DIMERIC PRODUCTS OF THE DEGRADATION OF COTTON LIGNIN AND RICE HULLS

L. S. Smirnova, S. Mukhamedova, and Kh. A. Abduazimov

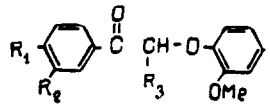
UDC 547.992.002.61

The conditions have been developed for the GLC separation of the dimeric products of the decomposition of lignins, and dehydroisoeugenol and 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-1-ol have been identified.

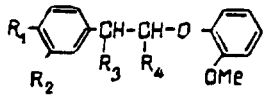
In a study of the products of cotton, Althea, kenaf, and rice lignins, the main information on the structural units of the lignin has been obtained from a consideration of the monomeric phenols produced by decomposition [1-4]. Continuing the separation of the total products of the hydrogenolysis of rice-hull lignin in the presence of a copper-chromium catalyst [4], after the separation of the monomers, we have fractionated the total oligomers on a preparative column of LH-20, using ethanol–water (9:1) as eluent and solvent. The course of separation was monitored on an analytical column under the same conditions using for calculating molecular masses the coefficients given in [5]. A fraction enriched with dimeric components was isolated.

The oligomeric products of the cleavage of lignin by sodium in liquid ammonia were separated by two methods: 1) similarly to the separation of the products of the hydrogenolysis of rice hulls; and 2) after the elimination of the monomers, the combined ethyl-acetate-soluble material [6] was separated on a column filled with silica gel, the substances being eluted first with chloroform and then with chloroform–methanol containing gradually increasing proportions of methanol. The process of separation was followed by TLC from elution volumes of the fractions on an analytical column of LH-20 gel, as in the case of the separation of the products of the hydrogenolysis of rice hulls. In this way, two combined products enriched with dimeric decomposition products were obtained.

TABLE 1



(I, II, VI, VIII)



(IV, V, VII, IX)

Model compounds	Composition	Mol. mass	Rel. retention time
I. 3-Syringylpropan-1-ol	$C_{11}H_{16}O_4$	212	1.0
II. R_1=OH, R_2=OMe, R_3=CH_3	$C_{17}H_{18}O_5$	302	4.3
III. R_1=R_2=OMe, R_3=CH_3	$C_{18}H_{20}O_5$	316	4.7
IV. R_1=R_3=OH, R_2=OMe, R_4=CH_3	$C_{17}H_{20}O_5$	304	4.9
V. R_1=R_2=OMe, R_3=OH, R_4=CH_3	$C_{18}H_{22}O_5$	318	5.3
VI. R_1=OMe, R_2=H, R_3=CH_2Ac	$C_{18}H_{20}O_6$	344	5.5
VII. R_1=R_2=OMe, R_3=OH, R_4=H	$C_{17}H_{20}O_5$	304	5.7
VIII. R_1=R_2=OMe, R_3=CH_2OH	$C_{18}H_{20}O_6$	332	6.0
IX. R_1=R_2=OMe, R_3=Ac, R_4=H	$C_{19}H_{22}O_6$	346	6.3
X. Dehydroisoeugenol	$C_{20}H_{22}O_4$	326	8.2
XI. Eudesmin [7]	$C_{22}H_{24}O_6$	384	13.8
XII. Diphyllin [8]	$C_{21}H_{16}O_6$	364	17.0

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 93-96, January-February, 1990. Original article submitted February 24, 1989.

0009-3130/90/2601-0076$12.50

To separate and identify the dimers we used the method of gas-liquid chromatography (Khrom-41 chromatograph with a flame-ionization detector). In developing the conditions of chromatography, the best separation of model compounds was achieved with the use of a 0.3 cm × 0.5 m column filled with 5% of OV-101 on Chromaton N super, with programming of the temperature from 200 to 310°C. The results of the separation are given in Table 1.

Under these conditions practically all the monomers issued together with the solvent. As a label we used the monomer of highest molecular mass, 3-syringylpropan-1-ol. Chromatography of compounds modeling lignin and of natural lignins showed their good separation. It can be seen from Table 1 that even substances of close chemical structures had different relative retention times (RRTs).

The chromatography under the same conditions of the total products of the hydrogenolysis of rice hulls gave 18 peaks, of which the following were identified from the agreement of their RRTs and the direct introduction of authentic samples: Dehydroisoeugenol (75% of the total) and 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-1-ol (IV, 1.0% of the total). The detection of the second substance showed that not all the Ar-O-alk bonds in lignin were cleaved on hydrogenolysis.

Among the products of the cleavage of cotton lignin by sodium in liquid ammonia (separation on LH-20 gel), 16 peaks were detected, among which the same substances were identified (10.1 and 5.65% of the total, respectively).

In the total material obtained after separation on a silica gel column 17 peaks were detected, among which the same two dimers were identified with yields of 4.3 and 1.2%, respectively.

The presence of a dimeric alcohol with a C—O—C bond confirmed that on cleavage with sodium and liquid ammonia the C—O—C bonds in lignin are not cleaved quantitatively. The detection of dehydroisoeugenol in all the decomposition products indicated the presence in the lignin molecule of such a fragment linked with the other sections of the lignin molecule by C—O—C bonds through one or two phenolic hydroxyls.

None of the total products contained substances in very large amount. The amounts of the individual components ranged from 1.5 to 13.5% (of the total).

EXPERIMENTAL

The total ethyl-acetate-soluble material obtained at pH 2 from the products of the hydrogenolysis of rice hulls was used. In the study of the products of the cleavage of cotton lignin by sodium in liquid ammonia we used the total ethyl-acetate-soluble material obtained at pH 2 [6]. Part of this total material was separated on a column of LH-20 gel. Another part of the same total material was transferred to a column filled with silica gel. The dimeric fraction was isolated when the column was eluted with chloroform—methanol (100:2).

GLC conditions: Khrom-41 chromatograph, 0.3 cm × 0.5 m stainless column filled with 5% of OV 101 on Chromaton N super (0.125-0.160 mm). Carrier gas helium at the rate of 60 ml/min. Temperature of the evaporator 300°C, initial temperature of the column 200°C (4 min), and then a rise in the temperature at the rate of 4°C/min to 270°C and at the rate of 6°C/min to 310°C and final holding at 310°C for 15 min.

LITERATURE CITED

1. N. A. Veksler, L. S. Smirnova, and Kh. A. Abduazimov, *Khim. Prir. Soedin.*, 100 (1977).
2. A. A. Geronikaki and Kh. A. Abduazimov, *Khim. Prir. Soedin.*, 93 (1977).
3. G. N. Dalimova, A. A. Geronikaki, and Kh. A. Abduazimov, *Khim. Prir. Soedin.*, 780 (1978).
4. Z. K. Saipov, T. S. Kaplunova, Kh. A. Abduazimov, and M. F. Abidova, *Khim. Prir. Soedin.*, 522 (1986).
5. L. S. Smirnova and Kh. A. Abduazimov, *Khim. Prir. Soedin.*, 505 (1978).
6. L. S. Smirnova, S. Mukhamedova, and Kh. A. Abduazimov, *Khim. Prir. Soedin.*, No. 3, 412 (1989).
7. D. M. Razakova, I. A. Bessonova, and S. Yu. Yunusov, *Khim. Prir. Soedin.*, 665 (1972).
8. É. Kh. Batirov, A. D. Matkarimov, and V. M. Malikov, *Khim. Prir. Soedin.*, 386 (1981).