9. B. J. Fergus and D. A. Goring, Holzforschung, 24, No. 4, 113 (1970).
10. B. Leopold, Acta Chem. Scand., 6, 38 (1952).
11. J. A. Pearl, J. Am. Chem. Soc., 72, 2309 (1950).
12. L. A. Kodina and V. N. Generalova, Zh. Prikl. Khim., 12, 2717 (1968).
13. J. C. Pew, J. Am. Chem. Soc., 77, 2831 (1955).
14. H. McNair and E. Bonelli, Basic Gas Chromatography, 4th ed., Varian Aerograph, Walnut Creek, Calif. (1968).

THE LIGNIN OF THE ALGA *Fucus vesiculosus*

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Until recently, the idea of the absence of lignin from plants having no mechanical and conductive tissues was generally accepted. Starting from this basic assumption, a theory of the genesis of fossils has been developed and ideas on the role of lignin in plants has been formulated. We have previously [1, 2] given definite evidence of the presence of lignin in peat mosses. Consequently, it was natural to consider it desirable to study the question of the presence of lignin at a lower degree of evolution in the algae. By the vibromilling method we have previously [3] isolated a preparation close in its physicochemical characteristics to lignin from brown algae (*Fucus vesiculosus*). However, to obtain indisputable evidence of the presence of the latter in algae additional information was necessary concerning the lignin arylpropane nature of the aromatic component of the plant tissue of the algae.

With this aim we have used the method of decomposition with metallic sodium in liquid ammonia which is applicable to the lignin of plants with a low degree of organization. Decomposition was carried out by the method of N. N. Shorygina et al. [4].

The ethereal extract of the decomposition products, separated into phenolic and acidic fractions, was analyzed by paper chromatography. In the phenolic fraction we identified six compounds: 3-(4-hydroxyphenyl)propan-1-ol (R_f 0.2), 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol (R_f 0.35), 4-hydroxy-3-methoxyphenylethane (R_f 0.46), 1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (R_f 0.65), 1-(4-hydroxyphenyl)propane (R_f 0.86), and 1-(4-hydroxy-3-methoxyphenyl)propane (R_f 0.89). In the acidic fraction we identified p-hydroxybenzoic and p-coumaric acids.

The decomposition products of phenolic nature were also analyzed by gas—liquid chromatography. The phenols were identified by their retention times and by the introduction of markers. Below we give the composition and residence times of the phenols obtained as the result of the decomposition of *Fucus vesiculosus* with metallic sodium in liquid ammonia:

	Retention time, min
Phenol	5.33
Guaiacol	10.62
1-(4-Hydroxyphenyl)propane	15.5
4-Hydroxy-3-methoxyphenylethane	15.72
1-(4-Hydroxyphenyl)propan-1-ol	18.28
1-(4-Hydroxy-3-methoxyphenyl)ethanol	19.01
1-(4-Hydroxy-3-methoxyphenyl)propane	20.62
Vanillin	22.72
1-(4-Hydroxy-3-methoxyphenyl)propan-1-ol	24.00
3-(4-Hydroxyphenyl)propan-1-ol	29.21
1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1-ol	37.25
3-(4-Hydroxy-3-methoxyphenyl)propan-1-ol	41.28

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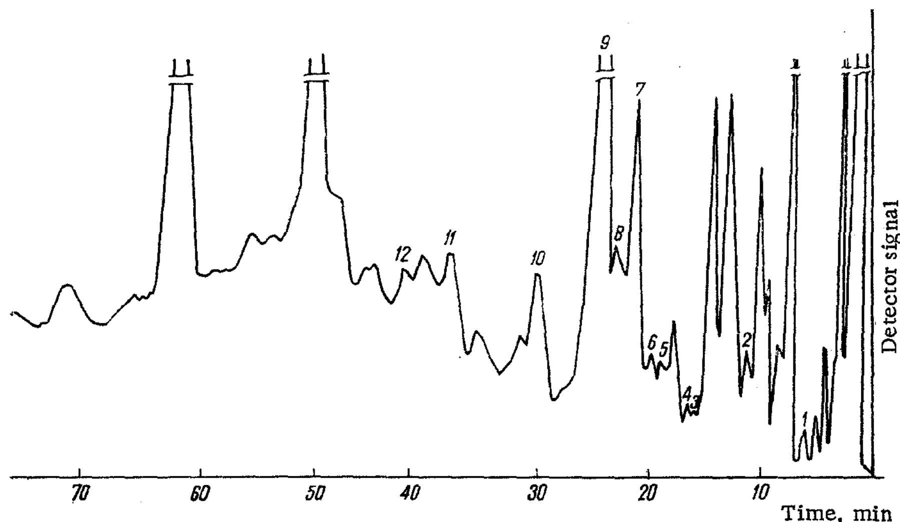

Fig. 1. Chromatogram of the products of the decomposition of the plant material from *Fucus vesiculosus* by a solution of metallic sodium in liquid ammonia: 1) phenol; 2) guaiacol; 3) 1-(4-hydroxyphenyl)propane; 4) 4-hydroxy-3-methoxyphenylethane; 5) 1-(4-hydroxyphenyl)propan-1-ol; 6) 1-(4-hydroxy-3-methoxyphenyl)ethanol; 7) 1-(4-hydroxy-3-methoxyphenyl)propane; 8) vanillin; 9) 1-(4-hydroxy-3-methoxyphenyl)propan-1-ol; 10) 3-(4-hydroxyphenyl)propan-1-ol; 11) 1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol; 12) 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol.

Thus, we have detected most of the phenols identified in lignins previously by various workers. p-Hydroxybenzaldehyde and vanillyl alcohol do not issue from the column under the chromatographic conditions used, and other compounds were not identified because of the lack of markers. In an analysis of the products of the nitrogenzene oxidation of the lignin preparation we detected syringaldehyde [3]. This fact and the presence in the products of decomposition by metallic sodium of 1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol shows that the uncondensed structures of the *Fucus* lignin are represented not only by p-hydroxyphenylpropane but also by guaiacylpropane and syringylpropane types.

EXPERIMENTAL

Decomposition with Metallic Sodium in Liquid Ammonia. The reaction with metallic sodium of the carefully comminuted and dried plant material previously extracted with ether and ethanol—benzene (1.2) was carried out at −(40-60)°C for 14-16 h. After elimination of the ammonia and neutralization of the aqueous mixture to Congo Red, four extractions with ether were performed. Dark-colored polysaccharides passed into the ether in the form of a viscous slime, which interfered with the separation of the ether. The ethereal fraction was separated from the settled (overnight) mass, which had given an appreciable separation of the layers, and it was freed from polysaccharides in a centrifuge. By treatment with a saturated solution of sodium bicarbonate, the ethereal extract was separated into acidic and phenolic fractions. The ethereal solutions of the phenols and of the acids were dried and evaporated in vacuum in a current of nitrogen. The yield of phenolic fraction was 0.8% and of acidic fraction 0.3%; ethanolic solutions of the phenols and acids were analyzed by paper chromatography.

Paper Chromatography. The descending paper chromatography of the phenols were carried out in the chloroform—n-hexane—methanol—water (7:5:2:1) system on Filtrak No. 15 paper for 6-8 h. After spraying with diazotized sulfanilamide, nine spots were detected, in which six phenols were identified from their coloration and R_f values in comparison with authentic samples.

Paper Chromatography of the Acids. The acid fraction was analyzed in benzene—acetic acid—water (6:7:1). The chromatogram of the samples under investigation and of vanillic, syringic, ferulic, hydroferulic, hydrocoumaric, p-hydroxybenzoic, and p-coumaric acid markers were treated sith diazotized sulfanilic acid (I) and with p-nitroaniline (II). p-Hydroxybenzoic acid (R_f 0.3, yellow coloration with reagent I, pink coloration with reagent II) and

p-coumeric acid (R_f 0.35, light blue coloration with reagent I, pink coloration with reagent II) were identified.

In addition, two spots fluorescing bright blue were detected on the chromatogram which did not change their color in UV light after treatment with ammonia and did not give colors in the azo coupling reaction (R_f 0.28 and 0.33).

Gas–Liquid Chromatography. The phenols and phenolic alcohols were separated on a Khrom-41 chromatograph with a flame-ionization detector; stainless-steel column with dimensions of 120 × 0.3 cm; liquid phase DS-550, 15%, on Chromaton N-AW DMCS (0.160-0.200 mm). Rate of flow of the carrier gas (nitrogen) 30 ml/min, temperature of the evaporator 255°C. Separation was performed with programming of the column temperature: a rise from 100 to 160°C at the rate of 5 °C/min, isothermal heating at 160°C for 2 min, and a rise from 160 to 230°C at the rate of 2 °C/min.

SUMMARY

1. The plant material of *Fucus vesiculosus* has been treated with metallic sodium in liquid ammonia. The total yield of products extractable by ether was 1.1%.

2. In the products of the decomposition of the lignin of *Fucus vesiculosus* 12 phenols and acids have been identified by paper chromatography and gas–liquid chromatography and it has thereby been established that the lignin of algae consists of p-coumaryl, guaiacyl, and syringyl structural units.

3. The composition of the decomposition products confirms the hypothesis expressed previously that the brown alga *Fucus vesiculosus* contains lignin.

LITERATURE CITED

1. V. M. Reznikov and N. F. Sorokina, in: The Chemistry of Wood [in Russian], Riga, No. 1 (1968), p. 103.
2. V. M. Reznikov and V. F. Novitskii, Khim. Prirodn. Soedin., 77 (1975).
3. V. M. Reznikov and M. F. Mikhaseva, Khim. Drev., 4, 76 (1976).
4. N. N. Shorygina, T. Ya. Kefeli, and A. F. Semechkina, Dokl. Akad. Nauk SSSR, 64, 689 (1949).

THE CHEMICAL COMPOSITION OF AQUEOUS EXTRACTS OF CONIFEROUS NEEDLES

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It follows from information in the literature that the chemical composition of conifer needles is complex and diverse [1-5]. The water-soluble fraction of the needles, which is used as a nutrient medium for the cultivation of organisms producing protein, has been studied inadequately. In the light of this fact, it appears of interest to study the group composition of the extracts, particularly of those of its compounds that are nutrients for microorganisms or exert a definite action on their development.

It can be seen from the results that we have obtained that in their quantitative and qualitative composition the components of aqueous extracts of pine and spruce needles differ insignificantly. So far as concerns the water-soluble fractions of the protein of pine and spruce needles, their amounts are practically identical. There are very slight differences also in their oligosaccharide contents. The presence of certain phenolic compounds apparently reduces the nutrient value of the aqueous extracts. This fraction of the extracts requires more detailed consideration, and it is possible that additional enrichment of the nutrient medium is necessary.

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