LIGNINS OF *Allochruza paniculata* AND *Glycyrrhiza glabra*

T. Sdykov[1] and Kh. A. Abduazimov[2]

UDC 633.88.547:992.022.61

The natural lignin of Allochruza paniculata *and* Glycyrrhiza glabra *is studied by catalytic hydrogenolysis. Three types of lignin structural units are present: guaiacyl, syringyl, and p-coumaryl, which are characteristic of annual and perennial herbaceous plants. The structure of DLA from these plants is confirmed by UV, IR and PMR spectra.*

Key words: *Allochruza paniculata, Glycyrrhiza glabra*, natural lignin, dioxanelignin, hydrogenolysis, phenolic substances.

Soaproot and licorice root have great economic significance and are used in medicine, food, light industry, construction, and as a cleaning agent [1, 2].

We studied the structure and properties of dioxanelignins (DLA) of soaproot (*Allochruza paniculata*, Fabaceae) and licorice root (*Glycyrrhiza glabra*, Caryophyllaceae). Their chemical compositions are listed in Table 1.

The elemental analyses and functional groups of the dioxanelignins were used to calculate the semi-empirical formulas per single phenylpropane structural unit (PPSU):

DLA of soaproot, $C_9H_{7.13}O_{1.39}(OCH_3)_{0.55}(OH_p)_{0.37}(OH_{al})_{2.03}(O_{CO})_{0.09}(OOH_{COOH})_{0.02}(O_{ar\text{-}al})_{0.63}$; OCH_3/C_9, 0.55; DLA of licorice root, $C_9H_{8.68}O_{1.89}(OCH_3)_{0.97}(OH_p)_{0.39}(OH_{al})_{0.86}(O_{CO})_{0.2}(O_{ar\text{-}al})_{0.61}$; OCH_3/C_9, 0.97.

A comparison of the semi-empirical formulas of the lignins isolated from these plants showed that they have different contents of functional groups. DLA of soaproot is less methoxylated than that of licorice root. This is consistent with it being more condensed. The semi-empirical formulas show that the contents of "free" oxygen not incorporated into OCH_3, OH, and CO groups are different. This oxygen probably belongs to all other ether bonds in lignin that may be alkyl—alkyl ether bonds of pinoresinol, syringaresinol, and diarylether bonds. The unequal quantity of hydroxyls and alkyl—aryl ether bonds indicate that the structures of the side chains and the reactivities of soaproot and licorice-root lignins are different.

The structure of natural lignin was studied using hydrogenolysis [3, 4] over a polymetallic catalyst. This catalyst was used previously for hydrogenolysis of natural lignin of rice and cotton-seed husks [5, 6]. The dioxane-soluble product from hydrogenolysis of natural lignin from soaproot and licorice root contained not only lignin-like substances but also carbohydrate decomposition products. Therefore, we separated phenolic substances, i.e., cleavage products of true lignin from the remaining dioxane-soluble components. Then, the total dioxane product was dissolved in NaOH (2%). After acidification to pH = 3, phenolic substances were extracted by hexane and ether (Table 2).

GC was used to study the hexane and ether extracts of lignin-cleavage products. The ether extracts consisted of mainly phenol and cresol whereas the hexane ones had a more varied composition (Table 3). It can be seen that guaiacyl-containing substances predominate. The presence of a large quantity of guaiacyl compounds with alcohol groups in the side chain may be due to partial hydrogenation of COOH and CO groups. The presence of compounds with shortened side chains indicates that C–C bonds were broken; the absence of syringic compounds in the hydrogenolysis products, that they are unstable to hydrogenolysis.

1) Complex Institute of Natural Sciences, Karakalpak Division, Academy of Sciences of the Republic of Uzbekistan, 742000, Nukus, pr. Berdakha, 41, fax (36122) 217 18 03; 2) S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75, e-mail: cnc@icps.org.uz. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 240-242, May-June, 2002. Original article submitted March 16, 2002.

 0009-3130/02/3803-0288$27.00

TABLE 1. Chemical Composition of Starting Material (% of Absolute Dry Mass)

Sample	Polysaccharides		Extractable substances	Cellulose	Komarov lignin	HCl Lignin	Saponins	Ash
	water-soluble	neutral						
Soaproot	14.5	9.1	2.18	22.4	10.6	13.32	29.7	4.85
Licorice root	3.0	-	13.3	30.7	27.5	25.1	8.0	4.02

TABLE 2. Yield of Hydrogenolysis Products of Soaproot and Licorice Root, %

Destruction products	Soaproot	Licorice root
Dioxane-soluble products*	18.6	31.6
Hexane extract**	12.3	8.2
Ether extract**	52.8	46.4
Hydrolignin**	24.5	36.4
Total % cleaved**	89.6	91.0

*of raw material

**of Komarov lignin

The hydrogenolysis products of soaproot and licorice root also contain hydrolignins (HLSR, HLLR), which are products of incomplete lignin decomposition. The IR spectra of the hydrolignins exhibit bands corresponding to substituted benzene (1600, 1510, 1470 cm^{-1}), OH (3450), CO (1720), OCH_3 (1330), and ethers (1280, 1230, 1040). Complete semi-empirical formulas of the phenylpropane core of the hydrolignins were calculated from the elemental and functional analyses:

HLSR: $C_9H_{10.23}O_{1.08}(OCH_3)_{0.53}(OH_p)_{0.46}(OH_{al})_{0.65}(O_{CO})_{0.30}(OOH_{COOH})_{0.05}$

HLLR: $C_9H_{9.86}O_{1.33}(OCH_3)_{0.55}(OH_p)_{0.44}(OH_{al})_{0.55}(O_{CO})_{0.35}(OOH_{COOH})_{0.06}$

The content of OCH_3 groups decreases and the hydrogen content increases in hydrolignin compared with DLA from the same plants. Hydrogenolysis over the polymetallic catalyst probably involves demethoxylation of syringic structures and saturation with hydrogen of phenolic products. This conclusion agrees with results from hydrogenolysis of rice husks [5].

Spectra of the DLA isolated from soaproot and licorice root were studied. The UV and IR spectra of lignins from these herbaceous plants are identical.

DLA of soaproot: UV spectrum (EtOH, λ_{max}, nm): 285; (λ_{min}, nm): 260 (log ε 2.85);

IR spectrum (KBr, ν, cm^{-1}): 1600, 1520, 1465 (benzene ring), 3480, 3410, 3400 (OH), 1730, 1660 (C=O), 1460, 1425, 1330, 1270 (OCH_3), 2930, 2855, 2850 ($-CH_3$), 1230, 1030 (–O–), and 1090 (primary and secondary OH).

Signals in the PMR spectrum were calculated and identified as before [10]. Of three theoretically free aromatic protons in the PMR spectrum of DLA from soaproot in the range 6.15-7.17 ppm, only 1.15 H are observed. Therefore, about 0.8 H of the aromatic core are involved in forming C–C or C–O bonds.

Protons signifying the number and nature of OH groups are found in the ranges 5.8-6.5 [Ar–CH–(OAc)–C] and 1.6-2.2 ppm. According to the PMR spectra (5.2-5.8 ppm), DLA of soaproot contains an insignificant quantity of coumarones (0.20) in condensed structures with lignin units.

DLA of licorice root: UV spectrum (EtOH, λ_{max}, nm): 280; (λ_{min}, nm): 260 (log ε 2.80);

IR spectrum (KBr, ν, cm^{-1}): 1600, 1510 (benzene ring), 3440, 1050, 1040 (OH), 1730, 1660, 1230 (C=O), 2940 (C–H), 2860 (OCH_3), 1470, 1455, 1430 (CH_2, OCH_3, Ar-Al-ethers).

Of three theoretically free aromatic protons in the PMR spectrum of DLA from licorice root, only 1.45 H are observed. Therefore, about 1.5 H of the aromatic core are involved in forming C–C or C–O bonds.

The unsubstituted C_3 side chain has 7H. Based on the empirical formula, 1.26 H are substituted by functional groups (0.4 H by C=O and 0.86 H by OH). Therefore, 5.74 H remain free. The PMR spectrum shows 3.27 free protons (0.2-1.6 and 2.5-5.2 ppm). Therefore, 2.47 H of the C_3 side chain in each licorice lignin PPSU forms bonds between its units.

TABLE 3. GC Analysis of Hexane Extract of Phenolic Substances from Natural Lignin of Soaproot and Licorice Root, % of Total

Substance	Soaproot	Licorice root
Phenol	4.6	8.1
Cresol	1.6	0.7
Guaiacol	6.4	4.8
p-Hydroxyphenylethane	3.3	1.3
Creosol	5.2	-
Guaiacylethane	0.8	5.6
Guaiacylpro pane	10.6	2.3
Guaiacylethan-1-ol	6.6	5.3
Guaiacylpropan-1-ol	54.3	30.6
Guaiacylpropan-3-ol	5.7	9.4
Unidentified	0.7	31.9

EXPERIMENTAL

UV spectra were recorded on a SF-26 spectrophotometer; IR spectra, on a UR-20 instrument; PMR spectra, on a JNM-4H-100/100 MHz spectrometer at room temperature, c = 20% (by mass) in $CDCl_3$.

Isolation of Dioxanelignin. DLA was isolated from ground (0.25 mm) plants that were extracted exhaustively with an alcohol—benzene mixture (1:1 by volume) and washed three times with hot water by the Pepper method [7]. DLA were purified by reprecipitation of aqueous dioxane solutions (1:9 by volume) in absolute ether and dried over P_2O_5 in a vacuum desiccator. The yield of soaproot DLA was 1.05%; of licorice-root DLA, 3.3% of the plant mass.

Elemental analyses of soaproot DLA: found (%): C 60.60, H 6.77, OCH_3 13.5; of licorice-root DLA; C 61.35, H 5.10, OCH_3 15.43.

Hydrogenolysis and subsequent treatment of the products were performed as before [5]; GC analysis, on a Chrom-4 instrument under previously described conditions [8].

The OH, CO, COOH, and OCH_3 contents were determined by literature methods [9]; cellulose, Komarov lignin, and extractable substance contents, by previously described methods [10].

REFERENCES

1. *Problems in the Study of Licorice in the USSR* [in Russian], Nauka, Moscow (1966), p. 38.
2. *Saponin-bearing Plants of Uzbekistan* [in Russian], Tashkent (1987), p. 16.
3. A. Sakakibara, M. Ohto, J. Wada, and M. Matsukura, *J. Jpn. Wood Res. Soc.*, **15**, 84 (1969).
4. C. J. Cosia, W. J. Schubert, and F. F. Nord, *J. Org. Chem.*, **26**, 5085 (1961).
5. T. S. Kaplunova, Kh. A. Abduazimov, Yu. S. Khakimov, and M. Abidova, *Khim. Prir. Soedin.*, 679 (1990).
6. E. N. Yanishevskaya, Author's Abstract of a Candidate Dissertation in Chemical Sciences, Tashkent (1990).
7. J. M. Pepper and M. Siddiqueullah, *Can. J. Chem.*, **39**, 390 (1961).
8. A. V. Novikov and S. V. Khokholko, *Khim. Drev.*, No. 4, 86 (1986).
9. G. F. Zakis, L. N. Mozheiko, and G. M. Telysheva, *Methods of Determining Functional Groups of Lignin* [in Russian], Zinatne, Riga (1975).
10. A. V. Obolenskaya, V. P. Shchegolev, G. L. Akim, E. L. Akim, N. L. Kossovich, and I. Z. Emel′yanova, *Practical Studies of the Chemistry of Wood and Cellulose* [in Russian], Lesnaya Promyshlennost′, Moscow (1965).