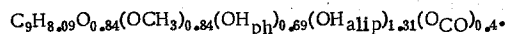
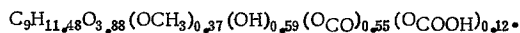


On the basis of functional-group and elementary analyses, the following formula of the C<sub>6</sub>-C<sub>3</sub> unit of the DLA was calculated (with a correction for the carbohydrates):



Gel chromatography of the DLA on a column of Sephadex G-75 with DMSO as eluent and solvent showed that it is monomodal and of high molecular weight (mol. wt. 28,000-26,000).

When the DLA was compared with the hydrolysis lignin obtained in the Yangiyul' Hydrolysis Plant it was found that in the latter the content of methoxy and hydroxy groups had fallen sharply and the amount of carbonyl groups and oxygen had risen:



The hydrolysis lignin is an almost black amorphous powder sparingly soluble in all solvents. In its IR spectrum the main absorption bands are resolved less sharply than in the lignins isolated under mild conditions: 3250 cm<sup>-1</sup> (OH), 1720, 1690 cm<sup>-1</sup> (carbonyls), 1600 cm<sup>-1</sup> (aromatic rings), 1450 cm<sup>-1</sup> (methoxyls).

The fraction of the hydrolysis lignin soluble in DMSO (3.8%) was, as shown by gel chromatography, poly-disperse with a wide range of molecular weights from 26,000 to 1000. The fraction insoluble in DMSO probably has a molecular weight greater than 26,000.

It is obvious that, under severe conditions of hydrolysis, processes of cross-linking [4] and of the degradation of the lignin molecule take place. The decrease in the amount of methoxy and hydroxy groups shows that in hydrolysis both the aromatic nucleus and the C<sub>3</sub> side chain in the lignin molecule are affected and the increase in the number of carbonyls and in the amount of oxygen shows the oxidative processes taking place on hydrolysis.

#### LITERATURE CITED

1. M. I. Chudakov, The Industrial Use of Lignin [in Russian], Moscow (1972).
2. N. N. Shorygina and Kh. R. Niyazov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2094 (1962).
3. N. A. Veksler, L. S. Smirnova, and Kh. A. Abduazimov, Khim. Prirodn. Soedin., 80 (1976).
4. V. M. Nikitin, Ref. Zh. Khim., No. 4, 4P5 (1072).

#### REDUCTIVE DEGRADATION BY METALLIC SODIUM IN LIQUID AMMONIA OF THE NATURAL LIGNIN OF *Althaea* spens

A. A. Geronikaki and Kh. A. Abduazimov

UDC 547.458.84+549.927.2

In the present paper we consider the results of a study of the decomposition by metallic sodium in liquid ammonia of the natural lignin of the stems of two species of *Althaea*: *Althaea rhyticarpa* and *A. nudiflora*. The products obtained on decomposition by this method [1-4] were extracted from the aqueous alkaline solutions at pH 8 with ether and then at pH 2. The concentrated and dried ethereal extract (pH 8; 1.27% and 1.42% of the initial raw material, respectively) was chromatographed on a "Khrom-4" chromatograph with a flame-ionization detector and a 370 × 0.3-cm stainless steel column filled with 15% of Apiezon L on Chromaton NAW DMCS (0.16-0.20 mm). The temperature of the column was 205°C, that of the evaporator was 255°C, and the rate of flow of the carrier gas (helium) was 40 ml/min. On the chromatograms the decomposition products (Table 1) were identified from their retention times and by the addition of standard substances. Quantitative estimation was performed by the method of normalizing areas [5].

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnkh Soedinenii*, No. 3, pp. 410-411, May-June, 1976. Original article submitted January 20, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

TABLE 1. Amounts of Phenolic Substances in the Decomposition Products, % on the Plant

Substance	Althaea rhyticar- pa (A <sub>I</sub> )	Althaea nudiflora (A <sub>II</sub> )
Phenol	—	0,0053
p-Hydroxybenzoic acid	0,009	—
4-Hydroxyphenylethane	—	0,0033
4-Hydroxyphenylpropane	—	0,0172
Total	0,009	0,026
Guaiacol	—	0,0049
Vanillin	0,1750	0,1890
Vanillyl alcohol	0,0050	0,0040
4-Hydroxy-3-methoxyphenylethane	0,0053	—
4-Hydroxy-3-methoxyphenylethan-1-ol	—	0,0029
4-Hydroxy-3-methoxyphenylpropane	0,2050	0,3890
4-Hydroxy-3-methoxyphenylpropan-1-ol	0,0470	0,0850
4-Hydroxy-3-methoxyphenylpropan-3-ol	0,0330	0,0530
Total	0,470	0,728
4-Hydroxy-3,5-dimethoxyphenylethan-1-ol	0,0130	—
4-Hydroxy-3,5-dimethoxyphenylpropane	0,6880	0,1880
4-Hydroxy-3,5-dimethoxyphenylpropan-1-ol	—	0,0811
4-Hydroxy-3,5-dimethoxyphenylpropan-3-ol	—	0,0606
Total	0,701	0,230

The total material extracted by ether from the acid solutions (pH 2; A<sub>I</sub> 3.76%, A<sub>II</sub> 1.56%) consisted of the products of incomplete decomposition. It follows from gel chromatograms on LH-20 with DMFA as eluent and solvent [6] that the combined ether-extracted material from the stems of A<sub>I</sub> consists of tetramers (57.09%), trimers (20.84%), and dimers (22.09%). Similarly, the ether-extracted material from the stems of A<sub>II</sub> consisted of oligomers (20.84%), tetramers (17.46%), trimers (18.20%), and dimers (43.50%).

Consequently, depending on the species of plant the amounts of the main structural units of the lignin vary: in A<sub>I</sub> syringyl structures predominate and in A<sub>II</sub> guaiacyl structures.

#### LITERATURE CITED

1. N. N. Shorygina, T. Ya. Kefeli, and A. F. Semechikina, Dokl. Akad. Nauk SSSR, No. 5, 689 (1949); Zh. Organ. Khim., 29, 1558 (1949).
2. N. N. Shorygina and A. F. Semechikina, Zh. Organ. Khim., 28, 3265 (1958); Trudy ILPIKhD Akad. Nauk LatvSSR, 19 (1960).
3. A. F. Semechikina and N. N. Shorygina, in: The Chemistry of Wood [in Russian], Vol. 1, Riga (1968), p. 57; Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 884 (1964); Zh. Obshch. Khim., 23, 1593 (1953).
4. Kh. R. Niyazov and N. N. Shorygina, Izv. Akad. Nauk SSSR, Otd. Khim., No. 3, 563 (1963).
5. H. McNair and E. Bonelli, Basic Gas Chromatography, fourth ed., Varian Aerograph, Walnut Creek, Calif. (1968).
6. H. Nimz, Chem. Ber., 102, 799 (1969).