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PREPARATION OF DIMERIC MODEL COMPOUNDS OF LIGNIN

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There are a number of reports in the literature on the study of the reactivity of the benzylic hydroxy groups of lignin [1-4]. These groups have a high chemical activity and play a large role in the formation of the wood substance [5].

We have shown previously that dimeric compounds are formed from *p*-hydroxyphenylpropan-1-ol, guaiacylpropan-1-ol, and syringylpropan-1-ol under comparatively mild conditions [6]. On continuing this work, we have obtained a dimeric substance from guaiacylpropan-1-ol and syringylpropan-1-ol. The reaction was conducted under the same conditions as in the preparation of the dimers synthesized previously: a mixture of one mole of each alcohol, one mole of aqueous ethanol, and one mole of hydrochloric acid was heated in the water bath or was left at room temperature. In the resulting reaction products TLC on Silufol plates in the solvent system hexane—diethyl ether (1:2.5) revealed four components, three of which were identified with the aid of markers as the initial guaiacylpropan-1-ol, diisoeugenol, and a dimer of syringylpropan-1-ol. To identify the fourth substance, the mixture of products was separated preparatively on Silufol plates. From its mass spectrum and its elementary composition, the fourth component proved to be a dimer of guaicylpropan-1-ol and syringylpropan-1-ol: 6-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-3-methoxy-2-methylindan. Composition $C_{21}H_{26}O_5$. Its mass spectrum — (*m/z*): M^+ 358, 329, 313, 299, 267, 253, 239, 225, 204, 175, 137) — was characteristic for substances of similar nature.

When the reaction products were separated on a silica gel column (the eluent being a mixture of hexane and diethyl ether) a dimer of guaiacylpropan-1-ol and syringylpropan-1-ol was isolated. The dimer was purified by reprecipitation from its ethereal solution in hexane. A light yellow resinous substance was obtained that could not be converted into a powder or be recrystallized. It dissolved well in all solvents except water and hexane. Its PMR spectrum was similar to those of diisoeugenol [4] and syringylpropan-1-ol [6]: PMR spectra (ppm, τ-scale) 0.09-1.1, doublet and multiplet, $2CH_3$; 1.4-1.7, triplet, $—CH_2—$; 2.2-2.5, quartet, —CH—; 2.75-3.0, quartet, —CH—; 3.35-4.0, three singlets, $3OCH_3$ and —CH—; 5.35-5.5, doublet, 2OH; 6.25-6.8, multiplet, aromatic 4H.

Since on TLC no material remained at the start and the spots obtained were sharp and well separated from one another, we calculated the areas of the spots and, from these, the amounts of the components in the mixture. Each reaction mixture was chromatographed in five different concentrations and in triplicate. Thus, the percentage amount of each component was calculated from 15 results (Table 1).

When the reaction mixture was not heated but was left to stand for 1-2 days, the mixture of products was shown by TLC to contain the spot of the initial syringylpropan-1-ol, which later disappeared. In the reaction products the amount of

TABLE 1. Amounts of the Reaction Products, % in the Mixture

Substance	Reaction conditions			
	7 days without heating	heating, h		
		1	2	3
Diisoeugenol	33.2	29.4	32.4	27.6
Guaiacylpropan-1-ol	27.3	25.4	25.2	21.9
Dimer of guaiacylpropan-1-ol and syringylpropan-1-ol	21.2	21.0	21.0	22.8
Dimer of syringylpropan-1-ol	18.7	24.0	21.7	27.6

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substances with guaiacyl nuclei was always far higher (by a factor of 1.5-2.4) than the amount of substances with syringyl nuclei. It is likely that, in an acid medium even without heating, syringylpropan-1-ol splits out one methoxy group.

As can be seen from Table 1, under the reaction conditions given above, the three possible dimers were formed, and there was always more diisoeugenol than the others. The mixed dimer amounted to 21-22.8% of the total reaction products.

The results obtained showed that the formation of dimeric compounds from phenolic 1-alcohols takes place in an acid medium not only on heating (as reported in [6-8]) but also at room temperature.

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