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OLIGO- AND POLYSACCHARIDES FROM *Cousinia umbrosa*

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Cousinia umbrosa Rgl. (Compositae) is a perennial weed that is widely distributed over Kyrgyzstan [1].

The overall properties of carbohydrates from *C. umbrosa* have been published [2].

Herein we communicate the structures of the oligo- and polysaccharides from *C. umbrosa* roots collected in Shamsy, Chui District, during fruiting.

Ground air-dried raw material was inactivated with alcohol (96°) to remove low-molecular-weight noncarbohydrate and colored compounds and then extracted twice with boiling alcohol (82°) at a 1:6 ratio. The combined alcohol extracts were worked up with grade OU activated charcoal (decolorizing carbon) for 10 min at 70°C, filtered, and evaporated to a syrup (yield 4.3%).

The monomer composition was studied by descending PC using *n*-BuOH:C_5H_5N:H_2O (6:4:3), 18 h development.

Development of the chromatograms with acidic anilinium phthalate detected glucose; with urea solution (5%), fructose, saccharose, and a series of D-fructoligosaccharides (FO) with R_f 1.0, 0.76, 0.68, 0.54, 0.43, 0.29, 0.2, and 0.14.

Of the FO listed above, the most abundant ones were those with R_f 0.76 (FO-1) and 0.68 (FO-2). These compounds were isolated by separating the syrup over a column of Sephadex G-25 (1.8 × 65 cm) with elution by water. Effluents (2 mL) were collected. The separation of FOs was monitored using the phenol:H_2SO_4 method [3] and PC. Effluents were collected separately, evaporated to dryness, and washed with acetone and ether to afford two pure FOs, FO-1 and FO-2 in yields of 24.6 and 31.7% (of the total GF), respectively.

FO-1: $[\alpha]_D^{20}$ +25.6° (*c* 1.0, water), fructose and glucose contents determined by the Holthoff method [4] were 66.4 and 33.2%. The quantitative ratio of monosaccharides suggested that FO-1 was a trisaccharide 1-kestose.

Methylation of FO-1 by the Hakomori method [5] produced the permethylate. Its acid-hydrolysis and formolysis products were analyzed by TLC on Silufol using C_6H_6:$(CH_3)_2CO$ (1:2) and markers to identify 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.

FO-2 contained according to hydrolysis fructose and glucose in the quantitative ratio 74.8:25.1% [4], which corresponded to the composition of nystose. The index of specific rotation was +14.6° (*c* 1.0, water).

The raw material remaining after isolation of sugars soluble in alcohol was extracted with water to afford water-soluble polysaccharides (WSPS) [6], yield 25%. WSPS were a hygroscopic white powder that was very soluble in water and did not give a color with iodine solution (0.1%). Acid hydrolysis and PC detected fructose and glucose. The predominant amount of fructose classified the WSPS as glucofructans (GF).

Crude GF was dissolved in water and fractionated with alcohol in order to produce homogeneous fractions [6]. Five fractions were obtained: GF-I, 2.0%; -II, 4.8, -III, 38.0; -IV, 50.5, and -V, 3.8. The main GF were fractions GF-III and GF-IV, the properties of which appear in Table 1. The MWs were determined over Sephadex G-75 as before [6].

GF-III and GF-IV differed in yield and MW whereas the specific rotations and fructose contents were similar. The periodate oxidation and Smith degradation products [6] in both fractions contained glycerine, which was consistent with the presence of both 2→1 and 2→6 glycosidic bonds in the GF. The negative specific rotations were consistent with a β-glycoside bond. The ^{13}C NMR spectra indicated that the GF contained 2→1 glycosidic bonds. The spectra contained signals corresponding to β-2→1 bonded fructofuranose units (Table 2).

Thus, GF from *C. umbrosa* roots consist of β-2→1 bonded fructofuranose units of the inulin type and differ in degree of polymerization.

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TABLE 1. Properties of Glucofructan Fractions

GF	$[\alpha]_D^{22}$ (*c* 1.0, water)	Fructose, %	MW	Periodate oxidation	
				$NaIO_4$	HCOOH
GF-III	38.9	97.7	16500	0.93	0.043
GF-IV	39.3	98.2	12800	0.95	0.042

TABLE 2. Chemical Shifts of C Atoms in ^{13}C NMR Spectra of *C. umbrosa* Glucofructans, ppm

GF	C atom					
	1	2	3	4	5	6
GF-III*	62.35	104.25	78.5	75.8	82.3	63.25
GF-III**	93.5	72.4	74.0	70.6	73.0	61.0
GF-IV*	62.1	104.45	78.3	75.5	82.1	63.10
GF-IV**	93.4	72.1	73.6	70.6	72.8	60.5

Unit: *-2-β-D-Fru*f*-1-, **-1-α-D-Glc*p*.

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