POLYSACCHARIDES OF *Polygonatum*

II. A STUDY OF THE DYNAMICS OF THE ACCUMULATION OF THE POLYSACCHARIDES OF *Polygonatum sewerzowii*

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Continuing an investigation of the polysaccharides of the family Liliaceae [1, 2], we have studied the amount and composition of the water-soluble polysaccharides (WSPSs) of various organs of *Polygonatum sewerzowii* Regel. according to vegetation periods. The plants were collected in 1978 in the Bostanlykskii region of the Tashkent oblast (Gal'vasai, environs of Khodzhikent) in the following phases of development: incipient vegetation (April 24), budding (May 10), flowering (May 19), green fruit (June 20), ripening of the seeds (July 14).

The isolation and purification of the WSPSs was carried out by the method described previously [1, 3]. Information on the amount of WSPSs is given in Table 1. The polysaccharides are distributed dissimilarly in the different parts of the plant. In the hypogeal organs over the whole period of development of the plant the amount of WSPSs is considerably greater than in the epigeal part. Samples of the WSPSs in the dried form consist of a white powder with a creamy tinge containing no nitrogen. The polysaccharides obtained from the roots and rhizomes form in water sticky highly opalescent solutions giving no color reaction with iodine, i.e., containing no glucan of the Starch type.

TABLE 1. Amounts of Water-Soluble Polysaccharides and Their Monosaccharide Compositions in Various Organs of *Polygonatum sewerzowii* in Various Vegetation Periods

Plant organs and date of collection	Yield of WSPSs, % on the wt. of the air-dry raw material	Monosaccharide composition: number of carbohydrate residues						
		Gal	Glc	Man	Fru	Xyl	Ara	Rham
Leaves								
24.IV	0,7	2,3	2,5	5,4	—	Tr.	1,0	—
10.V	0,2	7,3	2,3	13,7	—	1,0	2,5	—
19.V	0,7	9,3	13,5	23,3	—	1,0	9,0	—
20.VI	3,2	4,7	1,0	16,4	—	1,6	2,0	—
14.VII	2,3	4,0	1,5	5,6	—	1,0	5,3	—
Stem								
24.IV	1,0	13,5	1,0	6,4	—	2,6	8,2	2,2
10.V	0,7	17,3	1,0	6,0	—	4,2	11,7	2,9
19.V	0,2	38,5	Tr.	1,0	—	2,5	24,5	2,7
20.VI	1,3	16,8	3,7	7,5	—	5,1	13,2	1,0
14.VII	0,9	17,3	1,3	3,7	—	2,1	13,1	1,0
Fruit								
20.VI	2,5	6,0	2,3	7,6	—	1,6	4,5	1,0
Rhizomes								
24.IV	5,6	1,0	8,0	41,4	1,0	—	1,0	—
10.V	5,2	1,0	2,6	18,0	1,0	—	1,0	—
19.V	5,7	1,0	3,3	24,4	1,0	—	1,0	—
20.VI	4,8	1,0	4,2	47,6	1,0	—	1,0	—
14.VII	4,5	1,0	1,2	10,6	1,0	—	1,0	—
Root								
24.IV	6,5	1,0	3,4	29,2	1,0	—	1,0	—
10.V	7,1	1,0	4,2	57,0	1,0	—	1,0	—
19.V	3,9	1,0	3,0	32,1	1,0	—	1,0	—
20.VI	5,3	1,0	4,4	45,6	1,0	—	1,0	—
14.VII	6,2	1,0	2,0	23,0	1,0	—	1,0	—

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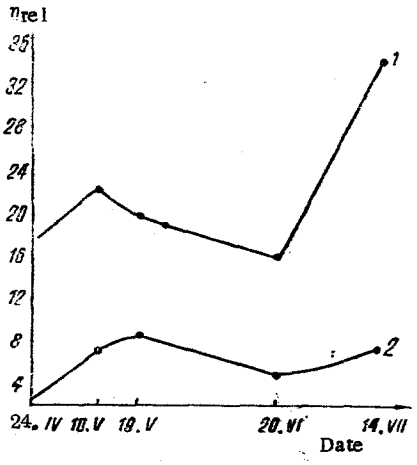

Fig. 1. Dependence of the relative viscosity of the water soluble polysaccharides on the vegetation period: 1) roots; 2) rhizomes.

A study of the change in the viscosity η_{rel} of the WSPSs from the roots and rhizomes in the different vegetation periods of the plants (Fig. 1) showed that the maximum viscosity of the polysaccharides from the roots is observed in the stage of the ripening of the seeds, and from the rhizomes in the flowering stage. At this time polysaccharides with high molecular weights probably accumulate.

To determine their qualitative carbohydrate compositions, the polysaccharides were subjected to complete acid hydrolysis and were analyzed by PC in systems 1 and 2 and by GLC in the form of aldononitrile acetates [4] (Table 1).

The polysaccharides isolated from the rhizomes collected on May 19 were treated with 70% ethanol, and from the soluble part a polysaccharide fraction was isolated with a yield of 36% which was purified via the copper complex. In a hydrolyzate of the latter, glucose and mannose were detected in a ratio of 1 : 10. Consequently the fraction soluble in 70% ethanol is a glucomannan.

As can be seen from Table 1, the predominating component in the polysaccharides of the stems is galactose and in the leaves, roots, and rhizomes it is mannose. The latter is rarely found in the free state in nature. A number of methods of isolating mannose is known [5-8]. We isolated D-mannose from the rhizomes and leaves with yields of 2.5 and 0.25%, respectively (on the air-dry raw material).

Thus, it has been established that the maximum amount of water-soluble polysaccharides is present in the leaves and stems in the fruit-bearing period, in the roots at the time of budding, and in the rhizomes at the time of flowering.

EXPERIMENTAL

For analysis we used air-dry raw material fixed with boiling methanol (1 : 10). The weights of the samples were 50 g for leaves, 30 g for stems, 20 g for rhizomes, and 10 g for roots. The water-soluble polysaccharides were isolated by a known method [1]. The solutions were evaporated in a rotary evaporator at 40-45°C. For PC we used FN-7 paper, descending method, in the following systems: 1) butan-1-ol–pyridine–water (6 : 4 : 3); chromogenic agent aniline hydrogen phthalate, and 2) butan-1-ol–phenol–acetic acid–water (20 : 20 : 8 : 40), chromogenic agent urea. Analysis by GLC was carried out on a Tsvet-101 instrument with a flame-ionization detector using a steel column (200 × 0.3 cm) filled with 5% of XE-60 on Chromaton N-AW, 0.200-0.250 mm, with helium as the carrier gas (50 ml/min) at a column temperature of 210°C. The samples of WSPSs were hydrolyzed with 1 N H_2SO_4 at 100°C for 8 h. The viscosities of the WSPS solutions were measured on an Ostwald viscometer (volume 10 ml) at 30°C (c 0.4; H_2O).

Fractionation of the WSPSs from the Rhizomes. The WSPSs (0.5 g) were treated with 70% ethanol at 80-90°C. The residue was separated by centrifuging and the solution was concentrated to a syrup and precipitated with three volumes of ethanol, after which the precipitate was washed with ethanol and was dehydrated with acetone and ether. Then it was dried in vacuum over P_2O_5. The yield of soluble fraction was 0.18 g.

Purification of the Fraction. The soluble fraction was purified via the copper complex. The yield from 0.1 g was 0.05 g. Glucose and mannose were detected in a hydrolyzate in a ratio of 1 : 10.

Isolation of D-Mannose. A. The water-soluble polysaccharides (2.5 g) isolated from the rhizomes (collected on April 24, 1978) were hydrolyzed with 1 N H_2SO_4 for 5 h, and were neutralized with $BaCO_3$. The solution was treated with activated carbon and evaporated to 50 ml. The hydrolyzate was treated with 2.3 ml of phenylhydrazine in 5 ml of 25% acetic acid. The mixture was kept in the dark overnight in the refrigerator and the D-mannose phenylhydrazone that had precipitated was separated off and was washed with cold water, ethanol, and ether. Yield 1.12 g; after recrystallization, mp 181-183°C; literature figures: mp 182°C [5], 188-190°C [9].

The mannose phenylhydrazone (1.1 g) was decomposed with benzaldehyde, and mannose was isolated with a yield of 0.5 g, mp 128-130°C; literature figure: 130-131°C [5].

B. The water-soluble polysaccharides (1.5 g) from the leaves collected on July 20 were treated by the method described above. Mannose was isolated with a yield of 0.125 g, mp 128-130°C.

SUMMARY

The amounts of water-soluble polysaccharides in various organs of Polygonatum sewerzowii in different vegetation periods have been determined and their polysaccharide compositions have been established.

The maximum amount of water-soluble polysaccharides is present in the leaves and stems in the fruit-bearing period, in the roots at the time of budding, and in the rhizomes at the time of flowering. The quantitatively predominating component in the polysaccharides of the stems is galactose, and in the leaves, roots, and rhizomes, mannose. D-Mannose has been isolated from the rhizomes and leaves.

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