

acetylated mannan), pectin substances, a glucan, a glucomannan, and starch. It follows from a comparison of the results obtained with those given in the literature [4, 5] that *U. vvedenskyi* differs with respect to its polysaccharide composition from other genera of the family Amaryllidaceae.

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#### POLYSACCHARIDES OF *Eremurus*.

#### VIII. A GLUCOMANNAN FROM THE TUBEROUS ROOTS OF

#### *Eremurus tadshicorum*

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A preliminary investigation of the polysaccharides of *Eremurus tadshicorum* Vved. has been reported previously [1]. We now give information on the study of the structure of a glucomannan isolated from the water-soluble fraction of *E. tadshicorum*.

According to the results of gel filtration on Sephadex G-100, the polysaccharide was polydisperse. To obtain a homogeneous fraction of the polysaccharide, an aqueous solution (1%, 500 ml) was precipitated with various volumes of ethanol (0.5; 1; 1.5; 4). The yields of the fractions were (%): T<sub>1</sub>, 1.7; T<sub>2</sub>, 75.1; T<sub>3</sub>, 9.8; T<sub>4</sub>, 3.0.

For further chemical studies we took fractions T<sub>2</sub> and T<sub>3</sub>, constituting the bulk of the water-soluble polysaccharide. In hydrolysates of T<sub>2</sub> and T<sub>3</sub> we detected glucose and mannose in ratios of 1:5 and 1:9.8 respectively. Fractions T<sub>2</sub> and T<sub>3</sub> proved to be homogeneous on gel filtration on Sephadex G-100; their molecular weights calculated on the basis of ultracentrifugation were 63,000 and 47,000, respectively and their specific rotations were  $[\alpha]_D^{22} -33^\circ$  (c 1.0; water) and  $[\alpha]_D^{22} -35^\circ$  (c 1.0; water), respectively. Their IR spectra (UR-20, tablets with KBr) contained absorption bands at 1730 and 1250 cm<sup>-1</sup> (ester group).

To determine the types of bonds between the monosaccharides, the glucomannans (T<sub>2</sub> and T<sub>3</sub>) were first acetylated and were then methylated by Haworth's [2] and Purdie's [3] methods, which gave permethylates of glucomannans with OCH<sub>3</sub> contents of 42.3% for T<sub>2</sub> and 41.54% for T<sub>3</sub>. The permethylates of T<sub>2</sub> and T<sub>3</sub> were subjected to formolysis and hydrolysis. In the hydrolysates, by TLC [4] and GLC [5] in comparison with standard samples, 2,3,6-tri-O-methylmannose and 2,3,6-tri-O-methylglucose as the main products, and also a very small amount of 2,3,4,6-tetra-O-methylmannose, were identified in both cases, which indicates completeness of methylation and linear structures for T<sub>2</sub> and T<sub>3</sub>. The hexose residues in the glucomannan molecules are linked by 1 → 4 bonds. There are mannose residues at their nonreducing ends.

To determine the configurations of the glycosidic bonds we used the method of oxidizing the acetylated polysaccharides with chromium trioxide [6]. When peracetates of the glucomannans T<sub>2</sub> and T<sub>3</sub> were oxidized with chromium trioxide, no mannose or glucose was detected in the oxidation products, which shows the presence of a β-glycosidic bond. This is in harmony with the values of the optical rotations of the polysaccharides.

The results of methylation were also confirmed by the results of <sup>13</sup>C NMR spectroscopy. To interpret the signals in the spectrum we used the results of the analysis of <sup>13</sup>C NMR spectra of other polysaccharides obtained previously [7]. The <sup>13</sup>C NMR chemical shifts (CSs) of the glucomannan T<sub>2</sub> are given below:

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	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
$\beta$ -D-Mannopyranose	101.5	71.6	72.9	77.85	77.5	62.0
$\beta$ -D-Glucopyranose	103.7	74.45	76.6	80.0	75.4	62.0

Weak signals with CSs of 21.7 and 173.5 ppm relating to the CH<sub>3</sub> and CO atoms of ester groups were detected in the spectrum.

Thus, the results of a chemical study and <sup>13</sup>C NMR spectroscopy permit the conclusion that the polysaccharides investigated were natively acetylated glucomannans possessing unbranched or only slightly branched chains the hexopyranose residues of which are linked to one another by  $\beta$ -(1 → 4) bonds and they differed from known polysaccharides [8] by their ratios of monosaccharides and degrees of polymerization.

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#### ACIDS OF AN AQUEOUS EXTRACT OF THE WOODY VERDURE OF THE PINE *Pinus sylvestris*

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Interest in the chemical composition of aqueous extracts of woody verdure is due to their use as a nutrient medium in the cultivation of protein-producing microorganisms. Aqueous extracts of the woody verdure of the pine and the spruce contain compounds necessary for the nutrition of microorganisms [1]. In addition to sugars, probable sources of carbon may also be organic acids [2]. We have studied the degree of assimilation of individual acids by the yeast *Candida krusei* VEH-11, which is capable of accumulating biomass on aqueous extracts of conifer needles. It was found that the culture studied assimilates as sources of carbon such acids as acetic, malic, succinic, and lactic. On the cultivation of aqueous extracts of woody verdure these acids could become an additional source of nutrient for microorganisms [3, 4]. In the study of the organic acids of an aqueous extract of the woody verdure of the pine *Pinus sylvestris*, we obtained the following results:

Acid	Amount, % of the total amount
Glyceric	13.5
Oxalic	0.4
Succinic	3.2
Benzoic	15.3
Fumaric	3.2
Malic	10.6
Glutaric	3.9
Cinnamic	0.4
Tartaric	2.0
Citric	5.2
Hemimellitic	0.6
Trimellitic	0.5

The aqueous extract of the woody verdure of the pine contained aliphatic mono-, di-, and tricarboxylic acids and benzenecarboxylic acids. Of the aromatic acids, the benzoic acid, which was found in the largest amounts, may lower the nutritional value of the extract. The aliphatic acids were represented by malic, citric, glutaric, and others. The concentration of malic acid amounted to 10% of the total acids, and the amount of