

The molecular weight of the PcSs was determined viscosimetrically [7] and was calculated from the equation  $[\eta] = KML = 1.1 \cdot 10^{-5} \cdot M_w \cdot 1.22$ . The weight-average molecular weight  $M_w$  of the PcSs was 47,500.

By chromatography on DEAE-cellulose it was found that the PcSs of Meyer's hawthorn were heterogeneous. As the results of the investigation showed, the pectin of the fruit of Meyer's hawthorn is similar to the pectin of the fruit of the silver hawthorn (*C. orientalis*).

#### LITERATURE CITED

1. V. B. Kuliev and L. V. Poletaeva, *Khim. Prir. Soedin.*, 647 (1982).
2. A. O. Arifkhodzhaev, D. A. Rakhimov, Z. F. Ismailov, *Khim. Prir. Soedin.*, 246 (1980).
3. V. V. Arasimovich, S. V. Baltaga, and N. P. Ponomareva, *Methods for Analyzing Pectin Substances, Hemicelluloses, and Pectinolytic Enzymes in Fruit [in Russian]*, Kishinev (1970).
4. G. N. Zaitseva and T. I. Afanas'eva, *Biokhimiya*, **22**, 1035 (1957).
5. G. V. Buzina, O. F. Ivanova, and L. B. Sosnovskii, *Khlebopek. Konditer. Promst.*, No. 4, 15 (1965).
6. V. V. Sharkov, N. I. Kuibina, and Yu. P. Solov'eva, *The Quantitative Chemical Analysis of Plant Raw Material [in Russian]*, Moscow (1968), p. 59.
7. S. G. Kovalenko and O. D. Kurilenko, *Ukr. Khim. Zh.*, No. 31, 175 (1965).

#### CARBOHYDRATES OF *Allium*.

##### V. GLUCOFRUCTAN OF *Allium cepa*

M. A. Khodzhaeva and E. S. Kondratenko

UDC 547.917

Continuing an investigation of the carbohydrates of plants of the family *Alliaceae*, we have studied the water-soluble polysaccharides (WSPSs) of the bulbs of *A. cepa* (garden onion).

The comminuted raw material, after the elimination of ballast substances with chloroform and 96% ethanol, was subjected to extraction with 80% ethanol. Fructose, glucose, and sucrose were detected in the ethanol-soluble fraction (9.7% on the absolutely dry raw material) by paper chromatography (PC, 1-butanol-pyridine-water (5:4:3) system).

Subsequent extraction with water, elimination of protein by Sevag's method [1] and precipitation in acetone gave the WSPSs (12% of the absolutely dry raw material). They consisted of a white amorphous powder readily soluble in water at 30-40°C, similar to inulin. When subjected to gel chromatography on Sephadex G-75 (61 × 1.8 cm), the initial WSPSs proved to be polydisperse. A homogeneous fraction was isolated by preparative gel chromatography on Sephadex G-50 (45 × 3.5 cm).

Six fractions (1-6) differing in elution volume and, therefore, in molecular weight were obtained:

	1	2	3	4	5	6
Elution volume, ml	135	166	198	267	340	470
Yield, %	20	2	1	35	20	11
Molecular mass	5000-6000	4000	—	2100	1000	320-700
2→6-Bound						
fructofuranose units	61.0	105.0 <sup>†</sup>	78.65	76.5 <sup>‡</sup>	81.65	64.7
α-D-Glucopyranose residues	93.5	72.5	73.9	70.8	73.0	61.0
	93.7					
β-D-Glucopyranose residues	97.15	72.7	73.2	70.5	72.5	62.1

\*Interpretation in accordance with [4].

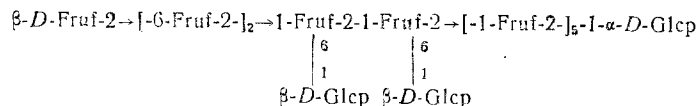
<sup>†</sup>For units within a chain 104.85 ppm.

<sup>‡</sup>For units within a chain 76.7 ppm.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnykh Soedinenii*, No. 1, pp. 105-106, January-February, 1984. Original article submitted July 5, 1983.

Methylation of the glucofructan by Hakomori's method gave a permethylate with  $[\alpha]_D^{22} -33.3^\circ$ , which was subjected to formolysis followed by hydrolysis. The product of the hydrolysis of the permethylate was subjected to thin-layer chromatography (TLC, benzene-acetone (2:1) system), and 2,3,4,6-tetra-O-methyl-D-glucose, 1,3,4,6-tetra-O-methyl-D-fructose, 1,3,4-tri-O-methyl-D-fructose, 3,4,6-tri-O-methyl-D-fructose, and 3,4-di-O-methyl-D-fructose were identified by comparison with authentic samples.

Analysis of the products of the hydrolysis of the permethylate confirmed the results of IR and  $^{13}\text{C}$  NMR spectra. On summarizing all the information derived the following structure can be suggested for the glucofructan from the bulbs of *A. cepa*:



Fraction 4 was homogeneous and had the highest yield on the initial WSPSs, which served as a basis for its deeper study.

In an acid-hydrolysate of fraction 4 fructose and glucose were detected with the aid of PC (system 1), the amount of fructose, determined by Koltoff's method [2], being 77%. Consequently, fraction 4 of the WSPSs was a glucofructan. Its IR spectrum had absorption bands characteristic for glucofructans of the mixed type [3].

In the  $^{13}\text{C}$  NMR spectrum of the glucofructan, chemical shifts of 105.0 ppm (C-2) and 76.5 ppm (C-4), which are characteristic for fructofuranose units within a chain joined by  $2 \rightarrow 1$  and  $2 \rightarrow 6$   $\beta$ -glycosidic bonds, were detected. The ratio of  $2 \rightarrow 1$  to  $2 \rightarrow 6$  bonds calculated from the intensities was 5.6:1.

The  $\alpha$ -GLCP residues had characteristic chemical shifts of 93.5 and 93.7 ppm and were present only at the "reducing" end of the glucofructan, attached to C-2 of the inulin units.

A chemical shift of 97.15 indicated the presence of  $\beta$ -D-Glcp also at the sixth carbon atom of the inulin part of the molecule, and from a comparison of integral intensities it follows that 20% of the inulin units were substituted by  $\beta$ -D-Glcp.

The assignment of the signals of the other carbon atoms is given below (solution  $\text{D}_2\text{O}$ ,  $60^\circ\text{C}$ , internal standard  $\text{CH}_3\text{OH}$  giving a signal at 50.15 ppm):

	C-1	C-2	C-3	C-4	C-5	C-6
2 $\rightarrow$ 1-Bound residues of fructofuranose units	62.35	104.5	78.3	76.1	82.6	63.7

#### LITERATURE CITED

1. M. G. Sevag, *Biochem. Z.*, **273**, 419 (1934).
2. I. N. Ivanov, *Methods in Plant Physiology and Biochemistry* [in Russian], Leningrad (1935), p. 122.
3. M. A. Khodzhaeva, Z. F. Ismailov, E. S. Kondratenko, and P. S. Shashkov, *Khim. Prir. Soedin.*, **23** (1982).
4. F. R. Seymour et al., *Carbohydr. Res.*, **72**, 57 (1979).