FRACTIONATION AND COMPOSITION OF THE CARBOHYDRATES OF *Ficus carica*

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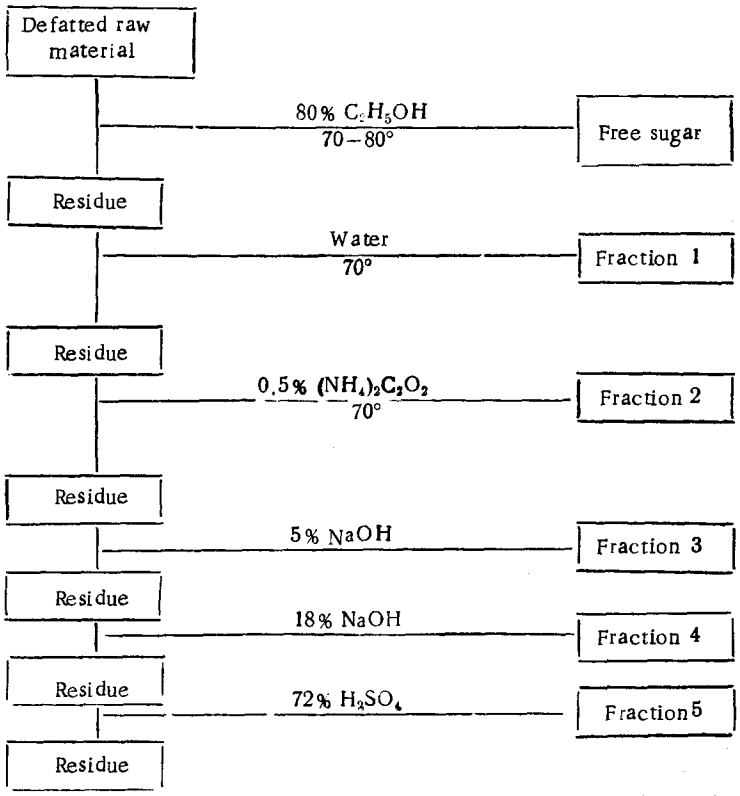
The fractional compositions of the carbohydrates of the four most promising varieties of *Ficus carica* L. — Smena, Kadota, Chumlakuri mtsvane, and Turetskii korichnevyi — have been investigated. The qualitative and quantitative monosaccharide compositions of the carbohydrates isolated have been determined. The bulk of the dry matter of the fruit consists of ethanol-soluble oligosaccharides — up to 74.53%. The composition of the residue obtained after the fractionation of the carbohydrates has been studied. It contains ligin bound to mineral elements.

The subtropical fruit-bearing plant *Ficus carica* L. (fig), family *Moraceae*, possesses peculiar biochemical and biological properties. This relates primarily to the biology of its flowering and fruit-bearing, the presence of a milky sap, and the high activity of a number of enzymes. Particular interest is presented by a study of the carbohydrate complex of the fruit which is responsible for the most important of its properties — taste, consistency, stability on storage, etc.

The carbohydrates of *Ficus carica* L. of varieties Smena, Kadota, Chumlakuri mtsvane, and Turetskii korichnevyi were studied in accordance with the scheme given below.



Scheme of the fractionation of Ficus carica

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TABLE 1. Carbohydrate Composition of *Ficus carica*

Extractant	Variety of fig	Carbohydrates, %		Monomeric composition of the carbohydrate, % on the total of oligo- and polysaccharides							
		in the fruit	on the dry matter	glucose	fructose	sucrose	arabinose	xylose	uronic acids	galactose	mannose
Ethanol	Smena	15,31	70,30	45,45	42,10	12,45	—	—	—	—	—
	Kadota	15,40	64,23	49,33	46,38	4,29	—	—	—	—	—
	Chumlakuri mtsvane	12,75	67,20	48,57	46,35	5,08	—	—	—	—	—
	Turetskii korichnevyi	17,70	74,43	49,54	43,62	6,84	—	—	—	—	—
Water	Smena	0,82	3,76	14,91	—	—	25,00	Tr.	36,89	22,50	—
	Kadota	0,86	3,59	19,10	—	—	23,00	Tr.	37,80	19,00	—
	Chumlakuri mtsvane	1,02	5,39	18,39	—	—	24,01	Tr.	38,50	17,70	—
	Turetskii korichenevyi	1,14	4,79	19,56	—	—	17,04	—	46,10	22,10	—
0.5% ammonium oxalate	Smena	0,75	3,44	16,01	—	—	14,06	13,61	32,22	23,30	Tr.
	Kadota	0,53	2,21	12,41	—	—	18,16	1,17	45,96	13,61	7,69
	Chumlakuri mtsvane	0,45	2,38	11,48	—	—	19,71	Tr.	50,91	17,01	—
	Turteskii korichnevyi	0,51	2,14	11,02	—	—	19,33	0,61	46,60	22,24	—
5% sodium hydroxide	Smena	0,34	1,58	29,06	—	—	28,94	24,01	—	17,49	Tr.
	Kadota	0,36	1,50	23,61	—	—	27,62	27,87	—	20,5	Tr.
	Chumlakuri mtsvane	0,36	1,80	26,90	—	—	31,82	23,64	—	17,34	Tr.
	Turetskii korichnevyi	0,39	1,64	26,58	—	—	24,22	25,90	—	23,29	Tr.
18% sodium hydroxide	Smena	0,43	1,97	23,12	—	—	30,12	39,47	—	17,09	—
	Kadota	0,68	2,84	22,61	—	—	35,94	41,25	—	Tr.	—
	Chumlakuri mtsvane	0,58	3,06	27,64	—	—	39,02	33,04	—	Tr.	—
	Turetskii korichnevyi	0,73	3,07	27,14	—	—	36,13	37,06	—	Tr.	—
Residue	Smena	0,13	0,59	98,5	—	—	—	Tr.	—	—	—
	Kadota	0,15	0,63	99,1	—	—	—	—	—	—	—
	Chumlakuri mtsvane	0,30	1,59	99,3	—	—	—	—	—	—	—
	Turetskii korichnevyi	0,25	1,05	99,6	—	—	—	—	—	—	—

Among the fractions obtained the largest was the ethanol-soluble fraction — up to 74.53% of the dry matter of the fig, consisting of free sugars. Thin-layer chromatography of the ethanolic extracts permitted the identification of the same qualitative composition of the carbohydrates in all the varieties of fig studied — glucose, fructose, and sucrose. Quantitative analysis showed some differences between the varieties (Table 1).

Information is given in the literature for green figs on the following indices: amounts of glucose, fructose, sucrose on the dry matter, which were 5.54, 4.00, and 0.0%, respectively. In fresh figs of technical ripeness, the proportion by weight of total sugars was between 13.1 and 18.2%, of reducing sugars 14.9%, and of sucrose 1.05%. Other authors have found 17.2% of reducing sugars and 2.9% of sucrose [1].

It is interesting to note that the fig varieties considered form a substantial source of fructose, which is widely used as one of the sucrose substitutes in the dietary treatment of patients with sugar diabetes, atherosclerosis, ischemic heart disease, etc. [2].

The water-soluble pectin fraction amounted to from 3.95% of the dry matter of the figs (Kadota variety) to 5.39% (Chumlakuri mtsvane variety). With respect to their monomeric compositions, the aqueous fractions of the varieties of fig mentioned were similar to one another. Hydrolysates of the polysaccharides mentioned with water were found to contain uronic acids and also neutral sugars — arabinose and galactose. On considering the monosaccharide compositions of the water-soluble fractions of the fig and of other fruits and vegetables we can see that, unlike apples of a summer variety, the fig contains galactose but no mannose, and unlike tomatoes the fig contains no rhamnose, while carrots do not contain glucose [3].

The polysaccharides isolated with ammonium oxalate were present in a smaller amount than the water-soluble fraction. Their hydrolysates consisted mainly of galacturonic acid, neutral sugars being present in smaller amounts.

A determination of the proportion by weight of protopectin showed that there was less of it in the dark variety Turetskii korichnevyi — 2.14% in the dry matter — which is possibly connected with the fact that it had been stored for the shortest time.

In addition to pectin substances, we made quantitative determinations of other structural polysaccharides in the fig — hemicelluloses and cellulose.

It was found that the main structural component of the plant cell walls responsible for their rigidity is cellulose. The cellulose fibers of the cells are cemented by a matrix consisting of three polymeric materials — hemicelluloses (HMCs), pectin, and extensin. The HMCs were investigated in alkaline extracts obtained by treating the residue with 5 and 18% NaOH. The fractions isolated by means of the 5% NaOH contained 1.50-1.90 and those by the 18% NaOH 1.97-3.07% by weight of the dry matter of the fruit.

Hydrolysates of hemicelluloses A and B of different varieties of fig had identical qualitative compositions of the monoses: glucose, arabinose, xylose, and galactose. The amounts of the individual monoses were different for the different varieties. The monosaccharide composition of the HMCs was richer than those of the HMCs of tomatoes and apples but poorer than those of carrots and sugar beets [3].

Glucose was the main product detected in acid hydrolysates of the residues after the extraction of the HMCs. The high level of glucose showed the presence of a glucan of the cellulose type, the amount of which was 0.56-1.53% by weight of the dry matter.

In order to investigate the residues, IR and UV spectroscopy were carried out after the fractionation and hydrolysis with H_2SO_4. The capacity of the chromophoric groups of the residue for absorbing rays in the 280 and 310-320 nm regions, and also sharp bands in the 1600 and 1500 cm^{-1} regions (stretching vibrations of aromatic rings) permitted the identification in the residues of a lignin similar to the lignins of other plant materials. The ash content of the residue was 0.70-1.93% on the dry weight of the fig.

EXPERIMENTAL

Fruit of *Ficus carica* of the varieties Smena, Kadota, Chumlakuri mtsvane, and Turetskii korichnevyi were gathered in the experimental garden of the Gurdzhani region of the GSSR in the technical stage of ripeness. The comminuted fruit was defatted with ether in a Soxhlet apparatus.

Fractionation of the Carbohydrates. The raw material (20 g) after the elimination of ether-soluble substances, was treated three times with 82% ethanol in the water bath at 70-80°C (liquor ratio 20). The solid phase was separated off by centrifugation and the extract was evaporated in vacuum. The residue was freed from ethanol by drying at 40-50°C. Treatment with water at 70°C was carried out similarly. The solution was separated off, and the polysaccharides were extracted from the residue with 0.5% ammonium oxalate solution at 70°C. Then it was extracted with 5% NaOH at room temperature, and the hemicellulose A fraction was obtained.

Treatment with 18% NaOH in the presence of 4% boric acid was performed similarly, giving the hemicellulose B fraction. The residue after all the extractions was washed with water until the wash-waters were neutral and was dried. Then it was treated with 72% sulfuric acid (liquor ratio 10) at room temperature for 2 h, after which water was added (1:15) and hydrolysis was carried out in the boiling water bath for 5 h.

The isolation of the polysaccharide from the water-soluble, the ammonium-oxalate-soluble, and the two alkali-soluble extracts was carried out by mixing each of these extracts with ethanol in a ratio of 1:4. In the case of the alkali-soluble fractions, they were first acidified with acetic acid to pH 4.5. The polysaccharides of each fraction were purified by two reprecipitations, for which purpose the precipitate of polysaccharides that had deposited was dissolved in a threefold amount of NaOH and were precipitated with ethanol, washed with ethanol, and dried over P_2O_5.

Hydrolysis of the Polysaccharides and Identification of the Monosaccharides. The polysaccharides were hydrolyzed with 2% HCl at 100°C for 6 h. The monosaccharides were identified by TLC and PC [4, 5]. The following solvent systems were used: butan-1-ol—benzene—pyridine—

water (5:1:3:3) and butan-1-ol—acetic acid—water (4:1:5). The revealing agent for aldoses was aniline phthalate (0.92 ml of aniline and 1.68 g of phthalic acid in 100 ml of ethanol) and that for ketoses was a mixture of 20 g of urea, 100 ml of ethanol, and 5 ml of concentrated HCl [6, 7].

IR spectra were taken on a UR-20 instrument in the wavelength intervals of 4000-2000 cm^{-1} (LiF prism) and 2000-700 cm^{-1} (NaCl prism). The samples were prepared by molding the polysaccharides in KBr [8]. The mineral composition was determined on the ash after the mineralization of the lignin [9].

SUMMARY

The carbohydrates of the fig *Ficus carica* L. varieties Smena, Kadota Chumlakuri mtsvane, and Turetskii korichnevyi contain ethanol-soluble sugars (fructose, glucose, and sucrose), water-soluble pectin and protopectin, hemicelluloses, and cellulose. Hydrolysates of the hemicelluloses were found to contain arabinose, xylose, glucose, and galactose.

Lignin in a complex with mineral elements was determined in the residues after fractionation.

For practically all the fractions of fig carbohydrates the monomeric composition of the polysaccharides can be regarded as a species characteristic, and variety differences are observed in their quantitative evaluation.

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