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Molecular weight characteristics and sorption properties of pectin extracted from different substrates

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Abstract: *The study of natural polymers is one of the most advanced tasks of modern chemistry. One of these polymers is the common polysaccharide pectin. Widespread acid hydrolysis was used to extract pectin from various substrates. Oxalic, citric and hydrochloric acids have been investigated for this purpose. The water-soluble pectin-containing fraction was extracted from the apples, sugar beet, lemon peel, pine needles. The optimal condition is heating the substrate in a boiling water bath for 1 hour with reflux in a solution of hydrochloric acid (pH 2–3). We neutralized the extract after cooling with an ammonia solution to isolate the dry powder of the pectin-containing component and the pectin was precipitated with ethanol. The study of pectin solutions by the method of gel permeation chromatography showed that they most often have three polymer fractions that are close in molecular weights: ~17–20, ~10–12 and ~0.5 kDa. The content of the last fraction in all selected samples is predominant. Solutions of pre-planted powders of the pectin-containing fraction significantly differ from the previously discussed results: the oligomeric fraction is practically absent in them. For a number of samples of pectin powders, the degree of esterification was determined by potentiometric titration. The dependence of the degree of esterification on both the feedstock and the isolation method was revealed. The method of reverse complexometric titration was used to study the sorption capacity of pectin. The analysis results suggest that there is an inversely proportional dependence of the degree of lead sorption of the pectin sample on its degree of esterification.*

Keywords: *pectin-containing fraction, degree of esterification, molecular mass characteristics, sorption capacity*

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Молекулярно-массовые характеристики и сорбционные свойства пектина, выделенного из разных субстратов

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Резюме: *Исследование природных полимеров является одной из передовых задач современной химии. Один из таких полимеров – полисахаридный пектин. Для его выделения из разных субстратов использовали широко распространенный кислотный гидролиз. Для этой цели исследованы щавелевая, лимонная и соляная кислоты. Водорастворимую пектинсодержащую фракцию выделяли из кожуры, ядрышек и жмыха яблок, жмыха сахарной свеклы, лимонной корки, хвои сосны. Оптимальным условием является нагревание субстрата на кипящей водяной бане в течение 1 ч с обратным холодильником в растворе соляной кислоты (pH = 2–3). Для выделения сухого порошка пектин-содержащего компонента экстракт после охлаждения нейтрализовали раствором аммиака и осаждали пектин этанолом. Исследование растворов пектина методом гельпроникающей хроматографии показало, что они имеют чаще всего три полимерные фракции, близкие по значению молекулярных масс: ~17–20, ~10–12 и ~0,5 кДа. Содержание последней фракции во всех выделенных образцах было преимущественным. Растворы предварительно высаженных порошков* *пектинсодержащей фракции заметно отличались от ранее обсужденных результатов: в них олигомерная фракция практически отсутствует. Для ряда образцов порошков пектина была определена степень этерификации методом потенциометрического титрования. Выявлена зависимость степени этерификации как от исходного сырья, так и от способа выделения. Для изучения сорбционной способности пектина, выделенного из разных субстратов, применяли метод обратного комплексонометрического титрования. Результаты анализа позволяют утверждать, что имеет место обратно пропорциональная зависимость степени сорбции свинца образца пектина от его степени этерификации.*

Ключевые слова: *пектинсодержащая фракция, степень этерификации, молекулярно-массовые характеристики, сорбционная способность*

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INTRODUCTION

Natural polymers are currently the most widely used. Pectin is a water-soluble biologically active polymer and has universal properties: sorption, radioprotective properties, gelling ability. It has various applications in the food industry, medicine and animal husbandry due to its physicochemical and functional properties [1–8]. Pectin poly-saccharides are especially common in fruit and vegetable materials [8–11]. Publications devoted to the isolation of pectin from various substances are numerous, however, the methods of isolation, and, accordingly, the properties of the isolated products differ markedly [9, 11–16]. There are different approaches to the analysis of important properties of pectins, presented both in articles on experimental data and in reviews [5, 8, 17–22]. It has been shown that the hydrolysis time affects the change in the size and branching of polymers [20]. In addition, the strength of acid affects the chain length: the stronger the acid acts in hydrolysis, the lower the molecular weight of the resulting molecule. At pH = 1, the extracts are especially rich in rhamnogalacturonan, the nature and amount of side chains also differ depending on the extraction conditions [23]. Gelation is one of the most important characteristics of pectin. A number of factors-pH, presence of other solutes, molecular size, degree of methoxylation, number and arrangement of side chains, and charge density on the molecule – influence the gelation of pectin. In low-methoxyl pectin, gelation results from ionic linkage via calcium bridges between two carboxyl groups belonging to two different chains in close contact with each other. In high-methoxyl pectin, the cross-linking of pectin molecules involves a combination of hydrogen bonds and hydrophobic interactions between the molecules [24]. Recent research has demonstrated how cross-linking of pectic polysaccharides to obtain gel formation can be promoted by enzymatic catalysis reactions [25]. In general, the chemistry and mechanism of pectin-based crosslinking are well understood from the point of view of pharmacy, biology and ecology. They are used as a immunostimulatory and anti-inflammatory drug [1, 26]. Even the bioactivity of pectin as antibiotics has been studied [27]. Crosslinked hydrogels have valuable properties such as volubility, swellability, solvability and hydrophilicity, which make them better alternative for wastewater treatment. The adsorption characteristics of pectin based hydrogels can be upgraded by using nanoparticles, which prompts to the development of hydrogel nanocomposites [2, 4, 7, 28].

The aim of this work is to obtain comparative data on a water-soluble pectin-containing fraction isolated by acid hydrolysis from various substances, by molecular weight parameters and sorption ability.

EXPERIMENTAL

Preparation of starting materials for the experiment. The raw materials were dried in a vacuum oven at a temperature of 45–50 ºC, crushed, treated several times with acetone to remove essential oils, sugars, wax.

Methodology of extraction of the pectin-containing fraction from various substrates. Pectin was extracted from the feedstock with a solution of acid with pH 2–3 (hydrochloric, boric, oxalic, phosphoric, acetic) under heating in a boiling water bath in a flask under reflux for 1 hour. The hot extract was separated by filtration through nylon tissue. The filter residue was washed with hot water until the ions of the acid residue were negatively reacted.

Methodology for isolating the pectin-containing component from the solution by evaporation of the solvent. The extract was placed in a flask of rotary evaporators and evaporated for 2–3 hours at 800 ºC under reduced pressure. Evaporation was continued to a volume of about 50–100 ml.

Methodology for isolating the pectin-containing component from the solution by reprecipitation. To isolate the dry powder of the pectin-containing component, the extract, after cooling, was neutralized with an ammonia solution and pectin was precipitated with ethanol. The pectin isolated on a filter from kapron tissue was washed with alcohol and then dried to constant weight.

Analysis of molecular mass characteristics. The determination of MMD was performed by Gel permeation chromatography (GPC) in the center of collective use of equipment of Lobachevsky State University using a Shimadzu CTO20A/20AC high-performance liquid chromatograph (Japan) with LC-Solutions-GPC software module. Separation was performed on a Tosoh Bioscience TSKgel G3000SWxl column with a pore diameter of 5 μm. An ELSD-LT II low-temperature light-scattering detector was used as a detector. An eluent was a 0.5 M solution of acetic acid. A flow rate of 0.8 ml/min. For calibration, finely dispersed dextran samples with a molecular weight range (MM) of 1000–410000 Da (Fluca) were used.

Method for determining the degree of esterification of pectin [10]. To determine the degree of esterification, a weighed portion of pectin 0.5 g of the powder was dissolved in water at a temperature of about 40 ºC. The resulting solution was titrated potentiometrically with a 0.1 M sodium hydroxide solution. Mass fraction of $\omega_1$free carboxyl groups was calculated by the formula:

$$\omega_1, \% = \frac{V_1(NaOH)\times C(NaOH)}{m}\cdot 0.45 \qquad (1)$$

V_1(NaOH) – equivalent volume of alkali, ml; C(NaOH) – alkali concentration, mol/l; m – pectin weight, g; 0.45 – conversion factor for the mass of carboxyl groups.

Then, 10 ml of 0.5 M NaOH was added to the neutralized sample and kept at room temperature for hydrolysis of methoxylated carboxyl groups. After 2 hours, 10 ml of 0.5 M HCl was added to the sample and its excess was titrated potentiometrically. The mass fraction of esterified groups of ω_2 was calculated by the formula:

$$\omega_2, \% = \frac{V_2(NaOH)\times C(NaOH)}{m}\cdot 0.45 \qquad (2)$$

The degree of esterification was calculated by the formula:

$$Q = \frac{V_2}{V_1 + V_2}\cdot 100\% \qquad (3)$$

Methodology for determining the sorption capacity (SC) of a pectin-containing fraction [10]. A weighed portion of pectin (0.3–0.5 g) was dissolved in distilled water, transferred to a 100–200 ml volumetric flask, 50 ml of a lead acetate solution with a concentration of 0.07 mol equivalents/l were added, and the volume was adjusted to the mark with distilled water. After an hour, the solution was filtered through a filter of nylon fabric. An aliquot of the filtrate (20 ml) was placed in a titration flask, 20 ml of 0.1 mol equivalents/l of complexon III solution, 15 ml of ammonia buffer solution (pH 10) and a few drops of the eriochrome black T indicator solution were added. It was titrated with 0.1 mol of zinc sulfate solution equivalents/l till the transition color. The control experiment was carried out similarly, but without the addition of pectin. The mass of lead ions remaining in the solution after sorption was calculated by the formula:

$$m\,(Pb^{2+}) = \frac{(C_1\ V_1 - C_2\ V_2)\times M(Pb^{2+})\cdot V_k}{Val} \qquad (4)$$

C_1, V_1 – concentration (mol equivalents/l) and volume (ml) of complexon III solution added to an aliquot of lead pectin solution; C_2, V_2 – concentration (mol equivalents/l) and volume (ml) of zinc sulfate solution; M(Pb^{2+}) – molar mass of lead equivalent, g/mol; $V_к$, V_{al} – volume of volumetric flask and aliquot volume, ml.; *m*(Pb^{2+}) – mass of lead lead ions, mg.

The mass of lead ions in the control solution was calculated by a similar formula.

The sorption ability of pectin was calculated:

$$\mathrm{CC} = \frac{m_k Pb^{2+} - m_p\ Pb^{2+}}{m(\text{pectin})},\ mgPb^{2+}/g \qquad (5)$$

Methodology for sample preparation and analysis on a scanning microscope. The structure of the obtained pectin product was studied using a JSM-IT300 scanning electron microscope (JEOL Ltd., Japan). Samples of dehydrated pectin of lemon raw material were visualized. Dehydration of the samples occurred directly in the JSM-IT300 chamber under low vacuum.

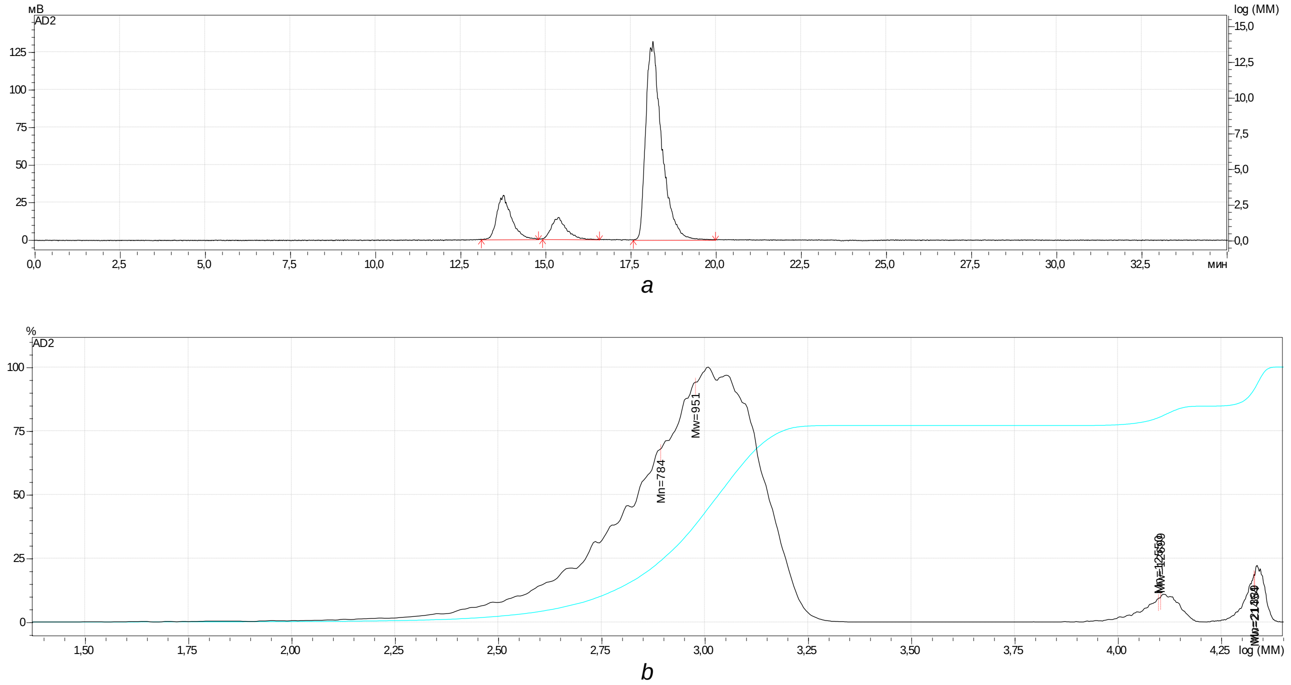
RESULTS AND DISCUSSION

Widespread acid hydrolysis was used to isolate pectin from various substrates [8, 11, 18]. A water-soluble pectin-containing fraction was isolated from apples, sugar beets, lemon peel, pine needles.

Pectin is a high molecular weight polysaccharide. Therefore, we analyzed GPC of isolated pectin, sample of which are demonstrated at the Figure 1.

First of all, it was interesting to compare the molecular mass parameters of the isolated biopolymers, because in the literature, this information is given most often for individual substrates (apples, or citrus fruits, etc.), while the conditions for the isolation of pectin and determination methods differ. The data on the molecular mass parameters of the solutions obtained by GPC are shown in Table 1: No. 1–13 are the solutions after isolation from various substrates, No. 14, 15 – are the powder solutions, No.16–18 are commercial pectins.

As can be seen from Table 1. the studied solutions of the isolated pectin-containing fraction (Table 1, No. 1–13) most often have three polymer fractions that are close in MM value: ~17–20, ~10–12 and ~0.5 kDa. The content of the last fraction in all selected samples is predominant. Obviously, this fraction of oligomers has, as a rule, a high coefficient of polydispersity (1.5–5.7). A similar ratio of fractions and MM values have commercial samples «Unipectin PG DS» and «Aidigo».



a

b

Fig. 1. GPC of sample No. 17 (see Table 1) "commercial apple pectin «Aidigo» (Russia)":
a – chromatogram type; b – type of molecular weight determination

Рис. 1. ГПХ образца № 17 (см. табл. 1) «коммерческий пектин «Айдиго» (Россия)»:
а – вид хроматограммы; b – вид молекулярно-массового распределения

Table 1. Molecular mass characteristics of pectin extracted from the studied samples by various extractants
Таблица 1. Молекулярно-массовые характеристики пектина, выделенного из исследуемых образцов различными экстрагентами

Sample number	Conditions of extraction from sample	M_w, kDa	M_w/M_n	%
1	Sugar beet in the boric acid medium	17.5 10.2 0.5	1.0 1.0 1.5	4 7 89
2	Sugar beet in the oxalic acid medium	17.2 8.2 2.9 0.4	1.0 1.1 1.2 5.7	4 12 16 68
3	Sugar beet in the acetic acid medium	17.5 10.4 0.4	1.0 1.0 2.9	9 10 80
4	Sugar beet in the phosphoric acid medium	16.3 5.6 0.5	1.0 1.2 5.2	8 8 83
5	Apple kernels in the boric acid medium	17.3 9.7 0.3	1.0 1.1 2.9	1 1 98
6	Apple peel in the boric acid in the medium	17.6 10.3 0.33	1.0 1.0 4.8	1 1 98
7	Apple peel in the acetic acid medium	17.5 10.0 0.35	1.0 1.1 2.9	1 1 98
8	Apple of variety «Bolotovskii» in the acetic acid medium	17.5 10.0 0.3	1.0 1.0 2.2	1 1 98
9	Apple of variety «Bolotovskii» in the boric acid medium	17.4 9.8 0.3	1.0 1.0 3.7	3 1 96

10	Apple of variety «Antonovka» in the acetic acid medium	17.6 10.2 0.35	1.0 1.0 4.1	1 1 98
11	Apple of variety «Antonovka» in the boric acid medium	17.7 10.2 0.34	1.0 1.1 6.3	0 1 99
12	Pine needles in the boric acid medium	21.0 12.0 0.4	1.0 1.0 3.7	6 5 89
13	Pine needles in the acetic acid medium	21.3 12.4 0.42	1.0 1.0 2.1	6 5 89
14	Pine needles in the acetic acid medium	21.0 13.0	1.0 1.0	81 19
15	Lemon peels in the hydrochloric acid medium*	22.0 12.7 0.9 0.2	1.0 1.0 1.0 1.2	4 90 2 5
16	Commercial citrus pectin «Unipectin PG DS» (Germany, France)	10.2 0.4	1.0 3.8	6 94
17	Commercial Apple Pectin «Aidigo» (Russia)	21.0 12.7 0.95	1.0 1.0 1.2	15 8 77
18	Commercial Apple Pectin «Pudov» (Russia)	20.0 12.5	1.0 1.0	87 13

*The solution is prepared from ethanol precipitated and dried pectin.

The solutions of pre-isolated powders of the pectin-containing fraction (Table 1. No. 14, 15) differ markedly from the previously discussed results: the oligomeric fraction is completely absent in sample 14, and is minimal in sample 15. Obviously, in this case the oligomeric fraction does not stand out in the form of powder but remains in the «solvent-precipitant” mixture. which is typical for the precipitation of any polymers [29]. The commercial sample «Pudov» has MM values close to these two samples.

Thus, the presented data on the analysis of the molecular mass parameters of the isolated pectin-containing fractions under comparable conditions indicate a significant similarity of these properties for all samples. There is interesting fact that the conducted studies allow us to conclude with a high degree of probability that commercial samples «Unipectin PG DS» and «Aidigo» are obtained by evaporation of the solvent from the solution. while the oligomeric fraction is not lost. The commercial sample «Pudov» does not have an oligomeric fraction which means it was isolated by precipitation from a solution.

The sorption and gelling properties of pectin are associated with the degree of esterification of its monomer unit – polygalacturonic acid: pectin with a small degree of esterification has better sorption characteristics, and with a greater degree – better gelling properties. For a number of samples of pectin powders the degree of esterification was determined by potentiometric titration (Table. 2).

As it follows from the data obtained (Table 2) the degree of esterfication depends on both the feedstock and the isolation method. Using an example of a sugar beet sample it can be seen that the reprecipitation of pectin leads to an increase in the degree of esterification. The degree of esterification for the studied substrates obtained by evaporation of the extractant increases in the sequence «sugar beets»<«Antonovka apples», for the precipitated samples «sugar beets»<«lemon (fruit with thin peel)»=«lemon (fruit with thick peel)». The commercial samples «Pudov» are also close to the latest samples in this parameter.

Table 2. The degree of esterification of some types of pectin

Таблица 2. Степень этерификации некоторых видов пектина

Source substrate	Degree of esterification, %
Sugar beet[1]	13–15
Sugar beet[2]	38–40
Lemon[2] (fruit with a thin peel)	78–80
Lemon[2] (fruit with a thick peel)	78–80
Apples («Antonovka»)[1]	55–65
Commercial pectin «Pudov»	60–80

Note. [1] – pectin obtained by evaporation of the solvent:
[2] – pectin obtained by isolation with ethanol after hydrolysis.

An important indicator of the quality of pectin used for the detoxification of metals is their sorption capacity (SC). This property is widely used in quality assessment in the production of medicines. flocculants. etc. This indicator corresponds to the mass of metal ions (mg of lead). which one gram of pectin can bind. The choice of lead is due to the fact that lead salts are the standard in the analysis of drugs for the content of heavy metals. To study the SC of pectin isolated from different substrates. the method of reverse complexometric titration was used. The results of the analysis are given in Table 3. Based on a comparison of the data of Table 2 (No. 1, 5) and Table 3 (No. 1, 2) it can be argued that there is an inversely proportional dependence of the degree of sorption of lead by pectin samples on its degree of esterification.

Table 3. Sorption capacity of pectin isolated from various raw materials
Таблица 3. Сорбционная способность пектина, выделенного из разного сырья

Source substrate	Sorption capacity Pb^{2+} mg/g
Sugar beet[1]	320–380
Apples («Antonovka»)[1]	170–220
Pine needles	160–170

Note. [1] – pectin obtained by evaporation of the solvent.

For a pectin sample isolated from a lemon peel by ethanol precipitation from an extract. the powder surface was studied by scanning electron microscopy. The fibrillar structure of the biopolymer is clearly visible. The resulting image is similar to those given in the works of other authors [2, 7, 9, 16, 22, 30]. The structure of pectin is an object of research by various instrumental methods [6, 7, 20, 31, 32].

CONCLUSIONS

A pectin-containing fraction was extracted by acid hydrolysisfrom sugar beets. apples. lemon peel. pine needles. Content of three polymer fractions with close MM values: 17–20, 10–12 and ~0.5 kDa was determinedusing GPC. In solutions of pre-precipitatedpowders of the pectin-containing fraction the oligomeric fraction is practically absent. The dependence of the degree of esterification on both the feedstock and the isolation method was revealed. The inverse proportion of the degree of sorption of lead by pectin samples on the degree of its esterification has been established.

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