STRUCTURAL UNITS OF LIGNINS OF Ricinus communis

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Continuing an investigation of the natural and dioxane lignins (DLA) of Ricinus communis L. (castor-oil plant), we have performed nitrobenzene oxidation (NBO) in an alkaline medium [1, 2] and cleavage with sodium in liquid ammonia [3, 4].

The total yield from the NBO was 8% (on the Komarov lignin) from the natural lignin, and 31.8% from the DLA. The following substances were detected in the isolation products by gas-liquid chromatography:

Substance	DLA, %	Castor-oil plant, % on the Komarov lignin
Phenol	–	0.25
p-Hydroxybenzaldehyde	0.21	0.03
p-Hydroxyacetophenone	–	0.04
p-Coumaric acid	0.18	0.63
p-Hydroxybenzoic acid	0.25	0.24
Guaiacol	0.17	0.13
Vanillin	14.84	2.27
Ferulic acid	0.03	–
Vanillic acid	1.68	–
Syringic acid	1.22	0.12
Syringaldehyde	8.54	2.21

The ratio of p-coumaryl, guaiacyl, and syringyl structural units was 0.48:1.00, 0.95 and 0.04:1.00: 0.58 for the natural lignin and the DLA, respectively.

The method of cleaving lignin by metallic sodium in liquid ammonia is milder and permits one to judge the structure of the C_3 side chain of the structural units [5].

The products of the cleavage of the products of the castor-oil plant lignins were extracted at pH 8 with ether and at pH 2 with ethyl acetate. The yields of the total ether-extracted products of cleavage by sodium in liquid ammonia from the natural castor-oil plant lignin and the DLA were 10% (on the Komarov lignin), 14% on the DLA.

By GLC analysis, the following were detected among the cleavage products:

Substance	DLA, %	Castor-oil plant, % on the Komarov lignin
Phenol	–	0.22
p-Hydroxyphenylpropan-1-ol	0.33	1.06
Guaiacol	0.51	0.50
Guaiacylethane	0.72	0.87
Guaiacylpropane	10.78	10.46
Guaiacylpropan-1-ol	1.23	4.88
Guaiacylethan-1-ol	–	0.08
Syringylpropane	4.43	9.93

The ratios of the structural units for the natural lignin and the DLA were 0.08:1.00:0.60 and 0.03:1.00:0.35, respectively.

Judging from the products of NBO and cleavage with sodium in liquid ammonia, the main structural units of castor-oil plant lignin are guaiacyl units.

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NIVALENOL IN A CULTURE OF AN ISOLATE OF *Fusarium graminearum* 15/2 VNIIVS

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Nivalenol (3,4,7,15-tetrahydroxy-12,13-epoxytrichotech-9-en-8-one), first described as a metabolite of *Fusarium nivale* Fn 2B [1], has recently been identified in a number of isolates of *F. graminearum* and of *Gibberella zeae* obtained in Japan [2].

In the present paper we report on the isolation of the total fraction of trichothecenes from the biomass obtained after the growth of an isolate of *F. graminearum* Schw. 15/2 VNIIVS on grain and the identification in it of nivalenol by TLC and chromato-mass spectrometry.

The biomass was extracted with a mixture of acetonitrile and water in a ratio of 5:1, and the extract was subjected to preliminary purification by filtration through a column with a two-layer filling of a mixture of activated carbon with Celite and of neutral alumina. The filtrate after concentration in vacuum to an aqueous phase was purified on a "PRE SEP C18" column (Czechoslovakia). The TLC analysis of the fraction isolated on the elution of the column with methanol–water (3:7) on Silufol with chloroform–methanol (7:1), benzene–acetone (1:1), and chloroform–acetone (3:2) as the mobile phases [3], followed by treatment of the plates with a 10% solution of $AlCl_3$ in ethanol and heating at 92°C for 10 min showed by a blue fluorescence in UV light at λ 366 the presence of substances having R_f values of 0.15, 0.08, and 0.02, respectively, coinciding with the R_f values of an authentic sample of nivalenol. To identify the substance, the dry residue from an eluate was dissolved in a mixture of N,O-bis(trimethylsilyl)acetamide, N-trimethylsilylimidazole, and trimethylchlorosilane in a ratio of 3:3:2, and the solution was heated at 60°C for 20 min and was analyzed on a Finnigan MAT 4615 chromato-mass spectrometer with a capillary column (0.32 mm × 20 m) containing the stationary phase OV-1 with programming of the temperature from 150 to 280°C at 4°C/min. Mass spectra were recorded under conditions of electron impact (EI) and of chemical ionization by positive and negative ions (CIPI and CINI), the reagent gas being ammonia at 0.7 mm Hg, with an ionizing voltage of 70 V.

The GC analysis of the trimethylsilylation product revealed the presence in it of a main component with retention time of 13.2 min, the EI spectrum of which contained weak peaks of the $(M - 15)^+$ ion (585, 2%) and the peaks of ions with m/z 482, 323, and 242, which are characteristic for the fragmentation of the TMS derivative of nivalenol [4]. In the CIPI mass spectrum, in addition to the peak of the ion of maximum intensity $(M + H)^+$ (601, 100%), there was a fragment $(M + NH_4)^+$ (618, 55%) and also the peaks of ions with m/z 511 (80%) and 397 (93%). The CINI mass spectrum was characterized by a weak peak of the M^- ion (600, 7%), the peak of a fragment with m/z 297, having the maximum intensity, and the peak of an ion with m/z 303 (20%), and coincided completely with the spectrum of the TMS derivative of nivalenol obtained previously [5].

The amount of nivalenol was 0.004% of the dry biomass. This is the first time that the identification of nivalenol in a culture of the isolate of *F. graminearum* Schw. 15/2 VNIIVS has been reported.

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