FRACTIONATION AND COMPOSITION OF THE CARBOHYDRATES OF LEAF VEGETABLES

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The qualitative and quantitative compositions of the carbohydrates of the leaf vegetables Lactuca sativa L., Spinacea oleracea L., and Rumex acetosa L. have been studied.

Particular interest is presented by the study of the carbohydrate complex of green leaf vegetables. Lettuce *Lactuca sativa* L. (variety Kucheryavets Odesskii), spinach *Spinacea oleracea* L. (variety Viktoriya), and sorrel *Rumex acetosa* L. (variety Odesskii-17) have been studied in accordance with the experiment described below. The results of the fractionation of the carbohydrates are given in Table 1.

Among the fractions obtained, the alkali-soluble ones, containing hemicelluloses A and B, were represented in the greatest amount. The hydrolysates of the hemicelluloses showed identical monose compositions for spinach and sorrel while for lettuce the hemicellulose A fraction lacked arabinose and the hemicellulose B fraction lacked rhamnose. The amounts of individual monoses varied for the different vegetables. The monosaccharide compositions of the hemicellulose of spinach, sorrel, and lettuce were richer than a number of well-known fruits — apples and figs — and even than some vegetables — tomatoes, sugar beet, etc. [2].

Of the oligosaccharides known under natural conditions, only a few are of interest as food factors possessing very great nutritional value. The most easily digestible carbohydrates such as glucose, fructose, and sucrose are represented in the vegetables investigated in only small amounts — from 0.39 to 0.92% of their crude weight or 6.29 to 9.78% of their dry weight — which permits these vegetables to be recommended for use in diets with a reduced oligosaccharide content.

The water-soluble pectin fraction amounted to 4.5% for lettuce, 1.9% for spinach, and 0.57% for sorrel. The monomeric compositions of the aqueous fractions of these vegetables were similar to one another. A hydrolysate of the polysaccharides extracted by water was found to contain uronic acids and also neutral sugars — arabinose (spinach, sorrel), glucose, galactose, and pentoses. On comparing the monosaccharide compositions of the leaf vegetables with other fruits and vegetables [2] it can be seen that, in contrast to apples of the summer variety, they contain galactose and no mannose, while for tomatoes and carrots the compositions are identical although fluctuations in the quantitative level of monoses are observed.

The amount of polysaccharides isolated with the aid of ammonium oxalate was smaller than that in the water-soluble fraction, with the exception of sorrel, but here considerable differences were observed in the monomeric composition of the fractions from different vegetables. For lettuce, the hydrolysate consisted mainly of galacturonic acid (72.4%), while the hydrolysate of sorrel contained only 13.3% of galacturonic acid.

A determination of the mass fractions of protopectin showed that its amount was smaller for spinach and sorrel, at 0.92 and 0.81%, respectively, on the dry weight, as compared with lettuce.

Together with pectin substances, we determined other structural polysaccharides — hemicelluloses and cellulose — quantitatively in the vegetables under investigation. The hemicelluloses were investigated in alkaline extracts obtained by treating the residue with 5% and 18% NaOH. The fractions isolated by 5% NaOH contained 9.25-12.4% and those by 18% NaOH 7.83-21.2% on the weight of the dry matter of the vegetables.

In acid hydrolysates of the residues, after the extraction of the hemicelluloses we found mainly glucose. The high glucose content indicated the presence of a glucan of the type of cellulose, the amount of which was 5.8-12.90% on the weight of the dry matter.

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TABLE 1

Extractant	Species of vegetable	Carbohydrates, %		Monomeric composition of the carbohydrates, % on the sum of the oligo- and polysaccharides							
		per 100 g of product	on the dry weight	glucose	fructose	sucrose	rhamnose	xylose	galactose	arabinose	uronic acids
Alcohol	Lettuce	0,39	6,29	60,73	14,54	24,72	—	—	—	—	—
	Spinach	0,60	7,16	59,54	30,95	9,49	—	—	—	—	—
	Sorrel	0,92	9,78	66,59	11,41	21,98	—	—	—	—	—
Water	Lettuce	0,28	4,5	15,94	—	—	7,45	14,8	13,98	—	47,8
	Spinach	0,160	1,9	13,1	—	—	8,8	3,6	29,5	15,2	29,5
	Sorrel	0,053	0,57	6,43	—	—	10,14	4,1	10,40	8,69	60,2
0.5% ammonium oxalate	Lettuce	0,18	2,9	—	—	—	21,3	4,49	22,1	—	50,3
	Spinach	0,077	0,92	12,7	—	—	10,52	6,32	10,24	22,37	37,3
	Sorrel	0,075	0,81	9,11	—	—	—	24,54	22,15	30.8	13,3
5% sodium hydroxide	Lettuce	0,658	10,48	25,14	—	—	6,46	36,8	21,08	—	10.50
	Spinach	0,777	9,25	17,73	—	—	3,13	20,86	11,23	14,37	32,65
	Sorrel	1,146	12,40	17,98	—	—	3,45	17,14	17.98	29,1	13,72
18% sodium hydroxide	Lettuce	0,6	9,67	Tr.	—	—	—	32,2	19,1	44,94	37,4
	Spinach	0,657	7,83	19,4	—	—	4,85	26,6	22,6	10,19	16,18
	Sorrel	1,95	21,20	11,55	—	—	31,98	19,36	7,77	12,43	16.88
72% sulfuric acid	Lettuce	0,800	12,90	99,3	—	—	—	—	—	—	—
	Spinach	0,48	5,80	99,0	—	—	—	—	—	—	—
	Sorrel	0,76	8,45	98,2	—	—	—	—	—	—	—
Residue	Lettuce	1,279	20,6	—	—	—	—	—	—	—	—
	Spinach	1,699	20,2	—	—	—	—	—	—	—	—
	Sorrel	1,16	12,28	—	—	—	—	—	—	—	—

The residues after fractionation and hydrolysis with H_2SO_4 were subjected to IR and UV spectroscopies. The capacity of the chromophoric groups of the residues for absorbing UV light in the 280 and 310-320 nm region, and also sharp bands in the 1600 and 1500 cm^{-1} regions (stretching vibrations of aromatic rings) permitted a lignin similar to the lignins of other plant materials to be identified in the residues. The ash content of the residues amounted to 1.02-2.14% on the dry weight of the leaf vegetables.

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument in the wavenumber 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 [7]. The mineral composition of the ash after the mineralization of the lignin was determined [8].

The vegetables were gathered in the Lenin Sovkhoz [communal farm] in Odessa province at the stage of technical ripeness. The comminuted vegetables were defatted with ether in a Soxhlet apparatus.

Fractionation of the Carbohydrates. After the elimination of the ether-soluble substances from 100 g of raw material, it was treated three times with 82% ethanol with heating 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 alcohol 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 a 0.5% solution of ammonium oxalate at 70°C. Then extraction was carried out with 5% NaOH at room temperature, giving the hemicellulose A fraction.

The treatment with 18% NaOH in the presence of 4% of boric acid, giving the hemicellulose B fraction was carried out similarly. 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, and after the addition of water (1:15) hydrolysis was conducted in the boiling water bath for 5 h.

The polysaccharides were precipitated from the water-soluble extract, the ammonium oxalate extract, and the two alkali-soluble extracts by mixing each of them with ethanol in a ratio of 1:4. The alkali-soluble fractions were first acidified with acetic acid to pH 4.5. The polysaccharides from each fraction were purified by two reprecipitations, for which purpose the precipitated polysaccharide residue was dissolved in a threefold amount of NaOH and was precipitated by alcohol, 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 4 h. The monosaccharides were identified by TLC and PC [3, 4]. 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). For the revealing agent, see [5, 6].

REFERENCES

1. V. I. Smolyar, *Rational Nutrition* [in Russian], Naukova Dumka, Kiev (1991).
2. N. V. Al'ba and L. S. Dorofeeva, *Biochemical Investigations of Plant and Animal Materials* [in Russian], Saransk (1977).
3. A. A. Akhrem and A. I. Kuznetsova, *Thin-Layer Chromatography* [in Russian], Moscow (1964).
4. *Methods for the Quantitative Paper Chromatography of Sugars, Organic Acids, and Amino Acids in Plants* [in Russian], Moscow—Leningrad (1962).
5. A. M. Grodzinskii and D. M. Grodzinskii, *Short Handbook on the Plant Physiology* [in Russian], Kiev (1973).
6. M. S. Dudkin and N. A. Denisyuk, *Khim. Prir. Soedin.*, No. 1 (1984).
7. I. Kössler, *Methods of Infrared Spectroscopy in Chemical Analysis* [Russian translation], Moscow (1964).
8. E. I. Solov'eva, *The Laboratory Control of the Preserving, Vegetable-drying, and Food Concentrate Industries* [in Russian], Moscow (1974).