On the basis of functional-group and elementary analyses, the following formula of the C_6-C_3 unit of the DLA was calculated (with a correction for the carbohydrates):

$$C_9H_{8.09}O_{0.84}(OCH_3)_{0.84}(OH_{ph})_{0.69}(OH_{alip})_{1.31}(O_{CO})_{0.4}.$$

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:

$$C_9H_{11.48}O_{3.88}(OCH_3)_{0.37}(OH)_{0.59}(O_{CO})_{0.55}(O_{COOH})_{0.12}.$$

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^{-1} (OH), 1720, 1690 cm^{-1} (carbonyls), 1600 cm^{-1} (aromatic rings), 1450 cm^{-1} (methoxyls).

The fraction of the hydrolysis lignin soluble in DMSO (3.8%) was, as shown by gel chromatography, polydisperse 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_3 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 Prirodnykh Soedinenii, No. 3, pp. 410-411, May-June, 1976. Original article submitted January 20, 1976.

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

Substance	Althaea rhyticarpa (A_I)	Althaea nudiflora (A_{II})
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_I 3.76%, A_{II} 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_I consists of tetramers (57.09%), trimers (20.84%), and dimers (22.09%). Similarly, the ether-extracted material from the stems of A_{II} 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_I syringyl structures predominate and in A_{II} 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. Semechkina, Zh. Organ. Khim., 28, 3265 (1958); Trudy ILPiKhD Akad. Nauk LatvSSR, 19 (1960).
3. A. F. Semechkina 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).