The main chain of the araboglucuronoxylan isolated from buckwheat husks is constructed of residues of β-D-xylopyranose units connected at the position of the 1 → 4 carbon atoms. In side chains there are residues of α-D-glucuronic and 4-O-methyl-α-D-glucuronic acids, attached to the main chain at the position of the second carbon atom, and the residues of β-D-xylopyranose and α-L-arabopyranose attached to the main chain at the position of the third carbon atom.

LITERATURE CITED

1. M. S. Dudkin, G. V. Tatarkina, and N. G. Shkantova, Khim. Prirodn. Soedin., 695 (1971).
2. I. Ehrenthal, K. Montgomery, and F. Smith, J. Am. Chem. Soc., 76, 5509 (1954).
3. E. L. Hirst, L. Hough, and J. K. Jones, J. Chem. Soc., 928 (1949).

THE GLUCAN OF THE BLUE-GREEN ALGA *Microcystis aeruginosa*

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UDC 547.917

A number of representatives of the blue-green algae contain a branched glucan [1-3] diffusely deposited at the periphery of the cell in the chromatoplasm [4, 5].

From the freshwater blue-green alga *Microcystis aeruginosa* we have isolated a glucan containing no protein and consisting of D-glucose residues. The glucose was identified chromatographically in a hydrolyzate and by converting it into the osazone with mp 209°C.

With iodine, the polysaccharide forms a colored complex. UV spectrum: λ_{max} (in water) 480 nm, which is characteristic for glycogen. The complex of the glucan with protein does not give a coloration with iodine. After the treatment of the polysaccharide with α-amylase, D-glucose and maltose were identified in the hydrolyzate. In the IR spectrum (Fig. 1) there are characteristic absorption bands in the frequency regions 750 and 930 cm^{-1}, due to the vibrations of pyranose rings, and 844 cm^{-1} — deformation vibrations of C_1—H groups found for polysaccharides with α-1,4 bonds [6]. The absorption band of the hydroxy groups in the 3100-cm^{-1} region is shifted to low frequencies which is possibly caused by a high density of intermolecular hydrogen bonds.

On periodate oxidation, the following numbers of moles of periodate were consumed by one mole of D-glucose residues: after 24 h, 0.9; after 48 h, 0.98; after 72 h, 1.15; and after 96 h, 1.15, which shows the ready oxidizability of the polysaccharide and also the presence of several terminal groups in the molecule.

After the reduction of the oxidized polysaccharide with sodium tetrahydroborate and hydrolysis of the resulting polyol, glycerol and erythritol were found in the solution by chromatography. There was no free glucose.

Among the products of the hydrolysis of the completely methylated glucan the following were identified by the use of methods of paper, thin-layer, and gas—liquid chromatography in parallel (Fig. 2) 2,3,4,6-tetra-O-methyl-D-glucose, 2,3,6-tri-O-methyl-D-glucose, and 2,3-di-O-methyl-D-glucose in a ratio of 5:14:4. The reducing capacity of the polysaccharide was 4.34%, which corresponds to a molecular weight of 3740 and a degree of polymerization SP of 23. From the number of units of 2,3,4,6-tetra-O-methyl-D-glucose and the total number of glucose residues in the molecule it is obvious that there are five D-glucopyranose units to each terminal group.

Judging from the facts given, the glucan of the blue-green alga is constructed from α-D-glucose residues in the pyranose form connected by 1—4 bonds in the main chain and 1—6 bonds at the branching points.

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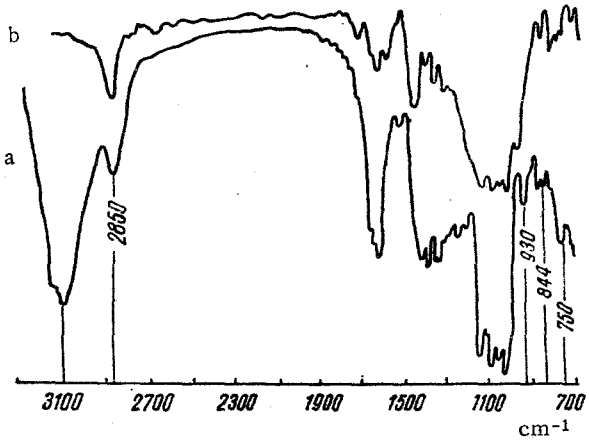

Fig. 1

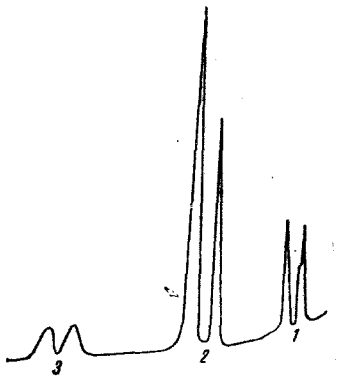

Fig. 2

Fig. 1. IR spectra of the glucan (a) and of the methylated glucan (b).

Fig. 2. Gas–liquid chromatograms of the products of the methanolysis of the methylated glucan (α and β isomers): 1) 2,3,4,6-tetra-O-methyl-D-glucoside; 2) 2,3,6-tri-O-methyl-D-glucoside; 3) 2,3-di-O-methyl-D-glucoside.

EXPERIMENTAL

The UV spectra were taken on an SF-4A instrument in 10-mm cells at a concentration of the polysaccharide in aqueous solution of 0.057% and an iodine concentration of 0.025%. The IR spectra were taken on an IKS-14 instrument in tablets of KBr. The conditions for the GLC of the products of the methanolysis of the methylated glucan were as follows: LKhM-8MD model 5 chromatograph; column (2 m × 3 mm) filled with 5% of XE-30 on Chromaton N-AW (0.2-0.25 mm); column temperature 170°C; flame-ionization detector; carrier gas helium (45 ml/min).

Isolation of the Glucan. The algal mass was washed three times with hot water and was dried, and 20 g of the dry residue was treated with 30 ml of a 25% aqueous solution of KOH with heating in the boiling-water bath and stirring for 30 min. The polysaccharide fraction was precipitated from the solution with five volumes of methanol. The residue was washed three times with methanol and was dissolved in 500 ml of water at 40°C. To eliminate the acid polysaccharides, 50 ml of 10% Cetavlon was added to the solution. The precipitate that deposited was separated by centrifuging. The glucan was isolated from the solution in the form of the copper complex by the addition of Fehling's reagent (15-20 ml of "one-and-a-half" Fehling's reagent). The precipitate was washed with water, and the complex was decomposed with 2 N HCl. The polysaccharide was precipitated from the hydrochloric acid solution with three volumes of a mixture of methanol and acetone (1:1), twice reprecipitated from aqueous solution, washed with acetone and ether, and dried.

The glucan was a colorless pulverulent product. Yield 1.6%, $[\alpha]_D^{20}$ + 170° (c 0.4; water). The homogeneity of the product was checked by gel filtration on Sephadexes G-75, G-100, and G-150. In all cases a single polysaccharide peak was found on the chromatograms.

Periodate Oxidation. The polysaccharide was oxidized with a 0.3 M solution of sodium periodate at 20°C. The consumption of periodate was determined iodometrically, and the amount of formic acid liberated was found by titration with alkali in the presence of an indicator [7]. Oxidation was complete after 72 h, the consumption of periodate amounting to 1.15 mole, and the amount of formic acid liberated being 0.3 mole per mole of glucose residue.

Smith Degradation. The product of periodate oxidation was reduced with sodium tetrahydroborate for 18 h. The unchanged reagent was decomposed with acetic acid. The solution was evaporated to dryness in vacuum and the residue was treated with methanol. The polyol was hydrolyzed in sealed tubes – one part with 0.5 N HCl at 100°C for 8 h and another part with 0.1 N HCl at 100°C for 10 h. The hydrolysis products were separated by paper chromatography in the solvent benzene–1-butanol–pyridine–water (1:5:3:2.5). The chromatograms were stained with a saturated aqueous solution of potassium metaperiodate and then with 1% permanganate. Erythritol and glycerol were found. Markers were used for identification.

Methylation of the Polysaccharide. Hakomori methylation [8] was performed three times. The completeness of methylation was checked by thin-layer chromatography on alumina and by the IR spectrum of the methylated product. The completely methylated glucan did not absorb in the region of hydroxy groups.

Hydrolysis of the Methylated Glucan. The methylated product was hydrolyzed with 90% formic acid at 100°C for 1 h and then with 0.25% sulfuric acid [7]. The hydrolysis products were separated in parallel by paper chromatography in the solvent 1-butanol—ethanol—water (5:1:4) and by thin-layer chromatography on silica gel in the solvent benzene—acetone (2:1.5). By comparison with markers and by their R_f values, the 2,3,4,6-tetra-, 2,3,6-tri-, and 2,3-di-O-methyl derivatives of glucose were identified in a ratio of 5:14:4. The methylated polysaccharide was subjected to methanolysis with 4% HCl in absolute methanol, and the methanolysis products were separated by GLC. Three pairs of peaks were obtained which were identified by comparison with markers as α- and β-methyl 2,3,4,6-tetra-, 2,3,6-tri-, and 2,3-di-O-methyl-D-glucosides.

SUMMARY

The blue-green alga *Microcystis aeruginosa* contains a branched glucan constructed of D-glucopyranose residues with α-1,4 bonds in the main chain and α-1,6 bonds at the points of branching.

LITERATURE CITED

1. A. A. Elenkin, Blue-Green Algae of the USSR [in Russian], Moscow (1938).
2. L. Chao and C. C. Bown, J. Bacteriol., 105, 331 (1971).
3. L. Houg, J. K. H. Jones, and W. H. Wadmen, J. Chem. Soc., 3393 (1952).
4. M. A. Preshkov, in: The Biology of Blue-Green Algae [in Russian], Moscow (1964), p. 25.
5. R. M. Giesy, Am. J. Bot., 51, 388 (1964).
6. K. Nakanishi, Infrared Absorption Spectroscopy. Practical, Holden-Day, San Francisco (1962).
7. N. K. Kochetkova (editor), Methods of Carbohydrate Chemistry [in Russian], Moscow (1967), p. 466.
8. S. Hakomori, J. Biochem. (Japan), 55, 205 (1964).

THE USE OF THE SEPARATING CAPACITY OF UNIFORM-PORED SILICA GEL IN THE REFINING OF COTTONSEED OILS

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UDC 665.3036.7:62.001.6

At the present time, the refining of cottonseed oil is performed with aqueous solutions of sodium hydroxide. In this method of purification, ~10% of the triglycerides, the gossypol, the fatty acids, the phosphatides, the steroids, the tocopherols, etc., are lost. In order to eliminate this defect, it is desirable to use the selective adsorption of the substances composing the oil or ultrafiltration of a solution of the oil through pores or channels with definite dimensions of the separating layers.

The clarification of cottonseed oil with zeolites, ion-exchange resins, and bentonites has been described [1]. Analysis of the experimental results has shown that the types of sorbents studied have a number of defects. However, silica gel is favorably distinguished from the other sorbents by its chemical inertness, its high specific surface, its great

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