NITROBENZENE OXIDATION AND CLEAVAGE WITH SODIUM IN LIQUID AMMONIA OF THE LIGNINS OF COTTON PLANTS OF THE VARIETY AN BAYAUT-2

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In order to determine the structural units of the dioxane lignins (DLAs) from the stems [1] and bolls [2] of cotton plants of the variety AN Bayaut-2, we have carried out the alkaline nitrobenzene oxidation of these lignins and their cleavage with metallic sodium in liquid ammonia.

The nitrobenzene oxidation and the identification of the reaction products were performed by generally adopted methods [3]. The total yield of aldehydes from the DLA of the stems was 44.54%, and from the bolls 54.20%. The total yield of acids from the DLA of the stems was 26.61% and from the bolls 15.80%. As we see, in the nitrobenzene oxidation of the lignin of the stems the total amount of products was higher than the total amount of the same products from the boll lignin, which indicates a greater degree of condensation of the boll lignin. The following substances were identified among the products of nitrobenzene oxidation by GLC (% on the DLA):

Substance	Stems	Bolls
p-Hydroxybenzoic acid	0.35	0.23
p-Coumaric acid	–	0.41
Vanillin	18.75	17.28
Vanillic acid	3.94	2.35
Ferulic acid	0.31	1.14
Syringaldehyde	11.94	8.07
Syringic acid	2.44	0.95

It follows from these figures that each of the two lignins was constructed of three typical structural units – p-coumaryl, guaiacyl, and syringyl – but in different proportions. Their ratio in the stem lignin was 0.02:1:0.63, and in the boll lignin 0.03:1:0.43.

The cleavage of the two lignins with metallic sodium in liquid ammonia was performed as in [4]. The total monomeric phenols (16.44%) and the total oligomers (23.56%) were obtained from the stem DLA. The yields of the corresponding total materials from the boll DLA were 7.68% and 30.0%. The results of identification by TLC and of calculations of the amount of each substance are given below (% on DLA):

Substance	Stems	Bolls
p-Hydroxyphenylpropan-3-ol	0.98	0.81
Guaiacol	0.31	0.06
Guaiacylethane	0.39	0.21
Guaiacylpropane	4.43	3.00
Guaiacylpropan-1-ol	0.56	0.68
Syringylpropane	3.61	1.40

The ratios of p-coumaryl, guaiacyl, and syringyl structures in the products of the cleavage of the stem and boll DLAs of cotton plants of the variety AN Bayaut-2 were 0.17:1:0.63 and 0.21:1:0.35, respectively.

Thus the alkaline nitrobenzene oxidation and cleavage with sodium in liquid ammonia of the DLAs from the stems and bolls of cotton plants of the variety AN Bayaut-2 have shown that they consist of three types of structures – guaiacyl, syringyl, and p-coumaryl, the

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guaiacyl structures being the main ones. The total yields of degradation products and the ratios of the structures in them have confirmed the greater degree of condensation of the boll DLA.

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IDENTIFICATION OF 3-ACETYL- AND 15-ACETYL-SUBSTITUTED DEOXYNIVALENOLS IN A CULTURE OF Fusarium graminearum

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Deoxynivalenol (3,7,15-trihydroxy-12,13-epoxytrichothec-9-en-8-one) and its acyl derivatives are known as biosynthetically linked metabolites of a number of isolates of Fusarium graminearum (Gibberellaceae) [1].

In the biomass obtained after the growth of the isolate F. sp. 579a VNIIZ of F. graminnearum Schw. on grain (29°C, 40 days), together with deoxynivalenol, we have identified 3-acetoxy-7,15-dihydroxy-12,13-epoxytrichothec-9-en-8-one (I) and 15-acetoxy-3,7-dihydroxy-12,13-epoxytrichothec-9-en-8-one (II).

The biomass, in an amount of 3.8 kg (equivalent to a dry weight of 0.7 kg) was extracted with acetonitrile—water (5:1). The extract so obtained was passed through a column filled with layers of activated carbon and of neutral alumina, and the eluate was concentrated and was evaporated in vacuum at 50°C to an aqueous phase. Sodium chloride (100 g/liter) was added to this aqueous residue and it was extracted with three volumes of ethyl acetate. The ethyl acetate solution was evaporated in vacuum to a dry residue (65.7 g), and this was subjected to column LC on silica gel L (100/400) with a gradient of the phases benzene and benzene—acetone (95:5 and 9:1). The eluate from the mobile phase benzene—acetone (9:1) was evaporated in vacuum to a dry residue (8.2 g) and this was subjected to column LC on silica gel L (100/400) with a gradient of mobile phases consisting of hexane with successive 5% additions of ethyl acetate. The compositions of the fractions were monitored by TLC on Silufol with the mobile phase ethyl acetate—hexane (3:1), the substances being detected from their blue fluorescence in UV light (366 nm) after the plates had been treated with a 20% solution of aluminum chloride in ethanol and had been heated at 92°C for 10 min.

The dry residue (0.75 g) that had been eluted with hexane—ethyl acetate (55:45) and contained, according to TLC, a substance with R_f 0.26 was subjected to reversed-phase HPLC on the sorbent LiChrosorb C_8 (10 μ) with the mobile phase acetonitrile—water (1:4). The eluate containing the main component of the fraction gave 0.21 g of substance (I) (yield 0.03% on the dry biomass). $[\alpha]_D^{22}$ + 25.6° (c 0.3; methanol). UV spectrum: $\lambda_{max}^{CH_3OH}$ 217 nm (log ε 3.7330). IR spectrum: ν_{max}^{KBr} 3548 (OH); 1742 (—O—C=O); 1684 (C=C—C=O). Mol. wt. 338 (mass spectrometry). The PMR spectrum [δ 2.20 ppm (3 H, CH_3CO)] and the ^{13}C NMR spectrum (in $CDCl_3$) coincided with those described for 3-acetoxy-7,15-dihydroxy-12,13-epoxytrichothec-9-en-8-one [1, 2].

The dry residue (1.28 g) that had been eluted by hexane—ethyl acetate (45:55) and contained, according to TLC, a substance with R_f 0.15 was subjected to HPLC under the conditions described for (I). The eluate containing the main component of the fraction gave 0.32 g of substance (II) (yield 0.05% of the dry biomass). $[\alpha]_D^{22}$ +22.2° (c 0.3; methanol). UV

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