitrolignin. The nitrolignin was washed free of acid and vacuum dried. The yields and chemical composition are recorded in Table III.

The pre-extracted dust was also nitrated in alcoholic media. The pre-extracted dust (50 g.) was refluxed with solution of nitric acid (125 ml) and ethyl alcohol (600 ml) for 2 hours. The reddish yellow solution was filtered and the filtrate was dropped into water to precipitate nitrolignin. The precipitate was filtered, washed and vacuum dried, under identical conditions methanol was also used instead of ethanol. Nitrolignins were analysed for their chemical composition. The yield and chemical composition are recorded in Table IV.



DISCUSSION

The results recorded in Table I and II indicate that by increasing the concentration of the acid, time, temperature and amount of sodium nitrate, the yield of nitrolignins increases. The increase in the yield of nitrolignin by addition of sodium is due to the liberation of HNO_2, which is very reactive in its nascent state. The low yield of nitrolignin (A) indicates that major part of the dissolved bamboo was converted into their water soluble products. The results recorded in Table III and IV indicate that yields of nitrolignins in non-aqueous media are higher than in aqueous medium showing the lesser drastic action of nitric acid in non-aqueous media.

The results recorded in Table I-IV, indicate that nitrogen content of nitrolignins lies in the range of 1.64-3.6 percent. Several workers have found that the nitrogen content of nitrolignins lies in the range of 2-4 percent[1]. The lower values of nitrogen substitution in aqueous medium as compared to non-aqueous medium is due to the side reactions which occur predominately suppressing nitration and resulting in the formation of acids and gaseous products containing nitrogen. The nitro content varies proportionally to the nitrogen content of the nitrolignin.

The results recorded in Tables I-IV indicate that the methoxyl content of nitrolignins prepared in non-aqueous medium is higher than in aqueous medium. It is observed that methoxyl content decreases more in aqueous than in non-aqueous media. The methoxyl content of bamboo dioxane lignin is 18.3[2]. The loss of methoxyl on nitration is due to the splitting of methoxyl by acid which forms the water soluble products. Several workers have found

TABLE—III YIELD & ANALYSIS OF PROTO-NITROLIGNINS PREPARED IN CARBON-TETRA CHLORIDE MEDIUM.

Sl. No.	Time of nitration Mts.	Yield of* protolignins %	Carbon %	Hydrogen %	Nitrogen %	Nitro %	Methoxyl %
1.	60	7.7	56.2	5.8	2.1	7.4	10.4
2.	120	8 2	54.6	5.2	2.6	8.1	9.8
3.	180	8.8	51.6	4.8	2.8	8.6	9.1

*expressed on the basis oven-dry bamboo.

TABLE—IV YIELD AND ANALYSIS OF PROTO-NITROLIGNINS PREPARED IN ALCOHOLIC MEDIA

Sl. No.	Solvent	Yield of* Proto-Nitro-Lignin %	Carbon %	Hydrogen %	Nitrogen %	Nitro %	Methoxyl %
1.	Ethanol	9.8	53.8	4.2	3.6	10.2	10.6
2.	Methanol	11.4	56.3	4.8	3-1	9.6	13.8

*expressed on the basis of oven-dry bamboo.

TABLE—V

Reaction Medium	Emperical Formulae
Aqueous*	$C_9 H_{14.8} N_{0.25} O_{6.1} (OCH_3) .06 (NO_2) 0.3$
Carbon-tetra-chloride**	$C_9 H_{10.3} N_{0.26} O_{4.5} (OCH_3) .11 (NO_2) 0.7$
Ethanol	$C_9 H_{8.3} N_{0.48} O_{4.7} (OCH_3)_{.7} (NO_2) .04$
Methanol	$C_9 H_{8.9} N_{0.39} O_{3.9} (OCH_3)_{.22} (NO_2) .11$

*Serial No. 1 B of Table I
**Serial No. 2 of Table III.

that nitration of lignin is accompanied by a widely varying decreases in methoxyl content .

As phenyl propane is the building unit of lignin, C_9 formulae of nitro lignins produced in aqueous and non-aqueous media have been worked out and shown in Table V. On perusal of Table V it is found that NO_2 per monomer is less than one indicating its substitution in 6 position[4].

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