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CARBOHYDRATES AND LIPIDS OF *Brassica oleracea*

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Lipids and polysaccharides have been obtained from the leaves of Brassica oleracea. *The qualitative and quantitative compositions of the lipid complex have been studied. The fatty acid compositions of the total neutral lipids and of the phospho- and glycolipids have been determined. The carbohydrate complex of cabbage includes water-soluble polysaccharides, low-methoxyl pectins, hemicelluloses, and free monosugars. The polypeptides have been characterized by their mannoside compositions.*

The pectins isolated from various sources of raw material differ by the size of their molecules and the degree of esterification or acetylation, and this explains the manifestation of different functional properties by them. An expansion of the variety of pectins is frequently connected with the search for new sources of raw material, and it is proposed to use cabbage waste (leaves) after the removal of the extraneous matter.

The lipids and carbohydrates were extracted successively from one sample of air-dry material [1, 2]. From the residual meal after the extraction of the lipids we isolated successively the water-soluble polysaccharides (WSPs), the pectin substances (PcSs) and the hemicelluloses (HMCs). All the samples of polysaccharides were purified by reprecipitation from aqueous solutions with ethanol.

We conducted a complete acid hydrolysis of the polysaccharide fractions and determined the nonpolysaccharide compositions by PC and TLC. The amounts of polysaccharides and their monosaccharide compositions are given in Table 1,

In the quantitative respect, in comparison with the WSPSs and HMCs the PcSs predominated in the leaves of *B. oleracea*, which induced us to investigate them in more detail.

The pectin contained 2.92% of methoxy groups and had $[\alpha]_D^{20}$ +227° (*c* 0.5; H_2O) and consisted of a white flocculent powder. It was readily soluble in water and practically insoluble in the majority of organic solvents. The pectin contained 51.3% of uronic anhydride, determined by a standard method [3]. The molecular mass (MM) was determined by the method of Kovalenko and Kurilenko [4], with calculation by means of the equation $/\eta/ = K \cdot M\ 1.1 \cdot 10^{-5}$ MW 1.22. The specific viscosity of the pectin for concentrations of 1.0, 0.5, 0.25, 0.125, and 0.06 was 13.6, 9.3, 6.5, 2.2, 1.6, and 1.3, respectively. MM 34,000 c.u. The ash content of the pectin was 2.1%. The titrimetric method gave the following characteristics of the PcSs (%): free carboxy groups, K_f, 10.8; methoxykated carboxy groups, K_e, 6.3; degree of esterification, λ, 46.3%.

In the products of the acid hydrolysis of the pectin we found mainly galacturonic acid and neutral sugars (Table 1).

The predominating sugar in the HMC A was xylose. This showed a predominance of xylan in the alkali-soluble polysaccharide.

Glucose was found as the main component of acid hydrolysates of the residues after the extraction of the hemicelluloses.

The pectin of the leaves of *B. oleracea* was similar to the pectin of its hulls and seeds [6], but differed by a low degree of esterification and a predominant content of rhamnose and xylose among the neutral sugars.

The lipid complex was isolated by Folch's method [1] The total lipids were separated into neutral lipids (NLs), glycolipids (GLs) and phospholipids (PLs) as in [7]. The lipid classes proved to be in the following ratio (wt.-%): NLs, 60.5; PLs, 20.2; GLs, 19.3.

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TABLE 1. Amounts and Compositions of Hydrolysates of Polysaccharides of *B. oleracea*

Polysaccharide	Yield, %	Ratio of the sugars					
		Rham	Ara	Xyl	Man	Glc	Gal
WSPSs	5.1	2.6	1.0	4.2	1.1	13.0	8.2
PcSs	7.8	7.6	1.0	4.1	Tr.	Tr.	2.0
HMCs A	2.4	1.0	2.0	9.0	–	–	Tr.
HMCs B	1.2	3.7	5.0	4.0	1.0	5.0	7.1
HMCs A_1	0.9	1.3	17.0	1.0	Tr.	2.0	1.0
HMCs B_1	1.7	2.1	1.0	11.0	4.0	30.0	2.0

TABLE 2. Composition of the Lipids of *Brassica oleracea*, % on the Weight of the Extract

Neutral lipids		Phospholipids		Glycolipids	
Hydrocarbons	4.6	N-Acylated phospholipids	6.8	Monogalactosyl diacylglycerols	28.7
Carotenoids	0.1	Phosphatidylglycerols	26.6	Sterol glycoside esters	16.4
Sterol esters	6.1	Phosphatidylethanolamines	25.0	Sterol glycosides	4.4
Wax esters	1.0	Phosphatidylcholines	20.8	Cerebrosides	30.2
Triacylglycerols	21.4	Phosphatidic acids	9.1	Digalactosyldiacylglycerols	20.3
Fatty acids	34.6	Phosphatidylinositols	7.8		
Fatty alcohols	0.9	Phosphatidylserines	3.9		
Sterols	18.4				
Diacylglycerols	10.3				
Xanthophylls	0.2				
Monoacylglycerols	2.4				

By the TLC method (solvent systems 2-4) 12 groups of compounds were detected in the neutral lipids with the aid of model specimens of plant lipids and characteristic color reactions for individual compounds. The quantitative composition of the total NLs was judged from the results of column chromatography (Table 2). The NLs were composed mainly of fatty acids, TAGs, and sterols.

In the PLs, seven groups of compounds were identified, among which the main ones quantitatively were phosphatidylethanolamines, phosphatidylglycerols, and phosphatidylcholines.

The glycolipids consisted of five groups of compounds, among which the main ones quantitatively were cerebrosides, MGDGs and DGDGs.

The fatty acid compositions of the total NLs, PLs, and GLs are given below (% on the total FAs):

	12 : 0	14 : 0	16 : 0	16 : 1	18 : 0	18 : 1	18 : 2	18 : 3	ES	EU
ENLs	1.7	2.3	51.4	4.6	5.3	17.5	10.2	7.0	60.7	39.3
PLs	2.1	2.8	44.8	4.4	5.4	17.1	19.2	4.2	55.1	44.9
GLs	2.6	3.1	54.4	3.8	4.8	16.6	12.4	2.3	64.9	35.1

In the FAs, eight components with C_{12}-C_{18} compositions were identified. The main ones quantitatively were palmitic among the saurated acids and oleic and linoleic among the unsaturated ones. The total GLs were more unsaturated than the other lipids.

Thus, containing a broad set of various lipid classes and pectin, the leaves of *B. oleracea* may be a source of physiologically active additives.

EXPERIMENTAL

The analytical chromatography of the sugars was conducted on Filtrak FN-3, 11 paper in system 1: butanol—pyridine—water (6:4:3). Monosaccharides were detected with acid aniline phthlate.

Solutions were evaporated in vacuum at 45°C. Viscosities of the solutions were measured relative to water in a VPZh-2 capillary viscometer with a diameter of 0.53 mm. GLC was conducted on a Chrom 5 chromatograph using glass columns (0.3 × 200 cm) packed with the phase 5% Silicone XE-60 N-AW-DMCS* (0.160-0.200 mm, 210°C, carrier gas He, 60 ml/min). Monosaccharides were analyzed in the form of aldononitrile acetates [8]. Relative amounts of the sugars were determined from the areas of the peaks on chromatograms.

For TLC we used Silufol and Chemapol 5/40 μm silica gel. The spots of the NLs were revealed with iodine vapor and by spraying with 50% H_2SO_4 followed by heating to 120°C for 3-5 min, those of the PLs by means of the Vas'kovskii and Dragendorff reagents and with ninhydrin, and those of the GLs with α-naphthol [9]. Solvent systems: 2) hexane—ether—acetic acid (70:30:1); 3) hexane—methyl ethyl ketone—CH_3COOH (43:7:1); 4) hexane—ether (3:2); 5) chloroform—methanol—ammonia (65:35:5); 6) chloroform—methanol—water (65:35:5); and 7) chloroform—methanol—acetone—CH_3COOH—water (10:5:4:2:1). For FAMEs, GLC was conducted in a Chrom 4 instrument using a stainless-steel column (0.4 × 250 cm) filled with Chromaton N-AW-DMCS and 17% of PEGS on Celite 545 at a temperature of 198°C.

The fatty-acid compositions of the total NLs and PLs were determined after mild alkaline hydrolysis, isolation, methylation, and GLC analysis [10]. The fatty acid composition of the total GLs was determined as described in [11].

Isolation of the Polysaccharides. The WSPSs, PcSs, and HMCs were obtained as described in [2] from the residual raw material after the isolation of the lipids. For the amounts of polysaccharides and their monosaccharide compositions, see Table 1.

Determination of Monosaccharide Compositions. The WSPSs, PcSs, and HMCs (0.1 g each) were hydrolyzed with 2 N H_2SO_4 at 100°C for 8-24 h. The resulting solution was treated with $BaCO_3$ to a neutral reaction and was centrifuged, evaporated, and analyzed by PC and GLC.

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