SUMMARY

In its antioxidant properties and capacity for binding peroxide radicals, lignin is not merely not inferior but is actually superior to some natural antioxidants.

The oxidation of lignin in solutions by oxygen and hydrogen peroxide takes place by a free-radical mechanism and is accompanied by chemiluminescence.

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AMINOMETHYLATION OF DIOXANE LIGNINS OF HEALTHY AND WILT-DISEASED COTTON PLANTS OF THE VARIETY TASHKENT-1

B. Kh. Pulatov and Kh. A. Abduazimov

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The products of the aminomethylation of dioxane lignins of healthy and wilt-diseased plants of variety Tashkent-1 according to the vegetation periods (ADLKhT-1-VII) have been studied. It has been established that the dioxane lignins of the wilt-diseased cotton-plant stems are less condensed.

The degree of condensation of lignin can be judged from the yield of vanillin and other aromatic aldehydes in the products of nitrobenzene oxidation, and also from the results of NMR spectroscopy [1, 2]. Mikawa et al. [3] have used the aminomethylation reaction to investigate the degree of condensation of thiolignin. By experiments with model compounds they established that, without exception, all the model compounds having a guaicacyl structure with a free phenolic hydroxy group take part in the reaction and give Mannich bases with the introduction of an aminomethyl group into position 5 of the aromatic ring.

Model compounds having substituents in position 5 of the aromatic ring do not take part in the reaction. A carboxy or a hydroxymethyl group in the para position to the phenolic hydroxy group is displaced by the aminomethyl group; the reaction does not take place when the phenolic hydroxy group is etherified or esterified and the other functional groups remain unchanged.

We have performed the aminomethylation of the dioxane lignins isolated previously [4] from healthy and wilt-diseased cotton plants of variety Tashkent-1 according to vegetation

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periods (DLKhT-I-VII) in order to investigate their degrees of condensation. The aminomethylated dioxane lignins of cotton plants of the variety Tashkent-1 (ADLKhT) are amorphous brown powders readily soluble in dioxane–water (9:1), and their salts with mineral acids are completely soluble in water.

The UV spectra of ADLKhT-I-VII are characteristic for lignins, having a maximum at 280 nm. In the IR spectra, in addition to the absorption bands of the functional groups of the lignin, the absorption of a C–N bond is observed in the 1030 cm^{-1} region.

On the basis of the results of elementary and functional analyses, for the aminomethylated dioxane lignins of the early period (8-12 leaves, ADLKhT-I), healthy and wilt-diseased stems of the vegetation period (ADLKht-VI and -III), and of the later period (after the gathering of the harvest, ADLKht-VI and -VII), and also of healthy and wilt-diseased bolls (after the gathering of the harvest, ADLKhT-IV and -V), we deduced semiempirical formulas of the phenylpropane structural units (PPSUs).

ADLKhT-I — $C_9H_{8.2}O_{3.28}(OCH_3)_{0.64}(OH_{ph})_{0.69}N_{0.56}$, mol. wt. of 1 PPSU 190.64; ADLKhT-II — $C_9H_{8.19}O_{3.04}(OCH_3)_{0.80}(OH_{ph})_{0.62}N_{0.57}$, mol. wt. of 1 PPSU 193.30; ADLKhT-III — $C_9H_{8.27}O_{2.30}(OCH_3)_{0.96}(OH_{ph})_{0.53}N_{0.43}$, mol. wt. of 1 PPSU 190.30; ADLKhT-IV — $C_9H_{6.31}O_{2.93}(OCH_3)_{0.79}(OH_{ph})_{0.72}N_{0.67}$, mol. wt. of 1 PPSU 183.30; ADLKhT-V — $C_9H_{6.57}O_{3.55}(OCH_3)_{0.77}(OH_{ph})_{0.69}N_{0.67}$, mol. wt. of 1 PPSU 193.48; ADLKhT-VI — $C_9H_{7.78}O_{2.2}(OCH_3)_{0.76}(OH_{ph})_{0.68}N_{0.45}$, mol. wt. of 1 PPSU 194.59; ADLKhT-VII — $C_9H_{9.47}O_{2.09}(OCH_3)_{1.02}(OH_{ph})_{0.61}N_{0.36}$, mol. wt. of 1 PPSU 198.06.

As can be seen from the semiempirical formulas, the amount of nitrogen introduced per PSU of the lignin macromolecule decreased with increasing age of the plant, which can be explained by the gradual methoxylation and formation of new bonds in the lignin molecule.

After comparing the semiempirical formulas of ADLKhT-II, -III, -VI, and -VII, it can be observed that in the aminomethylation products obtained from the wilt-diseased stems the amount of nitrogen introduced is smaller. This is probably connected with a relatively larger amount (per PPSU) of methoxy groups in the initial dioxane lignins isolated from the diseased stems [4].

If the difference in the amounts of methoxy groups in ADLKhT-II and -III and ADLKhT-VI and -VII is added to the amounts of nitrogen in ADLKhT-III and ADLKhT-VII, the amount of nitrogen introduced per PPSU will be greater in the aminomethylated dioxane lignins of the wilt-diseased cotton-plant stems, i.e., the dioxane lignins of the wilt-diseased samples are less condensed.

In ADLKhT-IV and -V, as in the initial dioxane lignins of the bolls [4], no changes in the functional groups are observed which is apparently due to the considerably smaller degree of wilt damage to the cotton bolls.

The semiempirical formulas of ADLKhT-I-VII, the yields of vanillin in the products of the nitrobenzene oxidation of the DLKhT-I-VII [5], and the comparatively low molecular weights of the lignins isolated from the diseased cotton-plant stems [4] permit the conclusion that the dioxane lignins from the diseased stems are less condensed than those from healthy plants.

EXPERIMENTAL

Aminomethylation of the Dioxane Lignins of Cotton Plants of the Variety Tashkent-1 (DLKhT-I-VII). The aminomethylated dioxane lignins (ADLKhT-I-VII) were obtained by the addition to 3 g of one of DLKhT-I-VII of about 60 ml of a mixture of piperidine, 35% formalin, and ethanol in a ratio of 5:6:12. The mixture was left for three days at room temperature, and was then concentrated in vacuum. The residue was dissolved in 3 ml of a mixture of dioxane and water (9:1) and was precipitated in absolute ether. The products were purified by reprecipitation in absolute ether and were dried over P_2O_5.

Functional groups were determined by standard methods [6]. UV spectra were recorded on an SF-4 spectrophotometer in a mixture of dioxane and water (9:1) as solvent. IR spectra were taken on an IR-20 spectrometer (tablets with KBr).

SUMMARY

Semiempirical formulas of aminomethylated dioxane lignins of cotton plants of the variety Tashkent-1 in different vegetation periods (ADLKhT-I-VII) have been deduced from the results of elementary and functional analyses and it has been established that dioxane lignins of wilt-diseased stems are less condensed than the lignins of healthy stems.

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SYNTHESIS OF [D-Phe^3(NH_2); Pro^3; D-Ala^6]- and [D-Phe^2(NO_2); Pro^3; D-Ala^6]LULIBERINS

S. V. Burov, O. A. Kaurov, V. F. Martynov, and M. P. Smirnova

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In order to study the influence of substituents of the aromatic ring of D-phenylalanine on the inhibiting capacity of luliberian analogs, we have synthesized two new analogs: [D-Phe^2(NH_2); Pro^3; D-Ala^6]- and [Phe^2(NO_2); Pro^3; D-Ala^6]luliberin. The synthesis was performed by the fragmentary condensation method using 2 + (3 + 5) and 2 + (5 + 3) schemes. A new and convenient method of obtaining the amide of the C-terminal tetrapeptide of the luliberin sequence has been developed. In the condensation of the fragments, both the azide and the carbodimide method of synthesis with the addition of 1-hydroxybenzotriazole were used. The guanidino group of arginine was protected by nitration, while the hydroxy groups of serine and of tyrosine were not protected. The complete elimination of the protective groups from the decapeptides was performed by catalytic hydrogenation over Pd on carbon and by anhydrous HF with the addition of anisole at 0°C. The protected octa- and decapeptides were purified by gel filtration on Sephadex LH-20 in ethanol or by preparative thin-layer chromatography on silica gel plates. The final peptides were purified by ion-exchange chromatography on Sephadex CM-25.

The releasing factor of the luteinizing hormone — luliberin — was first isolated in 1971 from extracts of porcine hypothalamus [1]. As was found, it consists of the amide of a linear decapeptide having the sequence:

pGlu-His-Trp-Ser-Tyr-Gly-Leu-Arg-Pro-Gly-NH_2.
1 2 3 4 5 6 7 8 9 10

By controlling the secretion of luteinizing and follicle-stimulating hormones, luliberin exerts a decisive influence on the course of ovulation processes.

The possibility of using both the releasing hormone itself and its analogs as pharmacological preparations is leading to great interest in the search for luliberin agonists and antagonists.

In the present paper we consider the synthesis of two new luliberin analogs that are potential inhibitors of the releasing hormone. The synthesis was carried out by using the classical method by a scheme permitting the building up of analogs modified in positions 2, 3, and 6 in large amounts and with good yields.

As is known, the introduction of D-(amino acid)s into position 2 of the luliberin molecule leads to compounds with a high antagonistic activity [2]. At the same time, in Yardley's

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