

LITERATURE CITED

1. I. V. Dovgan' and E. I. Medvedeva, *Khim. Prir. Soedin.*, 85 (1983).
2. H. Nimz, *Chem. Ber.*, 102, 799 (1969).
3. H. Nimz, K. Das, and N. Minemura, *Chem. Ber.*, 104, 1871 (1971).
4. L. S. Smirnova and Kh. A. Abduazimov, *Khim. Prir. Soedin.*, 505 (1978).
5. J. Skamla and J. Rybarik, *Drev. Vys.*, 20, No. 2-3, 107 (1975).
6. E. N. Yanishevskaya, B. Kh. Pulatov, and Kh. A. Abduazimov, *Khim. Prir. Soedin.*, 737 (1980).
7. G. B. Shtreis and Yu. A. Sevast'yanov, *Chromatographic Analysis in Wood Chemistry* [in Russian], Riga (1975), p. 61.

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

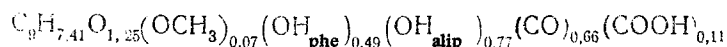
I. V. Dovgan'

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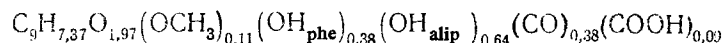
The PMR spectra of the dioxane lignins from the brown alga *Cystoseira* have been studied. It has been established that the lignins isolated from specimens of *Cystoseira* of different ages have different degrees of substitution of the C₃ side chain and differ in their degree of condensation. The most 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:

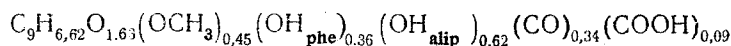
DLA-I (age up to one year)



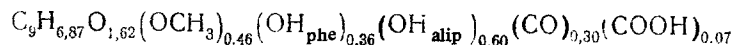
DLA-II (aged 2-3 years)



DLA-III (aged more than 3 years)



MWL (aged more than 3 years)



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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TABLE 1. Distribution of the Protons in the Phenylpropane Units of the *Cystoseira* Lignins*

Zone	Limits of the zone, ppm	MWL of <i>Cystoseira</i> more than 3 years old		DLA-III of <i>Cystoseira</i> more than 3 years old		DLA-II of <i>Cystoseira</i> 2-3 years old		DLA-I of <i>Cystoseira</i> up to 1 year old	
		A	B	A	B	A	B	A	B
I	2.0-3.7	18.67	2.30	13.72	2.14	12.34	2.01	11.98	1.68
II	3.7-4.2	3.61	0.51	3.68	0.54	2.41	0.37	2.27	0.30
III	4.2-4.8	1.50	0.20	1.71	0.27	2.49	0.40	3.58	0.53
IV	4.8-7.5	45.67	4.79	44.09	4.68	33.02	4.04	37.10	4.23
IVa	Protons† of OCH ₃ groups	10.02	1.38‡	9.83	1.35‡	2.44	0.33‡	1.83	0.21‡
	Other protons	35.65	3.41	34.76	3.33	31.58	3.71	35.27	4.02
V	7.5-7.9	7.05	0.92	7.24	0.97	7.91	1.03	8.55	1.31
VI	7.9-8.4	15.64	1.95	13.42	2.13	11.76	1.81	11.69	1.78
VII	8.4-9.5	7.86	0.99	13.64	2.16	30.05	3.64	24.83	4.80
	Sum	100	11.66	100	12.89	100	13.30	100	13.63

*A - Percentage content of the signal; B - number of protons per C₉ unit.

†Limits of the region of OCH₃ groups 6.0-6.8 ppm (region IVa in the spectrum).

‡Figures given found from empirical formulas.

lignins due to the irregular protonic environment of the carbon skeleton of the lignins, this method has come into wide use at the present time. Following Ludwig's procedure [3], the preparations of *Cystoseira* lignins were first acetylated.

The signals in the PMR spectra were identified in accordance with literature information [3, 4]. The quantitative evaluation of the PMR spectra was carried out as described by Veksler et al. [5]. The distribution of the protons in the phenylpropane units of the *Cystoseira* lignins is given in Table 1.

In view of the absence of signals of unscreened protons which lie below 2.0 ppm, in the PMR spectra of the lignins under investigation, the boundaries of the first zone were taken as 2.0-3.7 ppm. It is mainly aromatic protons that appear in this zone. Additional signals in this region may proceed from α -vinyl protons, but, according to Ludwig et al. [3], natural lignins contain insignificant amounts of conjugated α -vinyl groups. As follows from Table 1, the numbers of aromatic protons in the *Cystoseira* lignins of different ages are different. This shows the dissimilar degrees of substitution of the aromatic nuclei. The number of free aromatic protons is a maximum (2.30-2.14) in the lignins of the oldest *Cystoseira* alga, falling to 1.68 per C₉ unit in the young specimens. If it is borne in mind that the number of methoxy groups in the lignins changes in the same sequence [1], this shows a lower degree of condensation of the lignins of the mature specimens of the *Cystoseira*. The most highly condensed is the DLA-preparation of *Cystoseira* aged up to one year, since it contains the smallest number of aromatic protons and methoxy groups per C₉ unit.

The methods of calculating the percentages of condensed nuclei from the PMR spectra of lignins [6] are based on the assumption that in a natural lignin guaiacyl and syringyl structures predominate. However, such calculations cannot be performed for the alga under investigation, since on the degradation of the lignins of young specimens of *Cystoseira* considerable amounts of p-coumaryl structural units were observed [1, 2], which cannot be ignored. In region II ($\tau = 4.05$ ppm), signals corresponding to the protons of benzyl acetate groups are detected [6]. The number of these protons per C₉ unit ranges from 0.54-0.51 for the MWL and DLA-III of *Cystoseira* more than three years old (see Table 1) to 0.30 in DLA-I (up to one year old). This shows that in each second PPSU of the molecule of the lignin from *Cystoseira* more than three years old there is a hydroxy group present in the α position to the aromatic ring. In the DLA-II their number was 0.37, and in a specimen with an age of less than one year it was 0.30.

In zone III appear protons present in coumaran structures. It follows from Table 1 that the amount of such structures is a maximum in the lignins of the youngest specimens of *Cystoseira* and decreases with age. Phenylcoumaran structures are present in the condensed sections of the lignin molecule. Consequently, a decrease in their number in the lignins of mature specimens of the alga shows a lower degree of condensation of the latter.

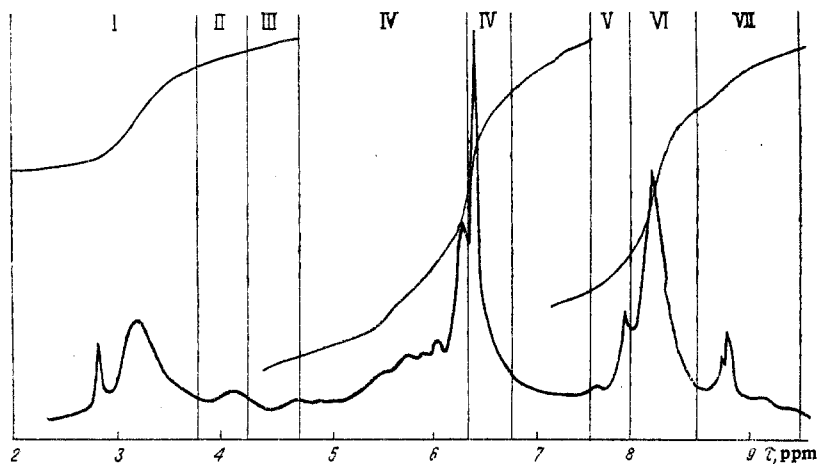


Fig. 1. PMR spectrum of the dioxane lignin from *Cystoseira* more than three years old (DLA-III).

Zone IV is due to the signals of the protons of methoxy groups and the α -, β -, and γ -protons of the C_3 side chain. The numbers of these protons in the *Cystoseira* lignin preparations were different, ranging from 3.33 to 4.02 protons per C_3 unit in DLA-III and DLA-I, respectively. A calculation of the total number of protons attached to the C_3 chain (zones II, III, and IV) also shows that their numbers are different. This indicates that the degrees of substitution of the side chains in the *Cystoseira* lignins are different. In DLA-III the number of aliphatic protons is the smallest (3.33), which means the degree of substitution of the side chains is the greatest. According to the biogenetic theory of lignin, the C_3 side chain should contain about four protons [5]. The figures in Table 1 show that this rule is observed for the *Cystoseira* lignins.

The signals in zone V are due to the protons of the methyl groups of aromatic acetoxy groupings, and in zone VI the protons of the methyl groups of aliphatic acetoxy groupings appear. From the numbers of protons in these regions it is possible to calculate the numbers of phenolic and aliphatic hydroxyls. In the PMR spectra of the MWL and DLA-III, the signals of the acetoxy protons (aromatic and aliphatic) are separated fairly clearly. In the spectra of young samples no clear separation is observed, because of their partial overlapping. Calculation of the numbers of protons in these regions showed that in the DLA-I there were 0.43 phenolic groups per C_3 unit, in DLA-II 0.33, and in DLA-III and MWL 0.33-0.31. These values are somewhat lower than the analytical figures from the amount of phenolic hydroxyls [1].

The number of aliphatic OH groups in the lignins of the mature samples of the alga is ≈ 0.7 per C_3 unit, and somewhat less in the young specimens. Some noncorrespondence of the figures obtained with the aid of PMR spectroscopy to the results of functional analysis of hydroxy groups is apparently connected with the partial overlapping of the signals in these zones. According to Smirnova et al. [7], the low values of the total numbers of hydroxyls obtained on the basis of the PMR spectra may be due to the intensity of the coloration of the DLA preparations.

On analyzing the total number of hydroxyls it can be seen that the DLA-I is more hydroxylated than the lignins of the mature samples of *Cystoseira* which, on the whole, confirms the analytical figures.

Considerable numbers of strongly screened protons (zone VII) were detected in the *Cystoseira* lignins. The signals in this region may be due to aliphatic methyl and methylene protons [3, 4, 6]. As compared with the *Cystoseira* MWL, the DLA preparations contain a considerably larger number of highly screened protons. This indicates that the preparations isolated by Pepper's method differ considerably from the natural lignins present in the *Cystoseira*. A high proton content in this zone of the PMR spectra of the dioxane lignins of wood as compared with the lignins of milled wood is also pointed out in [8].

EXPERIMENTAL

The lignin preparations were acetylated with a mixture of acetic anhydride and pyridine at room temperature for a day. The acetylated lignins were precipitated in water and, after

drying, were purified by reprecipitation from dioxane solutions in ether. The preparations obtained were carefully dried in vacuum over P_2O_5 .

The PMR spectra were taken on a JNM-4H-100/100 MHz instrument at 22-24°C, c 10-12% by weight, internal standard HMDS, τ scale, solvent deuteriochloroform.

SUMMARY

On the basis of an analysis of the PMR spectra of the lignins of *Cystoseira* of different ages, their chemical nonidentity has been confirmed and it has been established that they have different degrees of substitution of the C_3 side chain and different degrees of condensation through aromatic nuclei. The most highly condensed is the dioxane lignin of young specimens of *Cystoseira* (aged up to 1 year) and the least condensed the MWL of *Cystoseira* more than 3 years old.

LITERATURE CITED

1. I. V. Dovgan', in: Investigations in the Field of Wood Chemistry. Abstracts of Lectures [in Russian], Riga (1981), p. 36.
2. I. V. Dovran' and E. I. Medvedeva, Khim. Prir. Soedin., 85 (1983) [in this issue].
3. C. H. Ludwig, B. J. Nist, and J. L. McCarthy, J. Am. Chem. Soc., 86, 1186, 1196 (1964).
4. A. G. Zhuravlev, Yu. V. Gladkov, I. V. Sen'ko, and V. M. Reznikov, in: The Chemistry and Use of Lignin [in Russian], Riga (1974), p. 149.
5. N. A. Veksler, K. L. Seitanidi, L. S. Smirnova, Kh. A. Abduazimov, and M. R. Yagudaev, Khim. Prir. Soedin., 388 (1979).
6. C. Simionescu and A. Cernatescu, Celuloză și Hîrtie, 21, No. 6, 308 (1972).
7. L. S. Smirnova, K. L. Seitanidi, Kh. A. Abduazimov, and M. G. Yagudaev, Khim. Prir. Soedin., 116 (1980).
8. E. P. Swan, Pulp Paper Mag. Can., 67, No. 10, 456 (1966).

NEW CARBOXYL-CONTAINING DERIVATIVES OF DIBENZO-18-CROWN-6

A. K. Tashmukhamedova, I. V. Poleshko,
and I. A. Stempnevskaya

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New derivatives of dibenzo-18-crown-6 with carboxy groups in the side chain have been obtained by acylation with dibasic acids in the presence of polyphosphoric acid. Both 4',4''- and 4',5''-dicarboxydibenzo-18-crown-6's have been obtained by the oxidation of the corresponding diacetyl derivatives and have been separated into the isomers. The 4',4''- and 4',5''-diformyldibenzo-18-crown-6's have been obtained by the reaction of dibenzo-18-crown-6 with hexamethylenetetramine in polyphosphoric acid.

The present communication is a continuation of our papers [1-6] on the synthesis of functional analogs of natural ionophores belonging to the class of macrocyclic polyethers (crown compounds), which have proved to be useful tools in the study of the cationic permeability of biological and artificial membranes. Investigations on biological membranes [7, 8] showed that dibenzo-18-crown-6 derivatives are ionophores for univalent cations, especially for K^+ , and only some of their acyl derivatives possessed ionophoric activity with respect to the Ca^{2+} ion. We assumed that this effect is connected with the participation in complex-formation of the oxygens of the carbonyl groups in addition to the oxygens of the macrocycle itself. A neutral Ca^{2+} ionophore described in the literature [9] contains, in addition to the ether oxygen, amide and ester groups the oxygens of which also, apparently, participate in complex formation.

The introduction of carboxy groups into acyl derivatives of the benzo-crowns makes it possible to obtain a new series of compounds from which it is easy to pass to esters and

Institute of Bioorganic Chemistry, Academy of Sciences of the Uzbek SSR, Tashkent.
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