A STUDY OF THE DIOXANE LIGNINS OF Althaea nudiflora AND A. rosea

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The lignin was isolated by Pepper's method [1] from sawdust of the stems of Althaea nudiflora [2] and A. rosea (common hollyhock) collected in the experimental production section of the "Kibrai" sovkhoz, Tashkent oblast, from plants two years old.

The yield of dioxane lignin from A. nudiflora (DLA-I) was 6.4% of the weight of the initial plant or 46.5% of the Komarov lignin, and for the dioxane lignin from the double hollyhock (DLA-II) the corresponding figures were 6.2 and 46.6%. The DLAs I and II purified according to Björkman [3] contained 5 and 5.4% of carbohydrates, respectively. On the basis of determination of elementary compositions and functional groups of the DLAs I and II, allowing for the carbohydrates present, we calculated the semiempirical formulas of the phenylpropane structural units:

The DLA from A. nudiflora (mol. wt. 201) –

$$C_9H_{6,84}O_{1,83}(OCH_3)_{1,20}(OH_{alip})_{0,77}(OH_{phen})_{0,38}(O_{CO})_{0,41}(OOH_{COOH})_{0,08},$$

The DLA of the double hollyhock (M 205.8)

$$C_9H_{6,35}O_{1,61}(OCH_3)_{1,25}(OH_{alip})_{0,97}(OH_{phen})_{0,29}(O_{CO})_{0,30}(OOH_{COOH})_{0,056}.$$

The DLA-II contained less hydrogen, oxygen, phenolic hydroxyls, and carbonyl and carboxy groups and more methoxy and aliphatic hydroxy groups than the DLA-I.

The UV and IR spectra of the lignins were similar to those described previously [4]. By gel chromatography [4] it was established that DLAs I and II were polydisperse, the main fraction in DLA-I being a high-molecular-weight (15,000-23,000) fraction and in DLA-II a low-molecular-weight fraction [5].

The structures of DLA-I and II were studied by alkaline nitrobenzene oxidation [4] and by decomposition with metallic sodium in liquid ammonia [6]. The products of nitrobenzene oxidation were investigated by the GLC method [4] (the yields of aldehydes given are calculated on the weight of the plant and of the lignin, respectively),

Substance	A. nudiflora	Double hollyhock	DLA-I	DLA-II
p-Hydroxybenzaldehyde	–	–	–	2.02
p-Hydroxybenzoic acid	0.25	–	2.64	3.51
Ferulic acid	0.06	0.23	0.60	1.93
Vanillin	0.59	1.25	5.77	5.89
Acetovanillin	0.04	0.03	0.39	3.48
Sytingaldehyde	1.55	0.68	15.31	6.92
Sinapic acid	0.03	0.13	0.17	3.36

Among the products of the decomposition of the double hollyhock lignin by metallic sodium in liquid ammonia the following substances were found by GLC: phenol (0.004%), guaiacol (0.007%), (4-hydroxyphenylethane (0.001%), (4-hydroxyphenyl)propane (0.014%), vanillyl alcohol (0.001%), (4-hydroxy-3-methoxyphenyl)ethane

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(0.113%), (4-hydroxy-3-methoxyphenyl)propane (0.187%), vanillin (0.257%), (4-hydroxy-3-methoxyphenyl)propan-1-ol (0.184%), 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol (0.008%), (4-hydroxy-3,5-dimethoxyphenyl)propane (0.407%), (4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol (0.109%), and 3-(4-hydroxy-3,5-dimethoxyphenyl) propan-1-ol (0.0366%).

Thus, the results of nitrobenzene oxidation and decomposition of the lignin of the double hollyhock by metallic sodium and liquid ammonia confirm the presence of p-coumaryl, guaiacyl, and syringyl structures of the lignin units.

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ANTIMICROBIAL SUBSTANCES FROM Salvia officinalis

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On fractionating an acetone extract of the dried leaves of Salvia officinalis L. (garden sage) we detected two substances exhibiting considerable activity against Staphylococcus aureus. The two substances were isolated by chromatography on a column of silica gel of the "aqueous silicic acid" type with gradient elution by mixtures of diethyl ether and petroleum ether with increasing concentrations of diethyl ether (from 0 to 33%) and were finally purified by TLC on the same adsorbent in the ether–hexane (1 : 1) system, where they had R_f 0.48 and 0.63.

The substance with the higher chromatographic mobility, having $\lambda_{max}^{C_2H_5OH}$ 212, 233 and 284 nm (ε 21500, 9650 and 1690), ν_{max}^{KBr} 3500–2400, 1680 cm^{-1} was identified with a known component of sage, salvin (I) [1] on the basis of its conversion into a diacetate with mp 217-219°C (from methanol) (see [2]). This substance, which has also been described under the name of carnazolic acid [2] was readily esterified by diazomethane with the formation of monomethyl ester in which the two phenolic groups can be methylated under the action of methyl iodide and sodium hydride in dimethyl sulfoxide, as a result of which the trimethyl derivative (III) was obtained with $\nu_{max}^{CCl_4}$ 1730 cm^{-1}; δ^{CCl_4} 0.78 ppm (3H singlet), 0.97 ppm (3H singlet), 1.18 and 1.21 ppm (6H, 2 doublets J = 7 Hz), 2.67-2.93 ppm (2H, multiplet), 3.18 ppm (1H, septet, J = 7Hz), 3.58 ppm (6H, singlet), 3.64 ppm (3H, singlet), and 6.58 ppm (1H, singlet).

The second substance, present in the sage in larger amount (about 15% of the dry weight of the extract) consisted of an oil with $\lambda_{max}^{C_2H_5OH}$ 276 and 284 nm (ε 1570 and 1750); $\nu_{max}^{CCl_4}$, 3620, 3600–2400, 1740, 1690 cm^{-1}, δ^{CCl_4} 0.85 ppm (3H, singlet), 0.96 ppm (3H, singlet), 1.17 and 1.19 ppm (6H, 2 doublets, J = 7 Hz), 3.14 ppm (1H, septet, J = 7 Hz), 3.68 ppm (3H, singlet), and 6.38 ppm (1H, singlet); M^+ 346 (after treatment with D_2O, M^+ 348). For this compound we have established the structure (II) on the basis of the following facts. (See scheme on following page.)

On brief heating at 200°C it underwent oxidative decarboxylation with the formation of substance (IV) the NMR and IR spectra of which showed the absence of olefinic protons and carbonyl groups, while its UV spec-

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