

The most appreciable effect of modification was shown on promotion with metallic cerium: the amount of reducing substances in the hydrogenate fell by a factor of 5 and the time of hydrogenation by a factor of 4.

An improvement of known industrial catalysts by modification has permitted a rise in the selectivity of their action and a shortening of the reaction time with the production of high-quality xylitol.

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#### GLUCOFRUCTANS OF *Cousinia polycephala*

K. Turdumambetov, N. V. Plekhanova, D. A. Rakhimov,  
and M. R. Yagudaev

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The main polysaccharides of the roots of *Cousinia* are glucofructans [1, 2]. We have studied the structure of the glucofructans isolated from the roots of *C. polycephala* Rypr. [3]. The glucofructans were dissolved in hot water (10% solution, 80°C). On standing, a precipitate of the aqueous fraction (AF) deposited with a yield of 51%. The mother solution was concentrated and precipitated with ethanol to give an ethanolic fraction (EF) with a yield of 38%.

Gel chromatography on Sephadex G-75 showed that the aqueous and ethanolic fractions consisted of polydisperse polymers the molecular masses of which ranged from 12,000 to 21,000 and from 10,000 to 18,000, respectively. In order to obtain a homogeneous polysaccharide, the aqueous and ethanolic fractions were fractionated by precipitation from water (2% solution) with ethanol (Table 1).

Since AF-III, AF-VIII, and EF-VII formed the bulk of the polysaccharides, we studied their structures. Fructose and traces of glucose were detected in the products of the complete hydrolysis of the three polymeric fractions. By a standard method [4], 98.0, 96.2, and 98.3% of fructose were detected in the glucofructans AF-III, AF-VIII, and EF-VII, respectively. The values of  $[\alpha]_D^{22}$  (c 1.0; H<sub>2</sub>O) were as follows: -36.5° (AF-III), -39.3° (AF-VIII), and -37.2° (EF-VII). The negative values of the specific optical rotation confirmed the  $\beta$ -configuration of the glycosidic bonds of the fructose residues.

In the products of the Smith degradation of all the samples, PC showed the presence mainly of glycerol with very small amounts of fructose, which may indicate the presence of both 2  $\rightarrow$  1- and 2  $\rightarrow$  6-bonds between the fructofuranose residues and a small number of branches.

The glucofructans AF-III, AF-VIII, and EF-VII were methylated by Hakomori's method [5]. The completeness of methylation was checked by IR spectroscopy. The following methylated sugars were detected in the hydrolysates of all three completely methylated polysaccharides by TLC [in the benzene-acetone (2:1) system] and GLC (in the form of methyl glycosides): 2,3,4,6-tetra-O-Me-D-glucose; 1,3,4,6-tetra-O-Me-D-fructose; and 3,4,6-tri-O-Me-D-fructose (the main product), together with a very small amount of di-O-Me-fructose.

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Institute of Organic Chemistry, Kirghiz SSR Academy of Sciences, Frunze. Institute of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnikh Soedinenii, No. 3, pp. 427-429, May-June, 1989. Original article submitted September 7, 1988; revision submitted December 30, 1988.

TABLE 1.

Item	Ratio of water and ethanol							
	1:1	1:1,5	1:2	1:2,5	1:3	1:3,5	1:4	1:4,5
Aqueous fraction	I	II	III	IV	V	VI	VIII	VIII
Yield, % on total	—	9,7	34,6	6,0	9,0	4,4	—	22,5
Molecular mass	—	12000—21000	15000	15100	15000	15000—19000	—	17200
Ethanol fraction	I	II	III	IV	V	VI	VII	VIII
Yield, % on total	7,7	0,8	0,9	—	6,2	8,8	58,0	6,2
Molecular mass	11500	11000	10300	—	10600	10800	18800	12000

It was obvious from the analysis of the methylation products that in the polymer chains of the glucofructans studied there are 2 → 1-bound fructofuranose residues with a very small number of branches.

The  $^{13}\text{C}$  NMR spectra also showed the presence of 2 → 1-bonds in the glucofructans. The spectra contained signals corresponding to  $\beta$ -2 → 1-bound fructofuranose units (ppm):

Residues of $\beta$ -2 → 1-bound units	C-1	C-2	C-3	C-4	C-5	C-6
	Fructose					
AF-III	62,7	104,4	78,6	75,9	82,5	63,3
AF-VIII	62,0	104,1	78,3	75,6	82,2	63,1
EF-VII	62,3	104,3	78,6	75,9	82,4	63,3
	$\alpha$ -D- Glucopyranose					
AF-VIII	93,4	72,1	74,1	70,8	72,1	61,4
EF-VII	93,4	72,1	73,7	70,4	72,1	61,9

Glucose was present at the reducing ends of the polymeric chains, being attached to the C-2 atoms of fructofuranose residues as was shown by the position of the C-1 signal of  $\alpha$ -D-glucopyranose (93.4 ppm), which is characteristic for this type of linkage.

Thus, it has been established that the fructose residues in the glucofructans from the roots of *C. polycephala* are linked by the  $\beta$ -2 → 1, inulin, type of bond, and the polysaccharides differ by their degrees of polymerization. The chemical study of the glucofructans of *Cousinia* is proceeding.

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