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CLEAVAGE OF THE LIGNINS OF THE ALGA *Cystoseira barbata* BY THIOACETIC ACID

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UDC 547.992:002.61

The most complete cleavage of the aryl-alkyl ether bonds in *Cystoseira* lignins takes place under the action of thioacetic acid. It has been shown that the lignins of *Cystoseira* of different ages differ in the composition of the monomeric structural units. In the lignins of younger specimens of *Cystoseira* (age up to one year), p-coumaryl structures predominate and as the alga gets older a tendency is observed to an increase in the amount of guaiacyl structures and a decrease in the amount of p-coumaryl derivatives. It has been established that the β-arylalkyl ether bond is one of the main bonds between the structural units of *Cystoseira* lignin.

The structural units of the macromolecule of the lignin of specimens of the brown alga *Cystoseira barbata* of different ages are derivatives of the p-coumaryl and the guaiacyl series [1].

Continuing a study of the chemical structures of *Cystoseira* lignins, we have performed the thioacetic acid cleavage of lignins isolated from *Cystoseira* of different ages by Pepper's method (DLA) and by Björkman's method (MWL), and also of the natural lignins of the alga. This reaction leads to the more complete cleavage of the lignin macromolecule than the action of metallic sodium in liquid ammonia. According to Nimz [2, 3], under the action of thioacetic acid in the presence of BF_3 a selective cleavage of the arylglycerol β-aryl ether bonds of the lignin takes place without the formation of secondary C—C bonds as the result of condensation and polymerization. In this process, up to 92% of the initial lignin is cleaved [4].

The thioacetic acid cleavage of the MWL and DLA preparations and also of the natural *Cystoseira* lignins of different ages was performed as described in the literature [5, 6]. The combined monomeric degradation products were extracted with ether at pH 8 and were studied by the GLC method. After the extraction of the monomeric fraction, the solution was acidified to pH 2 and the remaining phenolic compounds were extracted. This fraction was studied by gel chromatography on Sephadex LH-20 in the methanol—water (9 : 1) system. Calibration of the analytical column was carried out on the basis of results obtained by Smirnova and Abduazimov [4].

As a result of the reaction with thioacetic acid, the *Cystoseira* lignin preparation was 86-96% cleaved. On cleavage with metallic sodium and liquid ammonia, the yield of phenolic products did not exceed 22% [1]. Below we give the yield of degradation products of the natural lignins and the dioxane lignins of *Cystoseira* of different ages (% on the initial amount):

Odessa Institute of Constructional Engineering, Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 88-91, 1983. Original article submitted February 10, 1982.

 0009-3130/83/1901-0084$07.50

Preparation	pH 8	pH 2	Sum
DLA-I (age up to one year)	14,0	72,0	86,0
DLA-II (2-3 years)	62,0	34,1	96,1
DLA-III (more than 3 years)	76 0	20,0	96,0
MWL (more than 3 years)	44,1	42,0	86,1
Cystoseira up to one year	1,6	8,1	9,7
" 2-3 years	3,8	6,4	10,2
" more than 3 years	7,7	3,4	11,1

The total yield of the degradation products of the natural *Cystoseira* lignin was also higher, and with an increase in the age of the alga the yield rose from 9.68 to 11.00%. This obviously indicates an increase in the amount of ether bonds and a decrease in the degree of condensation in the lignins of the older specimens of *Cystoseira*.

The compositions and yields of the monomeric products of the cleavage of the *Cystoseira* DLA and MWL were as follows (% in the mixture):

Substance	DLA (up to one year)	DLA (2-3 years)	DLA (more than 3 years)	MWL
Phenol	1,73	16,81	15,69	14,41
1-(4-Hydroxyphenyl)propane	1,03	1,29	3,47	2,73
1-(4-Hydroxyphenyl)propan-1-ol	3,32	—	4,49	—
Guaiacol	0 84	5,14	4,12	1,74
Vanillin	—	0,31	0,77	1,86
(4-Hydroxy-3-methoxyphenyl)ethane	3,52	4,09	4,90	6,21
1-(4-Hydroxy-3-methoxyphenyl)propane	—	29,95	45,29	50,68
1-(4-Hydroxy-3-methoxyphenyl)propan-1-ol	0,62	1,29	10,89	13,91
Ratio of p-coumaryl to guaiacyl units	1:0,82	1:2,25	1:2,83	1:4,34

The monomeric cleavage products of the natural lignins of *Cystoseira* of different ages were as follows (% in the mixture):

	Cystoseira		
	up to 1 year	2-3 years	more than 3 years
Phenol	0,60	—	5,45
1-(4-Hydroxyphenyl)propane	0,90	14,47	7,03
Guaiacol	0 80	9,93	—
(4-Hydroxy-3-methoxyphenyl)ethane	0,45	1,84	9,83
1-(4-Hydroxy-3-methoxyphenyl)propane	0,03	13,79	32,22
1-(4-Hydroxy-3-methoxyphenyl)propan-1-ol	—	3,41	2,97
Ratio of p-coumaryl to guaiacyl units	1:0,98	1:2,54	1:4,50

A comparison of the compositions of the cleavage products of the lignins of specimens of *Cystoseira* of different ages showed qualitative and quantitative differences between them. The quantitative ratios of the identified products changed: With an increase in the age of the alga the amount of guaiacyl structures became greater and the number of p-coumaryl derivatives decreased. The compositions and yields of the monomeric cleavage products of the natural *Cystoseira* lignins confirmed the rule deduced.

The monomeric products consisted of two types of structural units of lignin — p-coumaryl and guaiacyl. In the specimens studied, no derivatives of the syringyl series were detected, as was also the case in reductive degradation by metallic sodium in liquid ammonia [1]. The comparatively high content of guaiacyl derivatives in the products of the cleavage of the *Cystoseira* lignins, in spite of the low number of methoxy groups in this lignin, must be mentioned. This may be due to the fact that guaiacyl structures in the *Cystoseira* lignins are bound predominantly by arylglycerol β-aryl ether bonds which are cleaved most completely under the action of thioacetic acid. p-Coumaryl derivatives, in which position 5 of the aromatic ring is not occupied by a methoxy group, can participate in condensation processes with the formation of C—C bonds. According to Nimz [2, 3], these bonds are not cleaved under the action of thioacetic acid which probably leads to a decrease in the proportion of p-coumaryl derivatives in the cleavage products.

The phenolic products extracted by ethyl acetate at pH 2 were separated by chromatography on Sephadex LH-20 according to their molecular masses into five fractions: oligomeric, tetrameric, trimeric, dimeric, and monomeric (1-5). The percentage amounts of each fraction

are given below; since the bulk of the monomers was extracted with ether at pH 8, the amount of this fraction in the products extracted at pH 2 was low.

Preparation	Oligomers (fr. 1)	Tetramers (fr. 2)	Trimers (fr. 3)	Dimers (fr. 4)	Monomers (fr. 5)
Cystoseira aged up to 1 year	27,21	14,65	10,37	35,35	12,41
" 2-3 years	18,32	16,43	14,56	41,02	9,69
" more than 3 years	7,05	21,76	16,15	46,63	8,14
DLA-I	22,93	14,72	12,54	41,67	8,11
DLA-II	21,72	15,81	12,36	42,14	7,96
DLA-III	10,56	25,14	9,60	47,72	6,98
MWL	7,01	25,22	10,02	50,07	6,68

A comparison of the figures given above shows that the bulk of the degradation products consisted of dimers and monomers, and the total yield of monomeric phenols rose sharply with an increase in the age of the alga. Since thioacetic acid cleaves only aryl-alkyl ether bonds that belong to the C_3 side chain of the phenylpropane structures in lignin [3], the results obtained permit the conclusion that in the lignin preparations from *Cystoseira* more than three years only β-aryl alkyl ether bonds between the structural units predominated. This indicates a low degree of condensation of this material. The degradation products of the DLA-III and MWL contained mainly guaiacylpropane derivatives, and therefore the lignin of the mature specimens of *Cytoseira* also contained a larger amount of methoxylated units.

In lignin preparations of *Cystoseira* aged up to one year, the low yield of monomeric phenols reflects a decrease in the number of ether bonds in them. The proportion of C—C bonds and of diaryl ether bonds rose sharply, which indicates an increase in the degree of condensation of these lignins. In the degradation products of the lignin of *Cystoseira* aged up to one year, it was mainly p-coumaryl derivatives that were detected, and a consequence of this was a low yield of methoxy groups.

EXPERIMENTAL

Cleavage with Thioacetic Acid. A mixture of 0.5 g of a lignin preparation, 15 ml of freshly distilled thioacetic acid, and 0.5 ml of the ether complex of BF_3 was shaken at room temperature for 60 h. In the case of the cleavage of natural lignins, the reaction mixture contained 5 g of the comminuted (0.25 mm) plant that had been extracted with ethanol—benzene (1 : 1) and dried over P_2O_5, together with 40 ml of thioacetic acid and 1 ml of the ether complex of BF_3.

The excess of thioacetic acid was distilled off in vacuum, and the syrupy residue was dissolved in 25 ml of 8% caustic soda in aqueous ethylene glycol (1 : 3) and the solution was heated in a current of nitrogen at 60°C for 44 h. Then 75 ml of 8% caustic soda in aqueous ethylene glycol (1 : 3) and the Raney nickel catalyst obtained from 20 g of aluminum-nickel alloy were added to the reaction mixture, which was boiled with stirring in a current of nitrogen for 8 h. After the catalyst had been separated off, the solution was neutralized with a current of CO_2 to pH 8. The monomeric degradation products were extracted with ether and subjected to GLC analysis under conditions similar to those described in our preceding paper [1]. The residue was acidified with hydrochloric acid to pH 2 and extracted with ethyl acetate, the extracts were dried with sodium sulfate, evaporated in vacuum, and weighed.

The gel chromatography of the concentrated ethyl acetate extracts was performed on an analytical column (1 × 32 cm) of Sephadex LH-20, the solvent and eluent being methanol—water (9 : 1). The column was calibrated as described in a handbook [7].

SUMMARY

1. It has been established that the most complete cleavage of the aryl-alkyl ether bonds in *Cystoseira* lignins takes place under the action of thioacetic acid.

2. It has been shown that the lignins of *Cystoseira* of different ages differ by the composition of their monomeric structural units. With an increase in the age of the alga the ratio of the structural elements in the lignins changes: The number of guaiacyl structures increases and the number of p-coumaryl derivatives decreases.

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PMR SPECTRA OF THE LIGNINS OF *Cystoseira barbata* AT DIFFERENT AGES

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UDC 547.992:022.61

The PMR spectra of the dioxane lignins from the brown alga *Cystoseira* have been studied. It has been established that the lignins isolated from specimens of *Cystoseira* of different ages have different degrees of substitution of the C_3 side chain and differ in their degree of condensation. The most highly condensed is the dioxane lignin of young specimens of *Cystoseira* (age up to one year) and the least condensed the Björkman lignin of *Cystoseira* aged more than three years. All the PMR spectra of preparations of the lignin of the alga under investigation contain the signals of protons present in coumaran structures, their amount being the greatest in the lignins of the youngest samples and decreasing with increasing age of the alga.

Previously, from specimens of the Black Sea brown alga *Cystoseira barbata* of different ages we isolated preparations of dioxane lignins (DLA-I, DLA-II, and DLA-III), and lignin obtained by mechanical grinding (MWL). It was shown that with an increase in the age of the alga the functional composition and ratio of the structural units composing the macromolecule of the *Cystoseira* lignin changed [1, 2]. Below we give semi-empirical formulas of the preparations:

DLA-I (age up to one year)

$$C_9H_{7.41}O_{1.25}(OCH_3)_{0,07}(OH_{phe})_{0,49}(OH_{alip})_{0.77}(CO)_{0,66}(COOH)_{0,11}$$

DLA-II (aged 2-3 years)

$$C_9H_{7,37}O_{1,97}(OCH_3)_{0,11}(OH_{phe})_{0,38}(OH_{alip})_{0,64}(CO)_{0,38}(COOH)_{0,09}$$

DLA-III (aged more than 3 years)

$$C_9H_{6,62}O_{1.63}(OCH_3)_{0,45}(OH_{phe})_{0.36}(OH_{alip})_{0.62}(CO)_{0,34}(COOH)_{0,09}$$

MWL (aged more than 3 years)

$$C_9H_{6,87}O_{1,62}(OCH_3)_{0.46}(OH_{phe})_{0,36}(OH_{alip})_{0.60}(CO)_{0,30}(COOH)_{0.07}$$

Continuing a study of the isolated lignins of *Cystoseira*, we have investigated their PMR spectra. In spite of the difficulties in the interpretation of the PMR spectra of

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Odessa Institute of Structural Engineering. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 91-94, January-February, 1983. Original article submitted February 10, 1982.

