SYNTHESIS OF MODEL DIMERS OF LIGNIN FROM (1-HYDROXYALKYL)PHENOLS

L. S. Smirnova and Kh. A. Abduazimov

UDC 547.992.002.61

It has been shown that model (1-hydroxyalkyl)phenols of lignin condense in an acid medium with heating to form dimers of the indan and Ar—C_3—Ar series, depending on the substituents in the aromatic ring.

The condensation of guaiacylpropan-1-ol in an acid medium with heating to form diisoeugenol, 3-ethyl-6-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-5-methoxy-2-methylindan, has been reported previously [1]. In order to check the reactivity of an α-OH group and the sixth position in the aromatic rings of other lignin monomers with different substitutions of the aromatic rings and structures of the side chains, we have performed the condensation reaction with guaiacylethan-1-ol under the same conditions as in the synthesis of diisoeugenol (HCl, 80°C) [2]. This gave a crystalline substance S(recrystallization from ether) with a yield of 20.5%, mp 152-154°c, readily soluble in all organic solvents apart from hexane and petroleum ether, and insoluble in water. From its mass spectrum, MM 300, and composition, $C_{18}H_{20}O_4$ (here and below, compositions were determined as in [1]), it can be seen that, as in the case of guaicylpropan-1-ol, a dimer had been obtained: 6-hydroxy-1-(4-hydroxy-3-methylphenyl)-5-methoxy-3-methylindan. Its mass spectrum contained strong peaks with m/z: 300, 285, 283, 269, 253, 239, 237, 235, 221, 181, 176, 175, 161, 152, 151, 149, 145, 137, 115, 91.

The interpretation of the PMR spectrum of this dimer taken at 100 MHz showed that the substance obtained was an analogue of diisoeugenol [3] without methylene and methyl groups in the side-chain. The interpretation of the PMR spectrum is given in Table 1.

In order to perform the condensation reaction with syringyl and p-coumaryl lignin monomers, we attempted to synthesize the α-(hydroxyphenyl)-substituted alcohols syringylpropan-1-ol and p-hydroxyphenylpropan-1-ol by the Grignard reaction from syringaldehyde and p-hydroxybenzaldehyde with ethyl bromide using procedures described by Zakis [2]. In both cases, instead of the expected (1-hydroxyalkyl)phenols we obtained dimers of the corresponding phenolic alcohols, with yields of 51.04% from syringaldehyde and 7.6% from p-hydroxybenzaldehyde.

From syringaldehyde we obtained a crystalline substance with mp 146-147°C (recrystallization from ether) readily soluble in all organic solvents apart from hexane and petroleum ether, and insoluble in water. Its mass spectrum contained strong peaks with m/z: 388 (M^+), 373, 359, 343, 329, 327, 313, 299, 297, 283, 269, 255, 253, 234, 219, 205, 187, 167. Its composition was $C_{22}H_{29}O_6$. Its PMR spectrum confirmed its dimeric nature and showed that it was an analogue of diisoeugenol: 3-ethyl-6-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-5,7-dimethoxy-2-methylindan. The interpretation of its PMR spectrum is given in Table 1.

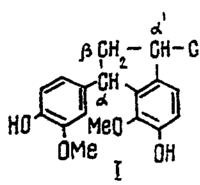
The dimer from p-hydroxybenzaldehyde was isolated in the form of a transparent slightly yellowish resin readily soluble in all organic solvents apart from hexane and petroleum ether, and insoluble in water. Mass spectrum: m/z 268 (M^+), 253, 239, 223, 209, 195, 194, 181, 178, 173, 145, 131, 107, 77. Composition of the dimer $C_{18}H_{20}O_2$. By analogy with the dimers obtained previously, it might have been expected that this substance would prove to be similar to diisoeugenol without the methoxy groups in the aromatic nuclei. However, analysis of the PMR spectrum showed the presence of eight aromatic protons, of a methyl at a double-bonded carbon atom also linked to a trisubstituted carbon, of a methine proton at a double bond (singlet), of a methine proton (triplet) adjacent to $-CH_2-$, and of methylene and methyl groups at $-CH_2-$, and also a signal from two phenolic hydroxyls in the form of a hump. Consequently, in the case of p-hydroxybenzaldehyde the condensation of the initially formed phenolic alcohol to give a dimer took place only through the phenylpropane chain without involving a proton from

---

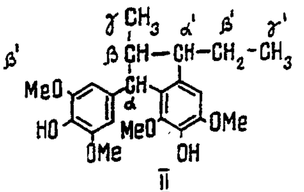
Institute of Chemistry of Plant Substances, Uzbekistan Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 564-567, September-October, 1992. Original article submitted January 6, 1992.

0009-3130/92/2805-0493$12.50

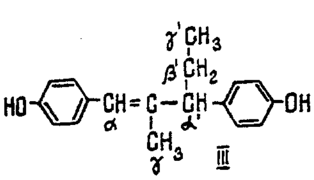
TABLE 1. Interpretation of the PMR Spectra of the Dimers



I



II



III

Formula	Proton	Amount	τ, ppm	Form of the signal*	Assignment
			Dimer from guaiacylethan-1-ol		
I	β'	3	1,1—1,3	d	—CH_3
	β	2	2,0—2,25	m	—CH_2
	α'	1	2,4—2,75	qn	—CH—
	α	1	4,05—4,3	t	—CH—
		6	3,65—3,9	d	2-OCH_3
		2	5,4—5,5	s	2 OH
		5	6,35—6,85	m	H arom
			Dimer from syringylpropan-1-ol		
II	γ, γ'	6	0,98—1,1	d	2—CH_3
	β'	2	1,4—1,7	t	—CH_2—
	β	1	2,2—2,5	q	—CH—
	α'	1	2,75—3,0	q	—CH—
	α	13	3,35—4,0	w	4-OCH_3, CH
		2	5,25—5,5	d	2-OH
		3	6,15—6,51	s	H arom
			Dimer from p-hydroxyphenylpropan-1-ol		
III	γ'	3	0,65—0,9	t	—CH_3—
	γ	3	1,4—1,6	s	—CH_3—
	β'	2	1,6—1,85	t	—CH_2—
	α'	1	2,9—3,1	t	—CH—
		2	5,2—6,1	br.s	2-OH
	α	1	6,15—6,35	s	—CH—
		8	6.5—7.1	2 d	H arom

---

*d) Doublet; m) multiplet; qn) quintet; q) quartet; t) triplet; s) singlet; br.s) broadened signal.

the aromatic ring. The interpretation of the spectrum of the 1,3-di(p-hydroxyphenyl)-2-methylpent-1-ene obtained is given in Table 1.

The UV spectra of the dimers obtained, taken in ethanol, showed that the spectrum of the dimer from p-hydroxybenzaldehyde differed sharply from those of the other dimers. In contrast to the spectra of diisoeugenol and its analogues, having λ_{min} 255-260 nm and λ_{max} 280-285 nm, the spectrum of this dimer had λ_{min} 235 nm and λ_{max} 260 nm.

The formation of dimeric compounds in the course of the Grignard reaction can be explained by the fact that in an acid medium during the decomposition of the organomagnesium complexes conditions are created for the dimerization of the phenolic alcohols formed. The yields of these dimers increase if the reaction products remain in the acid medium for a longer time.

As follows from [1], diisoeugenol was obtained from guaiacylpropan-1-ol. The same substance was isolated from the products of the Grignard reaction in the preparation of guaiacylpropan-1-ol from vanillin and ethyl bromide.

Consequently, in the production of (1-hydroxyalkyl)phenols by the Grignard reaction in an acid medium, condensation of the α-(hydroxyphenyl)alcohols takes place, when the rings are methoxylated, to give compounds of the indan type, while in the case of nomethoxylated phenol rings dimers with a double bond in the C_3 side-chain are formed. In view of the ease of dimerization of α-(hydroxyphenyl)alcohols, it is probable that compounds of such structure are always formed among lignin cleavage products if they remain in an acid medium for a sufficient time.

EXPERIMENTAL

TLC: Silufol plates; solvent system: hexane–ether (4:1, by volume); visualizers: I_2, UV_{254}.

UV spectra were taken on a SF-26 spectrophotometer in ethanol.

PMR spectra were taken in $CDCl_3$, 0 – TMS, on a BS 567 A instrument (Tesla, Czechoslovakia) at 100 Mhz. The "value" of one proton was calculated from the integral integrity and the number of protons in the empirical formula.

Mass spectra* were taken on an MKh 1310 mass spectrometer.

Production of the Dimer (I) from Guaiacylethan-1-ol. A mixture of 0.6 g of guaiacylethan-1-ol, 80 ml of 50% ethanol, and 2.5 ml of conc. HCl was heated in the water bath for 1 h. Then the reaction mixture was evaporated to 1/2-volume, and the residue was poured into 200 ml of ice water. A resinous precipitate deposited, which showed five spots on TLC. The resinous residue was separated on a column of silica gel with elution in 10-ml fractions, first with hexane and then, by adding ether, with mixtures of hexane and ether. After concentration, the fractions at a hexane:ether ratio of 4:1 deposited white acicular crystals showing a single spot on TLC. They were recrystallized from ether. Weight 0.154 g (20.5%).

Production of the Dimer (II) from Syringaldehyde. Syringylpropan-1-ol was obtained from syringaldehyde (3.3 g), ethyl bromide, and metallic magnesium by the procedure of [2]. The decomposition of the organomagnesium complex took place with the evolution of heat. The acid reaction mixture was left for a day. Then it was extracted with ether, and the extract was dried and evaporated, to leave a dark resin. This was dissolved in ether, and the ethereal solution was added dropwise to hexane. An amorphous precipitate deposited, which was separated and recrystallized from ether. Weight 1.96 g (51.04%).

Production of the Dimer (III) from p-Hydroxybenzaldehyde. p-Hydroxyphenylpropan-1-ol was obtained from p-hydroxybenzaldehyde (2.7 g), ethyl bromide, and metallic magnesium by the procedure of [2]. The decomposition of the organomagnesium complex took place with the evolution of heat. The reaction products were left in the acid medium for a day and were then extracted with ether. After the drying and concentration of the ethereal extract it was added dropwise to hexane. On standing, a clear oil separated out, which showed 10 spots in TLC. The oil was separated into its components on a column of silica gel with elution by hexane and then with mixtures of hexane and ether having increasing proportions of the latter. The eluate was collected in 10-ml fractions, with monitoring of the separation by TLC. In 14 fractions, TLC showed a single spot. After the solvent had been driven off, a clear light-colored resin remained. Attempts were made to crystallize it by the reprecipitation of ethereal solutions in hexane, of ethanolic solutions in water, and of acetone solutions in water. It was impossible to crystallize the resin. Its yield was 0.23 g (7.6%). We did not succeed in isolating this substance in the individual state from the other fractions, since it was always associated with 3-4 other substances.

LITERATURE CITED

1. L. S. Smirnova, S. Mukhamedova, and Kh. A. Abduazimov, Khim. Prir. Soedin., 732 (1991).
2. G. F. Zakis, Synthesis of Model Compounds of Lignin [in Russian], Riga (1980), pp. 102, 195.
3. G. V. Dobele, T. N. Skripchenko, G. É. Domburg, M. G. Liepin'sh, and T. N. Osadshaya, Khim. Drev., No. 6, 83 (1988).

---

*The elementary compositions and molecular masses of the dimers were determined mass-spectrometrically by Yu. M. Mil'grom.