

THE STUDY OF CARBOHYDRATES OF CORN RAW MATERIALS

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The aim. The aim of the study was to study the content of polysaccharide fractions depending on the dissolution, qualitative composition and quantitative content of sugars in corn silk, leaves and roots.

Materials and methods. To study different fractions of polysaccharides – water-soluble polysaccharides (WSPS), pectin substances (PS), hemicelluloses A (HC A) and B (HM B) used a gravimetric method based on the extraction of polysaccharide fractions with a suitable solvent followed by sedimentation and weighing of the sediment. Determination of the qualitative composition and quantitative content of monosaccharides in corn medicinal plant materials (MPM) was carried out by the method of gas chromatography-mass spectrometry (GC/MS).

Results. Conducted studies of corn silk, leaves and roots carbohydrates using the fractionation method indicate the following trend of BAS accumulation in the studied raw materials: the content of WSPS and PS in corn silk exceeded the content of these compounds in other types of raw materials – 4.07 ± 0.14 % and 7.20 ± 0.29 %, respectively; leaves accumulated the most HC A and HC B compared to the content of these fractions in other samples – 6.81 ± 0.21 % and 21.20 ± 0.84 %, respectively. It was established by the GC/MS method that 4 substances were identified in corn silk in the free state: arabinose, glucose, galactose and fructose. After hydrolysis 5 substances were identified in corn silk – arabinose, xylose, mannose, glucose, galactose. Among the free sugars 3 compounds were found in corn leaves – glucose, fructose and sucrose. After hydrolysis, 4 compounds were identified in in corn leaves – arabinose, xylose, glucose and galactose. In corn roots 3 compounds are found in a free form – glucose, fructose and sucrose. After hydrolysis 4 compounds were identified in corn roots – arabinose, xylose, glucose and galactose.

Conclusions. The obtained results indicate a significant content of polysaccharides and sugars in the raw materials of corn, which makes it possible to predict the anti-inflammatory, detoxifying, adsorbing, energetic activity of the studied types of corn plant raw materials

Keywords: corn, corn silk, leaves, roots, carbohydrates, fractionation, gas chromatography/mass spectrometry

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1. Introduction

Agricultural crops of plants began to be used not only for the needs of the food industry, but also as raw materials for the creation of feeds, medicinal substances, drugs and dietary supplements with various pharmacological activities. One of the important factors for the widespread use of agricultural crops is a sufficient raw material database of plants. The use of all parts of plants – fruits, green mass, underground organs, makes it possible to consume them without waste and in a wide range of industries.

Maize (*Zea mays* L.) belongs to these plants. All over the world, corn is used in the food industry. The following are obtained from seeds: groats, canned food, corn flakes, flour, starch, molasses, glucose, alcohol, syrups, honey, beer and many other products [1]. In various branches of industry, more than 40 types of various products are produced from the stalks, rods and wrappers of cobs – insulating pads, linoleum, cellulose, furfural, glue, paper, viscose, activated carbon and others [2, 3]. It is important to stock corn in animal husbandry [4, 5]. Corn grain, silage, straw, green mass, cob stalks are used to obtain fodder for feeding farm animals [6, 7].

Corn silks (*Zea mays* styli cum stigmati) is a pharmacopoeial [8] medicinal plant material that is used

as a hemostatic, choleric, diuretic, and hypotensive agent [9]. This type of corn raw material is rich in various groups of biologically active substances (BAS) – flavonoids, tannins, hydroxycinnamic acids, saponins, fatty acids, and carotenoids [1, 10, 11].

Recent studies confirm that maize roots and leaves are also BAS-rich raw materials with promising pharmacological activity. The leaves of maize contain triterpene saponins, steroids, carotenoids, chlorophylls, flavonoids, and hydroxycinnamic acids [12]. Phytochemical screening revealed the presence of various BAS such as tannins, flavonoids, terpenoids and alkaloids in aqueous extracts of maize roots [13]. Pharmacological studies of the ethanol extract of the roots and leaves of corn prove its anti-inflammatory and analgesic effect [14, 15].

The given data confirm the breadth of research on phenolic and terpene compounds of maize raw materials. But other BAS groups need further research.

Great importance in fodder production is attached to the quality of fodder, its chemical composition and nutritional value, absence of poisonous and harmful substances. This is important not only for the development, reproduction, and health of animals but also for providing people with high-quality food [4–7]. The pharmaceu-

tical and medical industries need carefully studied plant raw materials for obtaining medicines, dietary supplements, and plant substances of high quality and safety.

Carbohydrates, namely sugars, polysaccharides, are an important component of plants that have wide-ranging use. These compounds have an anti-inflammatory, immunostimulating, detoxifying, adsorbing, energetic effect on the body of humans and animals [16].

The study of carbohydrates of silks, leaves and roots of maize will allow to expand the range of medicinal plant raw materials for the development and creation of medicines and dietary supplements with different pharmacological activity.

The aim of the study was to study the qualitative composition and quantitative content of carbohydrates in silks, leaves and roots of corn, namely polysaccharides and sugars.

2. Research planning

The analysis of scientific publications indicates that research on the chemical composition of medicinal plant raw materials of maize (MPRM) is mainly devoted to the study of phenolic compounds, terpenes: flavonoids, hydroxycinnamic acids, saponins [1–3]. Carbohydrates – mono-, di-, polysaccharides – have not been studied enough, although they also determine the pharmacological activity of medicinal plant raw materials, they can be markers for its standardization. Roots, leaves, silks require an in-depth phytochemical study of carbohydrates. The study includes the following stages, shown in Fig. 1.

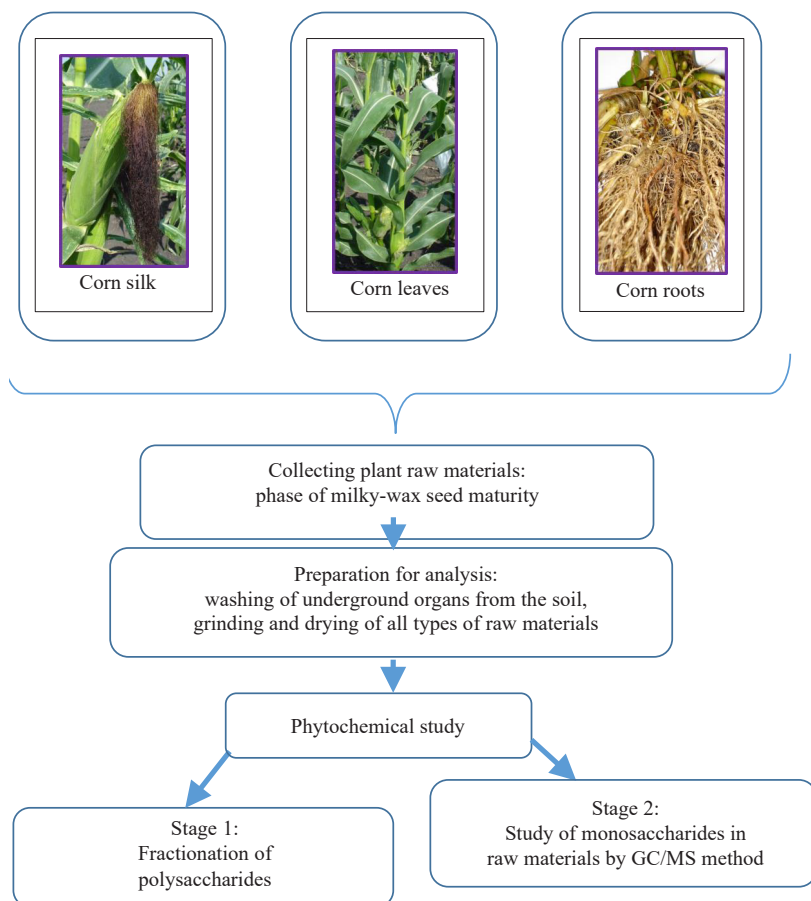


Fig. 1. Scheme of research of maize raw materials

3. Materials and methods

The objects for the study were the roots, silks and leaves of the maize, Svitlana variety as one of the most promising and the one included in the State Register of plant varieties suitable for distribution in Ukraine. The material of maize was grown on one research plot of the plant production institute named after V. YA. Yuriev of National Academy of Agrarian Sciences of Ukraine (Kharkiv). The raw materials were collected in 2021, crushed and dried by the air-shade method.

The plant raw material was harvested in the phase of milky-waxy seed maturity. The chosen phase of the growing season is consistent with the greatest accumulation of active substances in the silks with agricultural production. That is, both above-ground and underground parts of the plant can be harvested at the same time with further use in various fields: nutrition, fodder production, medicine, pharmacy.

Fractionation of polysaccharides was carried out according to a well-known technique, the gravimetric method, which is based on the defatting of raw materials with chloroform followed by the extraction of raw materials with various solvents for the precipitation of water-soluble polysaccharides (WSPS), pectin substances (PS), hemicelluloses A (HC A) and B (HC B) [17].

Determination of the qualitative composition and quantitative content of monosaccharides in raw corn was carried out by the method of gas chromatography-mass spectrometry (GC/MS) before and after complete acid hydrolysis [18, 19]. The research was carried out on an Agilent 6890N/5973 inert chromatograph (Agilent technologies, USA). Separation conditions: HP-5ms capillary column (30 m×0.25 mm×0.25 μm, Agilent technologies, USA), evaporator temperature – 250 °C, interface temperature – 280 °C. The separation was carried out in the temperature programming mode: start – 160 °C for 8 min; further changes in temperature – raised with a gradient of 5 °C/min to 240 °C; final temperature – 240 °C for 6 min. The sample volume is 1 μl, the flow split mode is 1:50; detection in SCAN mode in the range (38–400 a.m.); carrier gas flow rate – 1.2 ml/min. The identification of monosaccharides was carried out according to the retention time of the standards of these substances and using the NIST 02 mass spectrum library. The following mixture of standard samples of monosaccharides was used: ribose, rhamnose, arabinose, xylose, fructose, mannose, glucose, galactose. Among the disaccharides, a standard sample of sucrose was used. Quantitative analysis of identified substances was performed by adding a solution of the internal standard to the tested samples. Sorbitol solution was used as an internal standard. To obtain aldonitrile derivatives of monosaccharides, 32 mg/ml of

hydroxylamine hydrochloride in a pyridine-methanol mixture (4:1) was used as a derivatizing reagent. Acetic anhydride and dichloroethane were added for acetylation of aldonitrile derivatives of monosaccharides.

The mass of monosaccharide (X, mg/kg) was calculated according to the formula:

$$X = \frac{S_x \times C_{is} \times V \times 1000}{S_{is} \times m \times V_e} \tag{1}$$

where S_x – monosaccharide peak area;
 C_{is} – concentration of the internal standard, mg/ml;
 V – volume of solvent for extraction (hydrolysis of the sample), ml;
 S_{is} – peak area of the internal standard;
 m – weight of raw materials, mg;
 V_e – volume of extract for analysis, ml.

Statistical analysis. Results were the mean ± SD of three parallel measurements. All statistical comparisons and reliability were performed using the Student’s t test to determine the standard deviation at the 95 % significance level. Statistical processing of the obtained results was carried out by the method of least squares in accordance with the monograph of the SPhU “5. 3. N. 1. Statistical analysis of the results of a chemical experiment” (2015).

4. Research results

Fractionation of polysaccharides.

The results of fractionation of polysaccharides are shown in Table 1.

The results of the study indicate the following trend of BAS accumulation in the studied raw materials: the content of WSPS and PS in silks with receivers exceeded the content of these compounds in other types of raw materials and amounted to 4.07±0.14 % and 7.20±0.29 %, respectively; leaves accumulated the most HC A and HC B compared to the content of these frac-

tions in other samples – 6.81±0.21 % and 21.20±0.84 %, respectively. Analyzing the content of fractions in each type of raw material, we can state that HC B prevails in columns with silks, leaves and roots.

Table 1

Results of fractionation of polysaccharides of corn raw materials

Research objects	Quantitative content, %			
	WSPS	PS	HC A	HC B
Silks	4.07±0.14	7.20±0.29	3.84±0.17	17.02±0.82
Leaves	2.70±0.08	3.84±0.11	6.81±0.21	21.20±0.84
Roots	1.51±0.04	1.78±0.07	4.61±0.16	13.42±0.40

Determination of the qualitative composition and quantitative content of monosaccharides.

The results of studying the monosaccharide composition are shown in Table 2. The chromatograms are shown in Fig. 2.

In the free state, the raw material of maize, Svitlana variety ordinary had a much lower content of monosaccharides than after hydrolysis. In the silks, 4 substances in the free state were identified: arabinose, glucose, galactose and fructose; the largest amount contains fructose (38.90±1.17 mg/kg) and glucose (25.06±0.78 mg/kg) (Table 2). After hydrolysis, 5 substances were identified in the silks – arabinose, xylose, mannose, glucose, galactose, among which glucose 63.85±1.92 mg/kg was found in the largest amount.

Among the free sugars in the leaves of the maize, Svitlana variety, 3 compounds were found – glucose, fructose and sucrose, and the content of sucrose prevailed over the content of other leaf sugars – 15.14±0.63 mg/kg. After hydrolysis, 4 compounds were identified in the leaf – arabinose, xylose, glucose and galactose. Xylose prevailed in the content of other compounds identified in the leaf after hydrolysis – 61.24±2.20 mg/kg.

Table 2

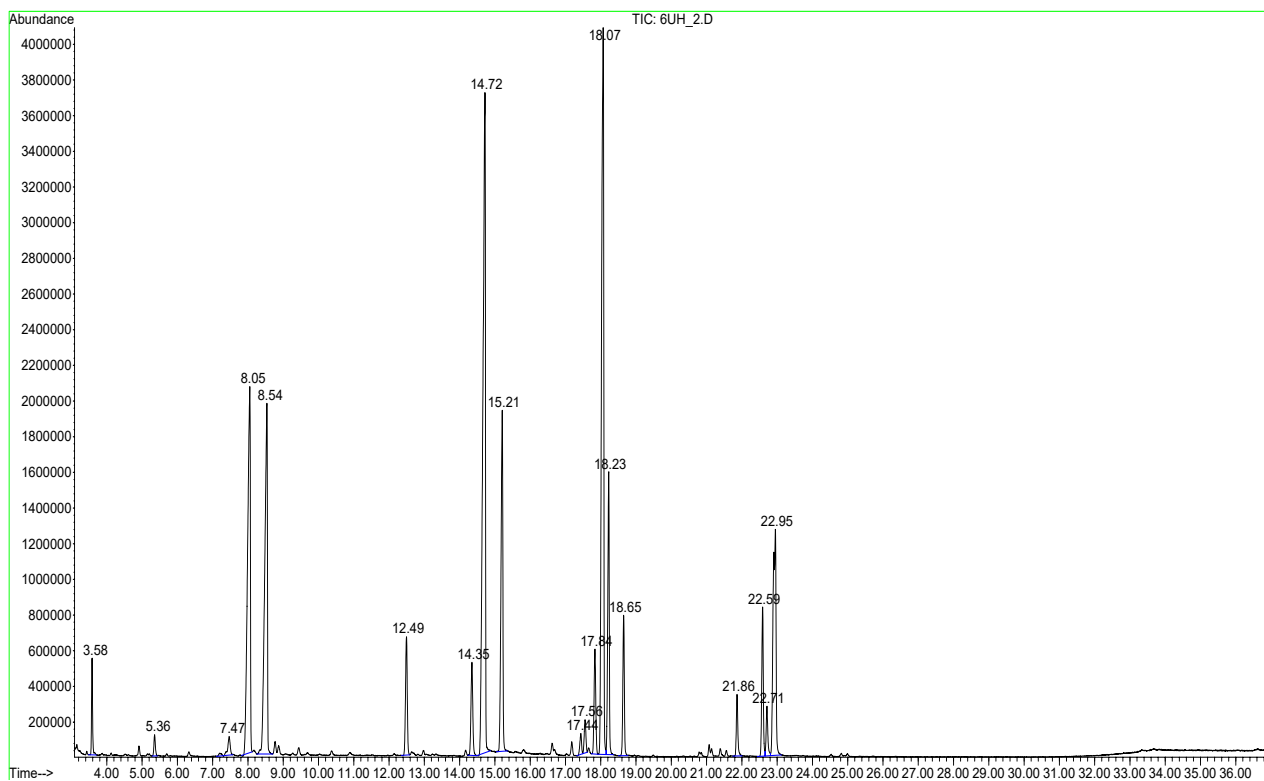
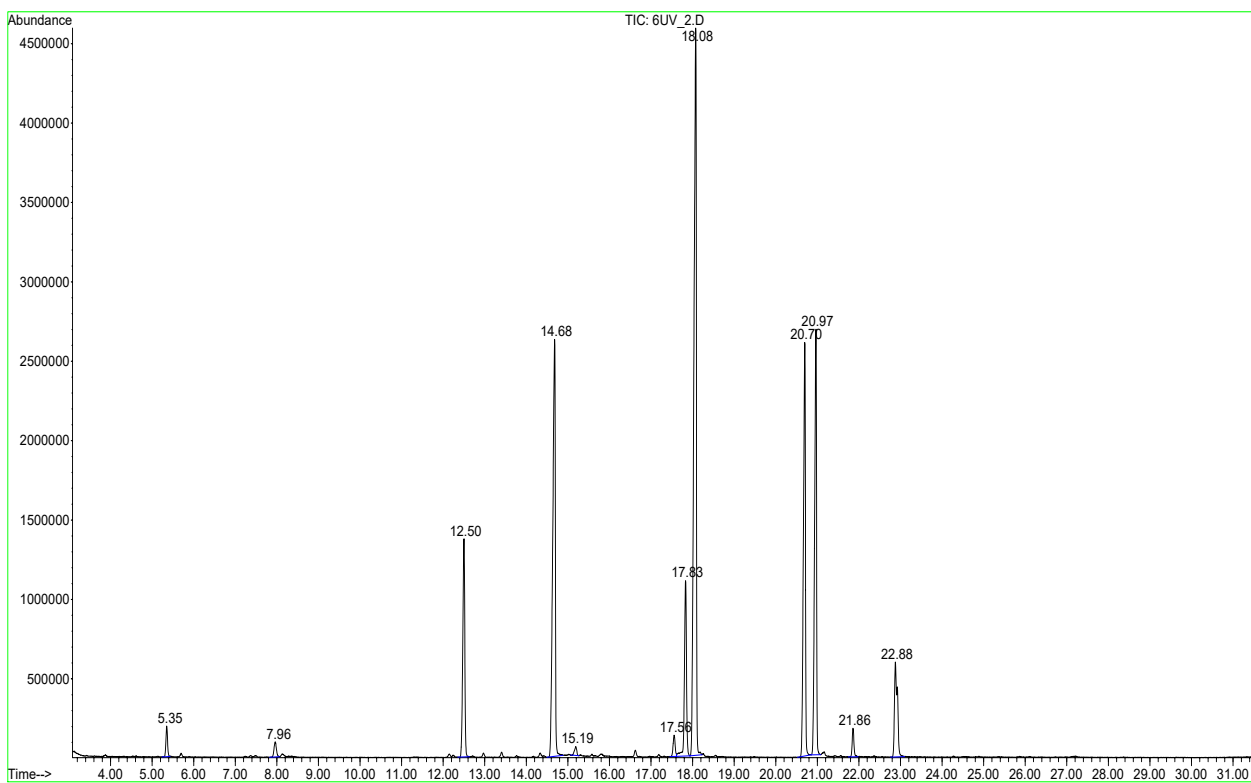
Content of free monosaccharides and monosaccharides after hydrolysis in corn MPRM (GC/MS method)

Carbohydrate standard	Type of raw material					
	Silks		Leaves		Roots	
	Retention time, min	Content, mg/kg	Retention time, min	Content, mg/kg	Retention time, min	Content, mg/kg
Free carbohydrates						
Arabinose	7.96	0.85±0.03	–	–	–	–
Glucose	14.68	25.06±0.78	14.61	2.96±0.11	14.65	56.62±1.70
Galactose	15.19	0.47±0.02	–	–	–	–
Sorbitol	18.07	i/s	18.06	i/s	18.06	i/s
Fructose	20.69 20.96	38.90±1.17	20.64 20.90	2.40±0.07	20.67 20.93	56.96±2.26
Sucrose	–	–	33.74	15.14±0.63	33.77	124.41±3.98
Carbohydrates after hydrolysis						
Arabinose	8.05	38.61±1.16	7.97	18.05±0.57	7.96	10.60±0.40
Xylose	8.53	36.27±1.08	8.50	61.24±2.20	8.47	45.20±1.44
Mannose	14.35	6.45±0.26	–	–	–	–
Glucose	14.71	63.85±1.92	14.64	42.17±1.77	14.67	94.61±3.78
Galactose	15.21	23.95±0.72	15.15	7.90±0.24	15.15	5.94±0.19
Sorbitol	18.07	i/s	18.08	i/s	18.07	i/s

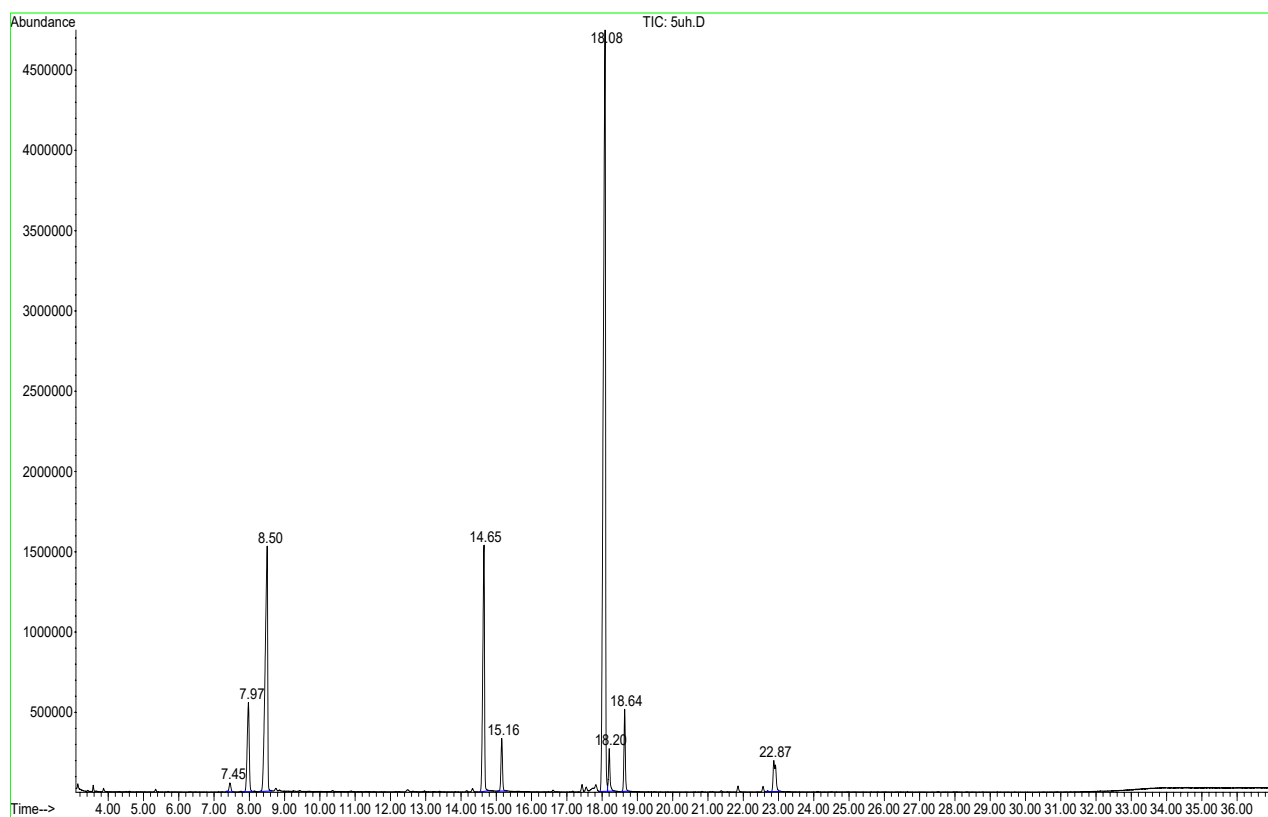
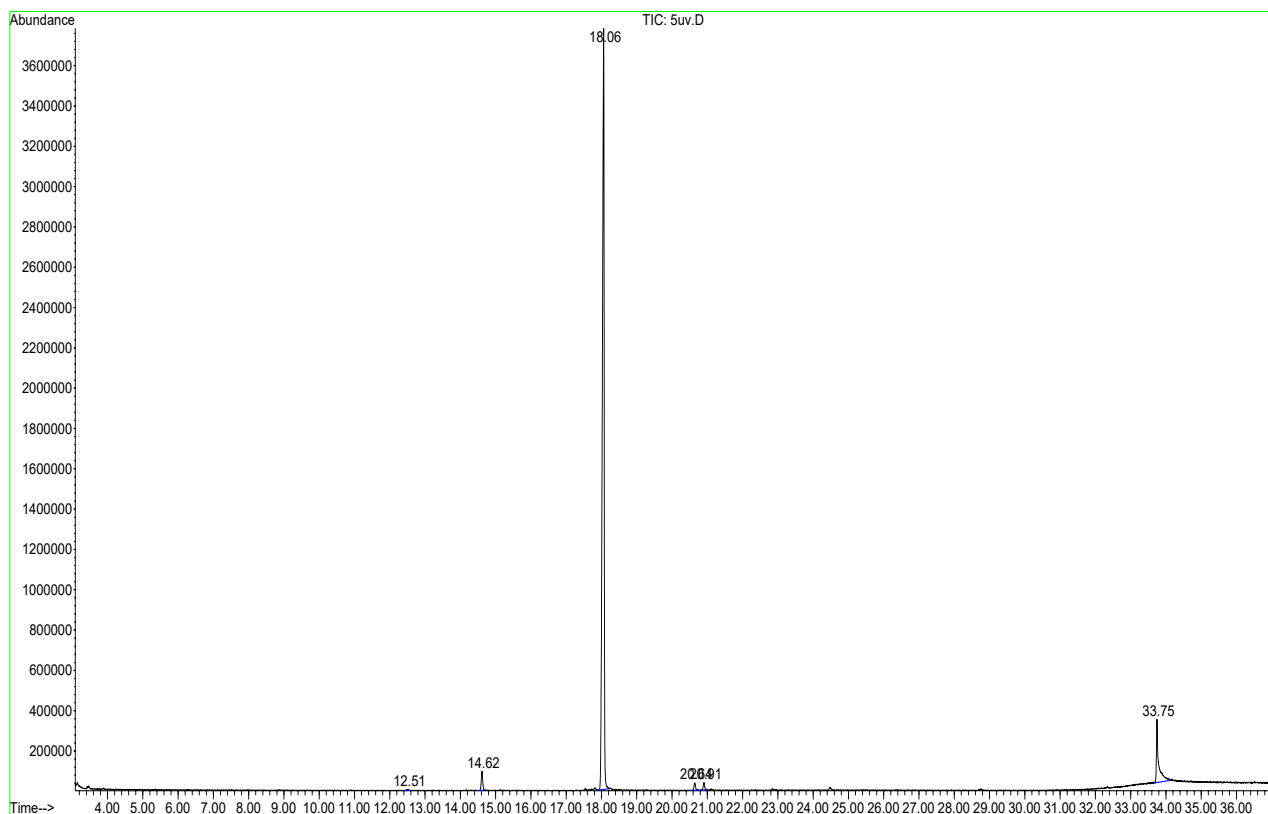
Note: i/s – internal standard

3 compounds – glucose, fructose and sucrose – were found in the roots of corn in a free state. A preference for sucrose of 124.41 ± 3.98 mg/kg was observed. After hydrolysis, 4 compounds were identified in corn

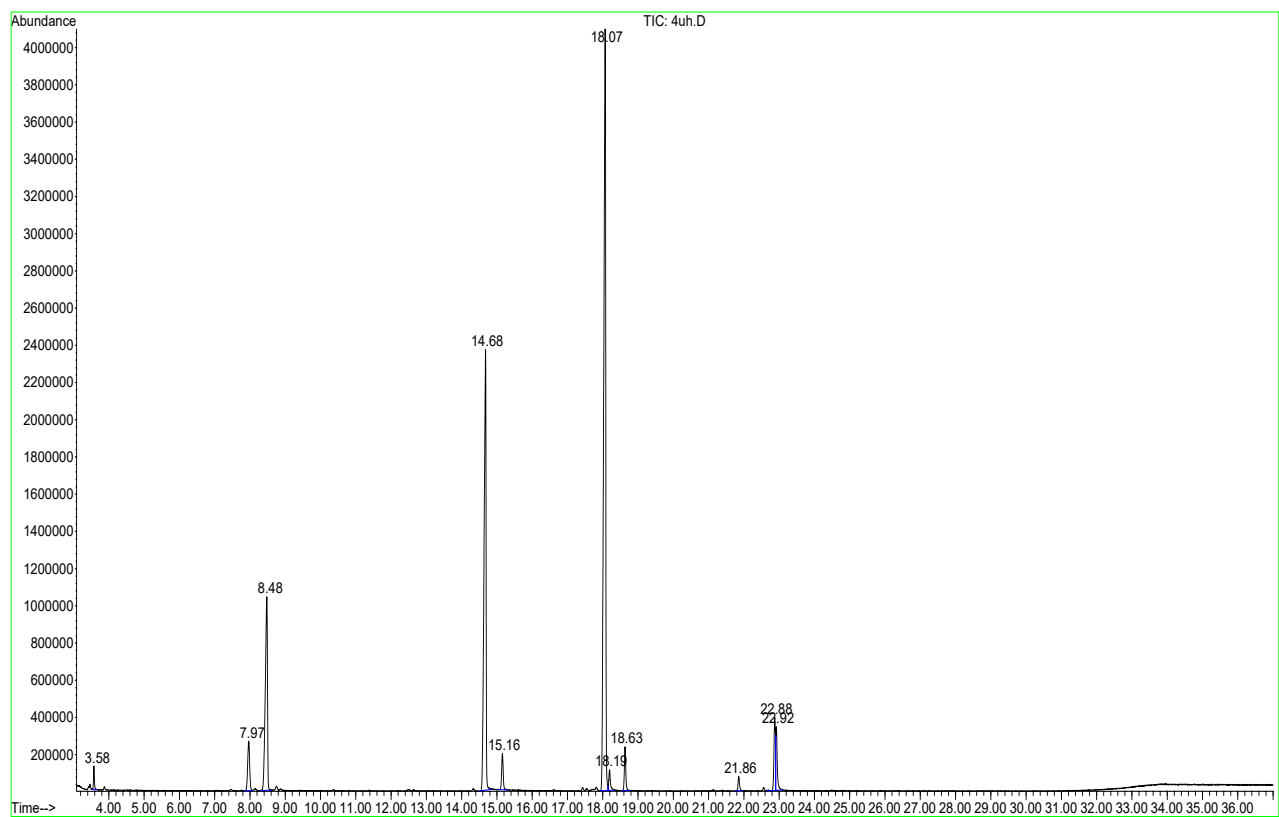
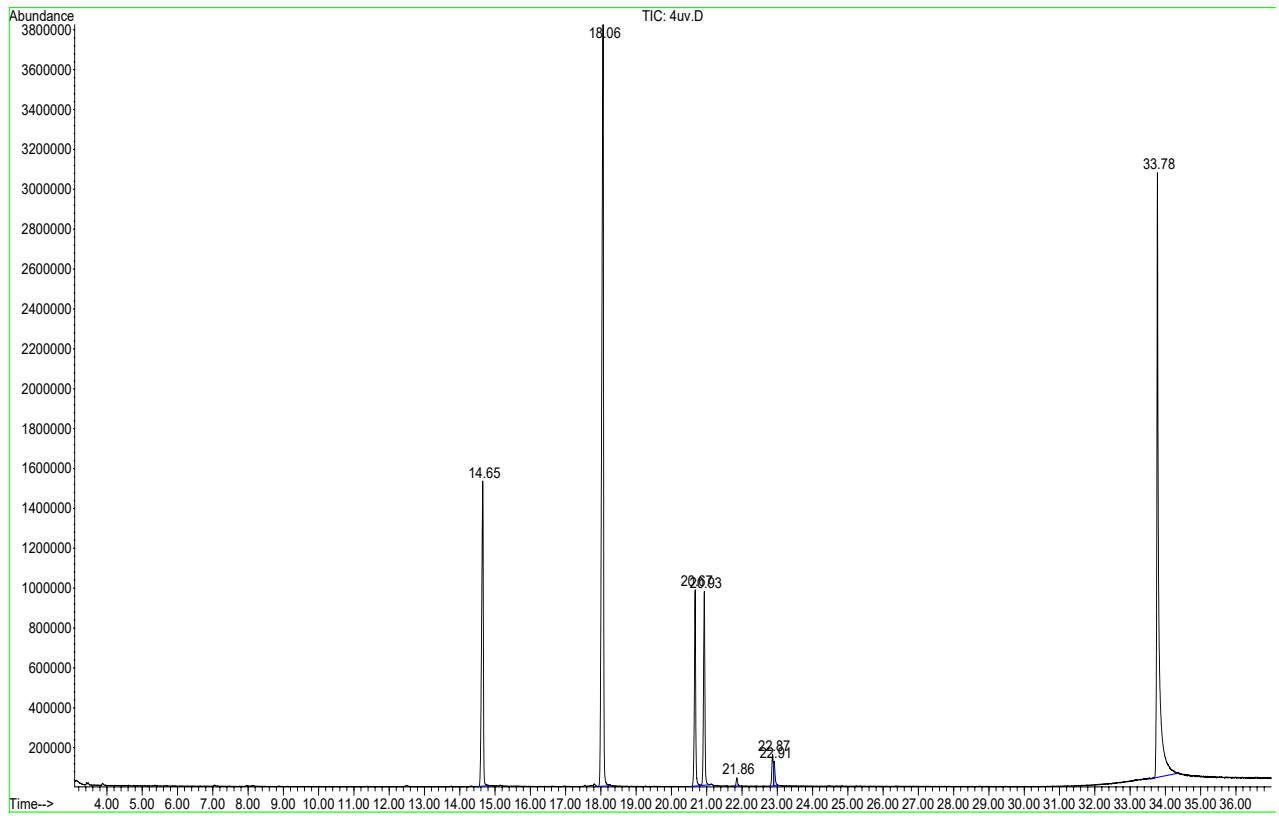
roots - arabinose, xylose, glucose and galactose. The content of glucose prevailed over the content of other identified compounds in the roots after hydrolysis – 94.61 ± 3.78 mg/kg.



a



b



c

Fig. 2. Schemes of chromatograms of free (1) and total (2) sugars of maize raw materials: a – silks; b – leaves; c – roots

5. Discussion of research results

Conducting studies of carbohydrates of silks, leaves and roots of maize by the fractionation method indicate the content in these types of raw materials of WSPS, PS and HC. The obtained results indicate a significant content of polysaccharides, which makes it possible to predict the anti-inflammatory, detoxifying, adsorbing, energetic activity of the studied raw materials of maize.

The precipitation method by scientists Liang Zhang et al. (2021) established the content of polysaccharides in corn silks at the level of 4.33 ± 0.08 %, which corresponds to our results [20].

The GC/MS method made it possible to establish the qualitative composition and quantitative content of mono- and disaccharides in the raw material of maize.

Among the MPRM, glucose and fructose in the free state dominated in silks, and sucrose in leaves and roots. The difference in the composition of monosaccharides of the raw materials of maize is also the presence of galactose and arabinose in a free state in silks, which are absent in leaves and roots.

Based on the results obtained after hydrolysis, we can predict that the polysaccharides of these types of MPRM belong rather to hetero forms. The presence of mannose in silks is also a feature. Mannose can become a marker for this type of raw material. It should also be mentioned the use of mannose for the prevention and treatment of infectious diseases of the urinary tract. It has been proven that mannose has an anti-adhesive effect, that is, it creates specific conditions for the existence of uropathogenic strains, namely, it prevents their binding to the urothelium. In the EU, medical products containing D-mannose are intended for the prevention of urinary tract infections. This may also explain the effectiveness of corn silks in diseases of the urinary tract [21, 22].

Leaves and roots are similar in the composition of identified monosaccharides before and after hydrolysis. This allows us to predict the possible similarity in the structure of polysaccharides and glycosides, which are part of these types of raw materials of maize.

Research by Bruce G. Abedon (2005) indicates the presence of normal glucose, xylose, arabinose, and galactose in the corn leaf, which are components of the cell wall, water-soluble polysaccharides, and pectin substances. Our studies of determining the composition of sugars after hydrolysis confirm the presence of arabinose, xylose, glucose, and galactose in the leaves of maize [23].

The advantage in the quantitative content of glucose, fructose and sucrose in the free state in the roots of corn, compared to other types of MPRM, may be related to the functions performed by the roots, namely storage.

Glucose, fructose, and sucrose are the most abundant free mono- and disaccharides in raw corn according to Garret Couture et al. (2021) [24], which is confirmed by the data of our study.

The leaves and roots had a simpler composition of monosaccharides, in contrast to the silks.

Carbohydrates, namely sugars, polysaccharides, are an important component of plants that have wide-ranging use. These compounds have an anti-inflammatory, immunostimulating, detoxifying, adsorbing, energetic effect on the human body and animals [16].

Study limitations. The method chosen for the study of raw material monosaccharides involves the derivatization of carbohydrates with the formation of their aldonitrile acetates, but during sample preparation after hydrolysis, ketoses cannot react, which is the main drawback of this method and does not provide a full understanding of the composition of complex compounds of leaves, roots and silks of maize - glycosides, polysaccharides [25].

Prospects for further research. Further research can be directed to the study of the qualitative composition and quantitative content of monosaccharides WSPS, PS, HC A and HC B.

6. Conclusions

1. The study of polysaccharides of the maize raw materials of the silks, leaves and roots, Svitlana variety, was carried out. It was determined that the content of HC B prevails in all studied objects and was 17.02 ± 0.82 %, 21.20 ± 0.84 %, 13.42 ± 0.40 %, respectively.

2. The conducted studies of the content of free monosaccharides by the GC/MS method made it possible to establish the superiority of fructose, sucrose and glucose in all the selected objects of ordinary corn of the Svitlana variety.

3. The data obtained after the hydrolysis of the raw material of maize confirm the presence of sugars as components of other compounds. We identified arabinose (0.85 ± 0.03 mg/kg), xylose (from 36.27 ± 1.08 to 61.24 ± 2.20 mg/kg), mannose (6.45 ± 0.26 mg/kg) and galactose (from 5.94 ± 0.19 to 23.95 ± 0.72 mg/kg) in raw maize only after hydrolysis.

4. Sugars have an energy function, participate in metabolism and can act as markers in the standardization of MPRM.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, including financial, personal, authorship or other nature, which could affect the research and its results presented in this article.

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Availability of data

The manuscript has no associated data.

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This manuscript is dedicated to the memory of professor Victor Ivanovych Gnoevoy (February 29, 1936 – March 1, 2021).

Sincere bow to professor Gnoevoy V. I. and gratitude for his scientific achievements, advice, ideas, vision, help. Bright memory...

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