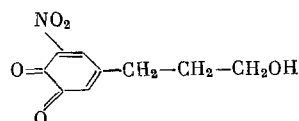


NITRATION OF METHYLATED LIGNIN

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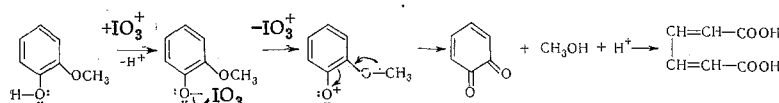
UDC 542.958.1+547.458.84

The nitration products of spruce lignin [1], which was isolated by a mechanical grinding method (MGL), were prepared earlier. It was noted that practically the same decrease in the contents of OCH_3 groups, which amounted to approximately one third of those originally available in the lignin, takes place when lignin is nitrated with various amounts of HNO_3 in various anhydrous mediums. This quantity closely corresponds to the content of the free phenolic hydroxyl groups in the original lignin. Similar data were also obtained when lignin hydrochloride was nitrated [2]. It was shown in [3] that an o-nitroquinone is formed in an $\sim 70\%$



yield of the original guaiacylpropanol when 1-guaiacylpropanol-3 is nitrated in absolute ether; the o-nitroquinone is decomposed with the rupture of the ring during further treatment with nitric acid. It has been proposed [1-3] that the demethylation of lignin under the nitration conditions proceeds basically analogously, i.e., through structural elements of the guaiacyl type. The COOH groups acquired by the lignin were basically attributed to the oxidation of the intermediately formed quinones with the rupture of the ring. The author of [4] showed that nitroquinone is formed when 4-methylguaiacol is nitrated with dilute nitric acid; it is decomposed when reacted further with nitric acid forming the following final reaction products: N_2 , N_2O , NO , NO_2 , CO , CO_2 , and $(\text{COOH})_2$. The authors of [5] observed the formation of o-benzoquinones during the chlorination of lignin. It was shown in [6 and 7] that 1 mole of methanol per mole of a guaiacylic compound is formed when oxidation of a guaiacol solution and solutions of its derivatives is carried out with sodium periodate. These results were used by the authors of [7] to determine the guaiacylic structures quantitatively in lignin preparations. The reaction probably proceeds through an ionic mechanism [8] (see Scheme 1):

Scheme 1



The o-quinone formed is oxidized further with excess periodate. Thus, cis-cis-muconic acid [7] is obtained by reacting periodate with guaiacol.

In order to prevent the formation of quinones during the nitration of the guaiacylic structures in lignin, and, consequently, their destruction, we nitrated MGL which had been preliminarily methylated. The lignin was methylated with dimethylsulfate in an aqueous acetone solution in the presence of KOH (the yield was 91% of the original weight taken). The elemental composition of the MGL after methylation was: C 65.08; H 6.34; and OCH_3 28.49%. The average elemental composition of the structural unit $\text{C}_6\text{-C}_3$ was: $\text{C}_9\text{H}_{7.16}\text{O}_{1.73}(\text{OCH}_3)_{1.84}$; mol. wt. 200. The average elemental composition of the structural unit $\text{C}_6\text{-C}_3$ of the original MGL was: $\text{C}_9\text{H}_{8.95}\text{O}_{2.74}(\text{OCH}_3)_{0.96}$; mol. wt. 190.6. The molecular weights of the methylated preparation determined ebullioscopically in dioxane and chloroform amounted to 2710 and 2745, respectively (the

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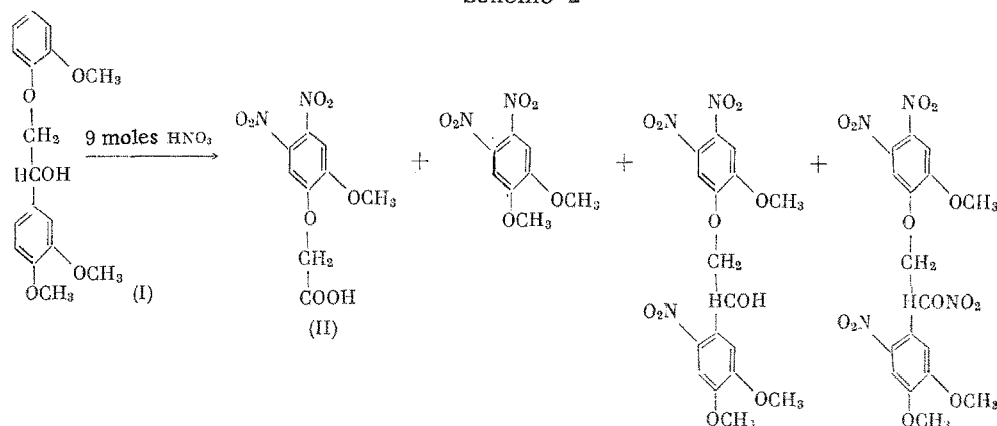
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degree of polymerization was 13.5). The molecular weight of the original MGL equalled 5200 (ebullioscopically in dioxane), which corresponds to a degree of polymerization of 27. Consequently, the degree of polymerization of the lignin is decreased by exactly one-half during the methylation with dimethylsulfate. A product (yield 110.5% of the original weighed sample) with the composition: C 47.97; H 4.41; N 6.94*; OCH₃ 19.11; and COOH 2.32% was obtained when the methylated lignin was nitrated in CCl₄ at room temperature for 1 h (9 mole of HNO₃ per mole of the structural unit of the methylated lignin). The average elemental composition of the structural unit C₆-C₃ was: C₉H_{6.79}O_{1.96}(OCH₃)_{1.64}(NO₂)_{1.32}(O₂COOH)_{0.14}; mol. wt. 264. When the product was fractionated in ethanol, an ethanol-insoluble nitrolignin (A) and an ethanol-soluble nitrolignin (B) were obtained in yields of 89.5 and 21.0% respectively on the basis of the original product. In addition, dinitroveratrol (yield 1.63%) and ~5% of other unidentified products were isolated. Oxalic acid was not detected in the reaction products. The composition of A is: C 47.84; H 4.30; N 6.74; OCH₃ 19.23; and COOH 1.83%. The composition of B is: C 48.60; H 4.86; N 7.80; OCH₃ 18.63; and COOH 4.40%. We did not succeed in determining accurately the amount of nitroester nitrogen in preparations A and B. However, it can be presumed from IR spectroscopic data that its quantity amounts to 0.3 to 0.2 and 0.4 to 0.3% respectively in the preparations.

The average composition of the basic units C₆-C₃ of these preparations are: A) C₉H_{6.52}O_{2.42}(OCH₃)_{1.66}(NO₂)_{1.29}(O₂COOH)_{0.11}; mol. wt. 267.6; B) C₉H_{7.96}O_{1.33}(OCH₃)_{1.56}(NO₂)_{1.45}(O₂COOH)_{0.25}; mol. wt. 263.6. The molecular weights of preparations A and B determined ebullioscopically in dioxane came to 2950 and 2755 and corresponded to an average degree of polymerization of 11.1 and 10.4. When the composition of the elemental structural units of preparations A, B, and the original methylated lignin are compared, it can be seen that the cleavage of the OCH₃ groups is insignificant when the methylated lignin is nitrated. Degradation manifested by a drop in molecular weight is also insignificant. The degree of polymerization prior to and after nitration is 13.5 and 11.1 respectively. It is interesting that the molecular weight of the nitrated unmethylated MGL [1] is 1265 (ebullioscopically in dioxane) and has a degree of polymerization of 4.6 in all. The presence of guaiacylic structures in the lignin molecule, consequently, facilitates its degradation under the conditions of the nitration.

It was shown earlier [9] that when the β-guaiacyl ether of α-veratrylglycol (I) is nitrated in an anhydrous medium, and electrophilic substitution of the side chain by a nitro group takes place in addition to nitration of the ring; (3,4-dinitro-6-methoxyphenoxy)acetic acid (II) and dinitroveratrol (Scheme 2) are formed

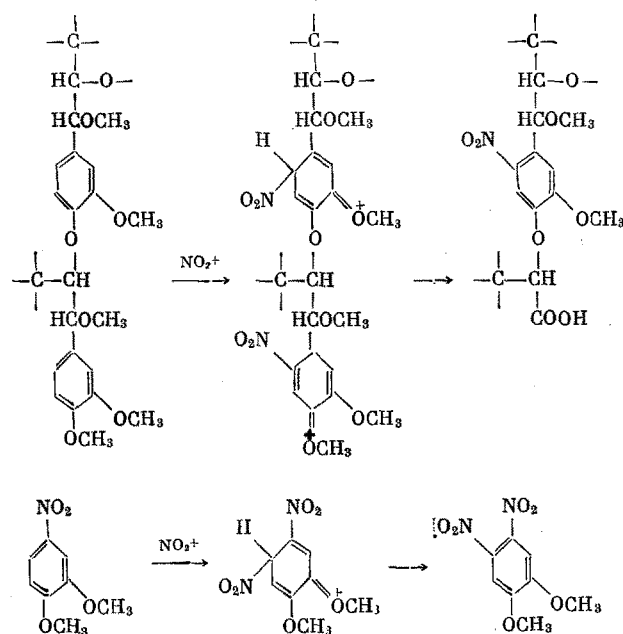
Scheme 2



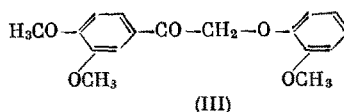
It was noticed that the β-alkylaryl ether bond is quite stable under the conditions of the nitration. It can be assumed that the formation of the COOH groups by the action of HNO₃ on the methylated lignin in anhydrous organic mediums proceeds basically according to Scheme 3 [10] and not through the step where a quinone is formed [2, 3], as occurs with lignins containing the guaiacyl structures

* Nitrolignin, which we obtained from the nitration of lignin hydrochloride with nitric acid under the same conditions, has a smaller amount of nitrogen in its composition, which probably is due to the higher degree of condensation of this lignin [2].

Scheme 3



The stability of the β -alkylaryl ether bond under the conditions of the nitration (9 mole of HNO_3 per mole of substance in CCl_4) was once more confirmed by nitrating ω -(2-methoxyphenoxy)acetoveratrone (III)



ω -(2-methoxy-4,5-dinitrophenoxy)-6-nitroacetoveratrone (IV) was obtained in a high yield (76.0% of the theoretical).

EXPERIMENTAL

The quantity of OCH_3 groups in all the preparations was determined by a modified Zeisel method [1], nitrate nitrogen by the Schultz-Timan method, the total nitrogen by the Dumas method, and the carboxyl groups by the calcium acetate method. The molecular weight was determined ebullioscopically on an ÉP-2 ebulliograph built at the N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR.

Methylation of Lignin. MGL, 3.0 g, with a composition: C 62.38; H 6.17; and 15.03% was dissolved in aqueous acetone (225 ml of acetone and 17 ml of water). To the mixture was added with constant stirring 77.15 ml of dimethylsulfate and an aqueous alkaline solution (KOH 8.6 and water 8.6 ml) over a 6 h period at room temperature. After decomposing the excess dimethylsulfate with alkali, the reaction mixture was poured into water (500 ml). The precipitate was centrifuged out, washed with water until neutral, and dried in vacuo to constant weight at 45°C . The product, 2.73 g, was obtained as a slightly yellow powder, highly soluble in ethanol, dioxane, acetone, chloroform, and in other organic solvents. The composition of the preparation was: C 65.08; H 6.34; and OCH_3 28.49%; mol. wt. 2710 and 2745 (ebullioscopically in dioxane and chloroform respectively); the yield was 91% of the original sample weight.

Preparation of ω -(2-Methoxyphenoxy)acetoveratrone (III). ω -(2-Methoxyphenoxy)acetoveratrone was prepared [12] by the scheme: veratrol $\rightarrow$ acetoveratrone ω -bromo-3,4-dimethoxyacetophenone $\rightarrow$ ω -(2-methoxyphenoxy)acetoveratrone. Found, %: C 67.55; H 6.16; and OCH_3 31.06. $\text{C}_{14}\text{H}_9\text{O}_2(\text{OCH}_3)_3$. Calculated, %: C 67.55; H 5.96; and OCH_3 30.89; mol. wt. 302. The melting point of the product was 93.5 to 94.5°C (from ethanol).

Nitration of Methylated Lignin. To a mixture containing 2.46 g of methylated lignin and 20 ml of CCl_4 and cooled to 0°C was added with constant stirring over a 15 min period 2.75 ml of HNO_3 (sp. gr. 1.52)

suspended in 6 ml of CCl_4 . The mixture was shaken at room temperature for 45 min. The dark brown resin which formed was isolated from the liquid, triturated in an agate mortar, transferred onto a glass filter, and successively washed with ether, benzene, and water until neutral. Two fractions were obtained by treating it with ethyl alcohol. The residue (fraction A), which was dried to constant weight in vacuo, was a light brown powder with the following composition: C 47.84; H 4.30; N 6.74; OCH_3 19.23; and COOH 1.83%. The mol. wt. was 2950 (ebullioscopically in dioxane). The yield was 91% of the original weighed sample. A light brown powder (fraction B), 0.46 g (21.0% of the original weighed sample), was obtained from the ethanol solution after evaporating it in vacuo; its composition was: C 48.60; H 4.86; OCH_3 18.49; N 7.80; and COOH 4.40%. The mol. wt. was 2755 (ebullioscopically in dioxane). A benzene solution was passed through a column packed with Al_2O_3 . Crystals, 0.04 g (1.63% of the original weighed sample), mp 128 to 129°C (from ethanol), were obtained when the column was eluted with benzene. No melting point depression was observed when a mixed melting point was run on a mixture of the crystals and 4,5-dinitroveratrol which had been synthesized.

Nitration of ω -(2-Methoxyphenoxy)acetoveratrone (III). To a mixture of 2.0 g of ω -(2-methoxyphenoxy)acetoveratrone and 20 ml of CCl_4 cooled to 0°C was added over a 10 min period with constant stirring 2.48 ml of HNO_3 suspended in 10 ml of CCl_4 . The mixture was shaken at room temperature for 1 h, then poured into water. The precipitate which formed was separated from the solution on a glass filter, washed until neutral, and dried in vacuo to a constant weight. A nitro compound, 2.2 g (76% of theoretical), mp 172°C (decomp.), highly soluble in acetone, was obtained; it was poorly soluble in other organic solvents: ether, benzene, chloroform, ethyl acetone, and CCl_4 . Found, %: C 47.02; H 3.69; N 9.60; mol. wt. 440 (ebullioscopically in benzene). $\text{C}_{18}\text{H}_{15}\text{O}_{11}\text{N}_3$. Calculated, %: C 46.70; H 3.44; N 9.60; mol. wt. 437.

CONCLUSIONS

1. When mechanically ground lignin was methylated with dimethylsulfate and alkali, a drop in its degree of polymerization by half was observed.
2. Methylated lignin is nitrated with an insignificant decrease in its degree of polymerization.
3. When methylated lignin was nitrated, electrophilic substitution of its side chains by the nitro group and oxidation of the α -carbon atoms with the formation of COOH groups was less pronounced than when non-methylated lignin was nitrated under the same conditions.

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