ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 5, pp. 955–962. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.A. Babkin, Yu.A. Malkov, E.N. Medvedeva, N.N. Trofimova, N.V. Ivanova, 2011, published in Rossiiskii Khimicheskii Zhurnal, 2011, Vol. 55, No. 1, pp. 10–16.

An Eco-Friendly Technology for Polysaccharide Production from Logging and Sawing Waste

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Received November 1, 2010

Abstract—A polysaccharide recovery technology was developed with intent to be used in integrated processing of larch biomass waste into practically significant arabinogalactan, pectin, and crystalline glucose suitable for medicinal, food-industry, and agricultural applications. Theoretical aspects were considered for arabinogalactan extraction from larch wood, in which procedure some of individual stages and the entire process cycle of arabinogalactan recovery on a pilot installation were optimized. The possibility of saccharification of larch wood-derived lignocellulosic residue into crystalline glucose was demonstrated. The results of a technological study on pectin polysaccharide isolation from larch bark were reported along with the findings concerning the membrane tropic activity of pectin and ability to form nanobiocomposites via interaction with transition and noble metal ions.

DOI: 10.1134/S1070363212050283

This study is dedicated to utilization of waste resulted from larch wood processing into building materials. In the existing methods used for wood processing into forest products, ca. 40% of this valuable raw material (bark, slab, sawdust) go to waste which is either burned or dumped. At the same time, the use of an integrated larch wood biomass processing scheme allows obtaining valuable products intended for medicinal, food-industry, and agricultural applications [1, 2].

At the present time, a commercial-scale technology for production of dihydroquercetin (flavonoid) from larch wood is being implemented with a view to further use of this pharmacological substance for preparation of diquertin (a pharmaceutical product), as well as of numerous bioactive food additives thereof [3]. Also, an economically viable and practically feasible technology of isolation of water-soluble polysaccharide arabinogalactan dominating in larch wood is currently under development [4]. Further, an integrated wood processing scheme allows utilization of lignocellulosic residue, a larch wood waste, into carbohydrate products, primarily, crystalline glucose [5].

A very rich source of biologically active compounds, in particular, of pectin polysaccharide, can be found in larch bark. Previously we proposed a scheme for larch bark processing into practically valuable products: wax, antioxidant complex [6], pectin, and sorbents.

Here, we present a technology for isolation of arabinogalactan from wood and also briefly discuss the basic aspects of the technology for preparation of crystalline glucose from larch wood lignocellulosic residue and of pectinaceous polysaccharides from larch bark.

The arabinogalactan content in larch wood may reach 15–20%; most enriched in arabinogalactan is the basis of tree (which goes to wood processing waste) [7–9].

Arabinogalactan exhibits a broad spectrum of biological activity which, combined with high membrane tropic activity and dispersive ability, offer wide prospects for medicinal and veterinary, as well as for food- and cosmetic-industry applications [10]. Membrane tropic activity of arabinogalactan (due to the galactose moieties in its macromolecule) makes it suitable as a kind of nanocontainer for medicines suffering from low bioavailability. For example, arabinogalactan is effective in photodynamic diagnostics and therapy of cancer, as well as in targeted delivery of functional genes in gene therapy [11–13]. As a polyfunctional polymer, arabinogalactan is a useful synton for preparation of a broad spectrum of biologically active substances [14–21]. Despite relative

availability of raw materials for this compound with unique properties, it has not yet achieved commercial production in Russia. At the same time, some foreign companies have been producing arabinogalactan from Western larch (Larix occidentalis Nutt.) and American larch [Larix laricina (Du Roi) K. Koch] wood for over 40 years. In the United States arabinogalactan serves as a source of efficient biologically active food additives with immunomodulating and prebiotic properties. This polysaccharide is successfully used as a fodder additive able to improve the livestock productivity [22].

As regards pectic substances contained in larch bark, they belong to a group of plant polysaccharides known as glycanogalacturonans and find extensive application due to a variety of useful properties, above all, physiological activity [23, 24].

Significantly enhanced larch biomass processing can be achieved through utilization (saccharification) of lignocellulosic waste into crystalline glucose.

Arabinogalactan: A Technology for Recovery from Larch Wood

The currently existing arabinogalactan preparation procedures are based on water extraction of this polysaccharide from chopped larch wood (wood chips, shavings, sawdust) at room, or elevated, temperature [7, 8, 25–27]. The degree of recovery of the substance extracted strongly depends on the raw wood material particle size. For example, within the first 10 min of extraction from sawdust (specific surface area 164 $cm^2 g^{-1}$), nearly 90% of arabinogalactan is extracted against only 10% in the case of extraction from wood chips (specific surface area 17 $cm^2 g^{-1}$) [9]. The extraction can be intensified by mechanochemical activation of wood and its processing with superheated steam (explosive autohydrolysis) [28]. The degree of arabinogalactan recovery significantly (more than twice) increases when larch sawdust is exposed to microwave-assisted water extraction or that with shock and acoustic treatment [29]. However, practical implementation of these methods seems to be unlikely so far because of the need in considerable investment.

An interesting (though lacking the physical embodiment) solution to the problem of arabinogalactan recovery [30] is represented by compression of ground fibrous raw material in the absence of solvent into a high-quality fibrous product.

Along with arabinogalactan recovery, water extraction of larch wood leads to isolation of phenolic compounds (low-molecular-weight and oligomeric flavonoids, lignin substances, and tannins) [8, 31, 32]. Also, the resulting extracts may contain dissolved iron salts [8]. The removal of arabinogalactan-related compounds from the water extracts is troublesome. The earlier proposed methods to solve this problem based on the use of active carbon or ion-exchange resins [33, 34], or a polyamide sorbent [27, 35] exhibit low efficiency. Oxidation of impurities with chlorine dioxide [36] is undesirable, because the finished product, intended for medical and food purposes, needs to satisfy relevant environmental and toxicological criteria.

Iron and (partially) phenolic compounds can be efficiently removed from the extract by treatment with active magnesium oxide at elevated temperatures and pH 9–10 [37]. This technique underlies the production of arabinogalactan available as Stractan 2 (the United States); its improved version based on the ultrafiltration purification procedure, gives a high-purity product [8]. A promising technique for purification of arabinogalactan extracts is that based on the use of nonionic flocculants and coagulants [38].

The domestic industrial technology for recovery of high-purity arabinogalactan from larch wood is underlain by a cost-effective, environmentally friendly procedure of preparation of dry arabinogalactan (95–97% basic substance) from larch wood chips [39, 49]. This process involves the following stages: extraction of arabinogalactan, removal of impurities from the resulting extract, and isolation of the dry product.

The development of this technology relied upon the results of relevant laboratory studies and data calculations.

Physicochemical Principles of Arabinogalactan Extraction

Water extraction of arabinogalactan from larch wood sawdust is a two-stage process comprised of a fast and a subsequent slow stage (Fig. 1).

The progress of the extraction process is determined by diffusion of arabinogalactan from the raw material into the liquid phase and also is involved with the wood chips impregnation. The time of almost complete recovery of arabinogalactan from sawdust is 30 min against several days in the case of wood chips at identical hydromoduli. The qualitative characteristics of arabinogalactan, as well as of other water-soluble wood components extracted, are unaffected by the wood particle size.

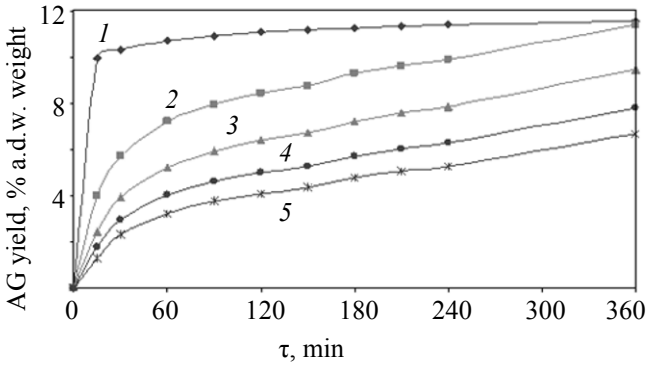

Fig. 1. Arabinogalactan yield in larch wood sawdust extraction vs. raw material particle size. The product yield was determined on a.d.w. weight. Particle size, mm: (*1*) 0.056, (*2*) 0.86, (*3*) 2.61, (*4*) 3.24, and (*5*) 5.37; the same for Fig. 2.

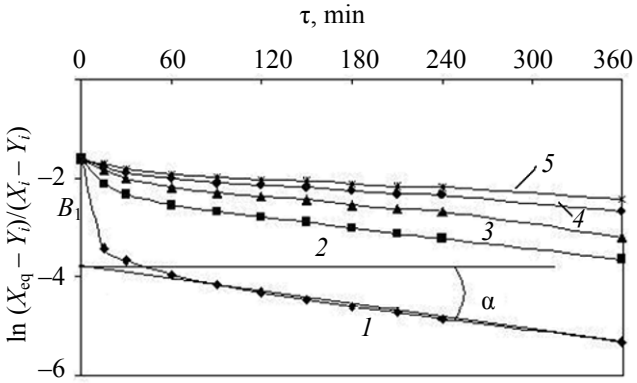

Fig. 2. Plot of the progress of arabinogalactan extraction in the equilibrium regime.

Based on the experimental data obtained, the diffusion coefficient and the mass-transfer coefficient were calculated, as well as the diffusion criterion Bi characterizing the rate of recovery as influenced by the hydrodynamic conditions. The extraction was run till the equilibrium was attained at which the concentration of the substance to be recovered in the solution filling the wood particle pores was identical to that in the resulting extract. At the time $\tau \to \infty$, for the diffusion Fourier criterion $Fo_g \to \infty$ is valid, correspondingly. Hence, the kinetic equation of the extraction process can be represented in the dimensionless form [41]:

$$\frac{X - Y_{eq}}{X_{in} - Y_{in}} = \sum_{n=1} A_n e^{-\mu_n^2 Fo_g}, \qquad (1)$$

where X is the average concentration of the substance extracted (arabinogalactan) in solution filling the pores of a solid (raw material particles) at a given moment τ, g cm^{-3}; Y_{eq}, equilibrium concentration of arabinogalactan in the extract, g cm^{-3}; X_{in}, initial concentration of arabinogalactan in the solution filling the pores of the solid, g cm^{-3}; Y_{in}, initial concentration of arabinogalactan in the extract, g cm^{-3}; and

$$A_n = \frac{6\mathrm{Bi}^2}{\mu_n^2(\mu_n^2 + \mathrm{Bi}^2 - \mathrm{Bi})}, \qquad (2)$$

where μ_n are the roots of the characteristic equation.

The mass-balance condition can be written as

$$Y_{eq} - Y_i = b(X - Y_{eq}), \qquad (3)$$

where Y_i is the concentration of arabinogalactan in the extract at a given moment τ, g cm^{-3}, and

$$b = G\varepsilon/(\rho V), \qquad (4)$$

where G is the mass of the solid (plant material), g; V, volume of the extracting agent, cm^3; ρ, density of the solid, g cm^{-3}; and ε, specific pore volume in the solid, filled with solution, cm^3/cm^3.

The right side of equality (3) determines the relative amount of arabinogalactan that passed into solution from the solid plant-based material during the period elapsed from the given moment till the end of extraction, and the left part determines the increment of the amount of arabinogalactan contained in the extract over the same period.

By substitution of $(X - Y_{eq})$ in Eq. (1) with expression (3) we obtain

$$\frac{X_{eq} - Y_i}{X_i - Y_i} = \sum_{n=1} B_n e^{-\mu_n^2 Fo_g}, \qquad (5)$$

where $B_n = bA_n$.

For the equilibrium extraction regime, the first member of the series in Eq. (5), i.e., $n = 1$, will suffice [41].

Based on the available experimental data we constructed the plot of ln $[(X_{eq} - Y_i)/(X_i - Y_i)]$ vs. τ (Fig. 2).

Extrapolation of the straight line

$$f(\tau) = \ln \frac{X_{eq} - Y_i}{X_i - Y_i}$$

to τ = 0 (see Fig. 2) gives the diffusion coefficient:

$$\tan \alpha = \mu_1^2 \frac{D\tau}{l^2}, \quad (6)$$

$$\tan \mu_1 = \frac{\mu_1}{b}, \quad (7)$$

where α is the angle of inclination of the straight line, with time as the abscissa, and *l*, particle size.

The intercept direct gives the ln B_1 value to be used for calculating criterion Bi by Eqs. (2) and (5)

$$B_1 = \frac{6\mathrm{Bi}^2 b}{\mu_n^2(\mu_n^2 + \mathrm{Bi}^2 - \mathrm{Bi})}. \quad (8)$$

Solving Eq. (6) (the characteristic equation) for μ_1 using expression (7) gives the diffusion coefficient *D*. For the experimental data obtained (see Figs. 1 and 2), the diffusion coefficient of arabinogalactan in extraction from larch wood sawdust (at 20–25°C) was estimated at 1.55×10^{-10}–2.67×10^{-10} $m^2\ s^{-1}$.

Using the calculated values of the diffusion coefficient and criterion Bi, the mass-transfer coefficient *K* can be determined as:

$$K = \frac{\mathrm{Bi}D}{l}. \quad (9)$$

Knowing the contact surface area and the concentration gradient it is possible to determine the amount of arabinogalactan extracted over period τ.

Technological Aspects

The mass-transfer characteristics obtained were used in extraction calculations for arabinogalactan recovery from ground larch wood in a similar hydrodynamic environment. The value of the diffusion coefficient *D* is suitable for extraction calculations in the case of technologically different processes that are differently implemented at the same temperature (20–25°C).

The experimental data were used for development of a mathematical model, on which basis the process technology optimization was carried out, as well as for calculation of the mass balance and determination of the best parameters for the extraction process [42].

The procedure developed consists in water extraction of larch wood chips (upon removal of dihydroquercetin and other phenolic extractive substances with an organic solvent) at 60–80°C in the continuous circulation mode for 2–3 h. The resulting extract is treated with a cationic flocculant solution to remove mechanical and colloidal impurities, and this makes unnecessary treatment of the extract with a coagulant. The clarified extract containing arabinogalactan is subject to additional purification by ultrafiltration with simultaneous concentration.

It was found that, in ultrafiltration through UAM150P cellulose acetate membranes [4], the filtration speed tends to decrease over time due to increases in the arabinogalactan concentration in solution and in the solution viscosity and to deposition of high-molecular-weight particles on the membrane surface [4, 43]. The process efficiency tends to decrease with increasing arabinogalactan concentration in solution and to increase with increasing pressure differential across the membrane. In the final stage of ultrafiltration the filtration speed approaches the stationary level, with the process efficiency being the lower the larger the pressure differential. This trend is due to the fact that, over identical time intervals, the concentration speed is higher at high pressures.

Examination of how the ultrafiltration process is affected by pressure showed that the degree of concentration was at a maximum at the pressure differential of 0.4 MPa. However, the process efficiency and the degree of concentration are optimally balanced at Δp = 0.2 MPa.

The ultrafiltration of the product involves, along with concentration of the arabinogalactan extract, removal of low-molecular-weight phenolic impurities which virtually exhaustively pass into the filtrate. The degree of removal of impurities depends on the composition of the initial extract, characteristics of membranes, and filtration conditions, as well as on the degree of concentration.

Based on the experimental data, the degree of concentration of arabinogalactan at different pressure differentials across the membrane was estimated at 82–87%.

Along with phenolic substances, the oligomeric fractions of arabinogalactan and metal cations pass from the extract to filtrate [4]. The total content of dry substances in the filtrates does not exceed 1–2.5%.

The ultrafiltration module efficiency was improved with the use of a UAM500P membrane. As shown by examinations of the dynamics of ultrafiltration of the clarified arabinogalactan extracts on these membranes, the filtration speed is inversely proportional to the initial concentration of arabinogalactan in the extract [43]. With large pore-size ultrafiltration membranes there is no need in pretreatment of arabinogalactan extracts with a flocculant. The process efficiency is comparable to that for the extracts clarified by

flocculation [43]. Therefore, in the case of ultrafiltration through UAM500P membrane, the pore blocking in the initial stage is not a limiting process, by contrast to the case of UAM150 membrane [44]. For optimum ultrafiltration conditions ensuring the viability of the technology, see [4, 43, 44].

The resulting ultrafiltration concentrate is dried in a drying installation.

As to the earlier proposed methods for dry product isolation by precipitation into alcohol or acetone [25, 26, 38], their commercial implementation is inexpedient from the technological, economic, and environmental perspectives.

After passing through an ultrafiltration membrane, the filtrate can be mixed with fresh water without additional treatment and reused for extraction of dihydroquercetin.

This procedure offers the following significant advantages over the existing technical solutions. First, arabinogalactan is extracted from larch wood which is freed from dihydroquercetin and resinous substance, and the resulting extract is characterized by a fairly high degree of purity. Second, the process involves a smaller number of stages, the use of expensive equipment is avoided, and the energy costs are reduced. Third, there is no need in expensive sorbents, as well as in toxic and flammable organic solvents. Fourth, the water consumption is decreased, and the amount of effluents is significantly reduced owing to the water recycling scheme applied.

To remove high-molecular-weight phenolic impurities from arabinogalactan, the water extracts are additionally treated with an eco-friendly oxidant, hydrogen peroxide [40]. The oxidation conditions for arabinogalactan-related substances were optimized so that the degradation of the polysaccharide macromolecules can be avoided. The optimal oxidation conditions vary with the arabinogalactan solution concentration and, e.g., for 5% concentration are as follows: temperature 60°C, H_2O_2 concentration 0.2 M in the presence of EDTA, and process time 1.5–2.0 h (depending on the heat-exchange conditions).

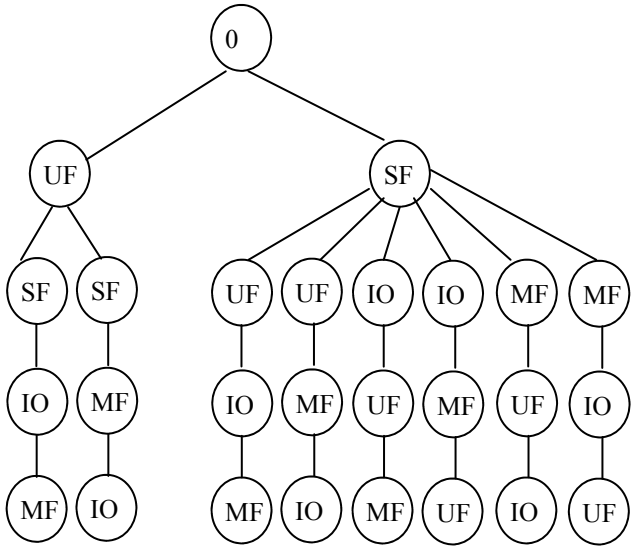

Fig. 3. Tree of variants of the sequence for arabinogalactan preparation steps. (0) Zeroth node of the tree of variants, (UF) ultrafiltration concentration, (SF) solution flocculation, (IO) impurity oxidation, and (MF) microfiltration.

The commercial product can be recovered from the concentrate by spray, freeze, or fluidized-bed drying procedures, of which options spray drying is optimal from the technical and economic perspective. Spray drying of arabinogalactan concentrate was examined in different modes; the varied parameters included the initial solution concentration, air temperatures at the drier inlet and outlet, and the pressure of compressed air used for spraying.

Assessment criteria for arabinogalactan preparation technology variants

Criterion	Variants[a]							
	1–2–3–4	1–2–4–3	1–3–2–4	1–3–4–2	1–4–2–3	1–4–3–2	2–1–3–4	2–1–4–3
Efficiency	1	1	1	1	1	1	7	7
Material and reagent consumption rate	3	3	3	3	3	3	1	1
Metal intensity	1	1	1	1	1	1	7	7
Labor intensity	3	5	3	5	7	7	2	1
Technological effectiveness	2	1	2	5	7	6	6	4
Total	10	11	10	15	19	18	23	20

[a] (1) Flocculation, (2) ultrafiltration, (3) impurity oxidation, and (4) microfiltration.

The most important process parameter is the temperature of the drying gas (air). Examinations of the drying efficiency in relation to the air temperature showed that the acceptable moisture content of the end product (<7%) can be achieved at air temperatures above 100°C. Also, nonuniform spraying of the product at the arabinogalactan concentrations above 30% was revealed and, as a result, sticking of large arabinogalactan particles to the walls of the drying chamber in the outlet tube was observed. The most efficient drying is achieved at arabinogalactan concentration of 20–25% and temperature of the drying agent (air) of 120–140°C.

The process scheme for production of dry high-purity arabinogalactan consists of the following operations: (1) flocculation of the solution of the product, (2) oxidation of impurities in the solution, (3) microfiltration of the solution, 4) ultrafiltration concentration of the solution, and (5) spray drying of the concentrate.

The main drawbacks suffered by the proposed scheme include a low efficiency of the process and a long time required to produce one unit of the product. In this connection, the process was optimized using the tree-search procedure [45–47] with the aim to determine the best sequential combination of process steps with the following restrictions imposed: spray drying is always the last stage and therefore is excluded from tree branching; microfiltration of arabinogalactan solution and oxidation stages go only after the flocculation stage. Figure 3 presents the resulting tree of variants of the sequence of process steps.

The performance of these variants was assessed against the following criteria: efficiency; material and reagent consumption rate; metal intensity (capital costs), labor intensity (work time expenditures), and technological effectiveness.

The normalized value (rank) for each criterion ranged from 1 to 7.

The optimal technology variant 2-1-3-4 (see the table) provides a four times higher efficiency and halved capital costs compared to the earlier adopted technology.

The improved process scheme was implemented at the pilot installation of the Khimiya Drevesiny Farma, Limited Liability Company (Irkutsk); pilot batches of the product were prepared. The produced arabinogalactan known as FibrolarS is a raw material permitted for use in production of biologically active food additives [48].

Crystalline Glicose Derived from Lignocellulosic Residue

Integrated processing of larch wood leaves a lignocellulosic residue which, after extraction with ethyl acetate and hot water, is comprised of chips whose main constituents include cellulose, lignin, and hemicellulose. Polysaccharides account for 65–75% of absolutely dry wood (a.d.w.) weight of larch wood chips [49], and water-soluble substances, for 10–16% (in some cases, up to 30%) [50]. The content of holocellulose in the lignocellulosic residue (minus water-soluble substances) is ~54% of a.d.w. weight against ~40% in the initial larch wood. The increment of the relative content of polysaccharides, calculated on the a.d.w. weight basis, is ca. 14%. Thus, the lingocellulosic residue can be regarded as a raw material "enriched" in polysaccharides, suitable for preparation of sugars and products thereof by acid hydrolysis.

The maximal yield of reducing substances from lignocellulosic residue hydrolyzed under mild conditions (dilute inorganic acids, 100–105°C) is 1.1% with 5% sulfuric acid used. This corresponds to 23% easily hydrolyzable polysaccharides in the lignocellulosic residue. The hydrolyzates contain 62.1% hexoses and 33.9% pentoses, including arabinose, galactose, xylose, mannose, and glucose. These are process solutions characterized by enhanced content of pentose sugars, which are suitable for manufacture of animal feeds [51, 52] and other products.

Of most interest are the results from experiments on low-temperature hydrolysis of lignocellulosic residue with concentrated sulfuric acid. The maximum yield of glucose (up to 64% of a.d.w. weight) is achieved at sulfuric acid concentrations of 65–80% [53].

An alternative can be found in conversion of cellulose into glucose via acid hydrolytic reaction preceded by delignification of the lignocellulosic residue by industrial procedures [54], which option can also give high-purity glucose syrups. One of the major advantages offered by this process is that the resulting glucose syrups have a purity quotient of no less than 85% and are not contaminated with water-coloring lignin-carbohydrate impurities and ash components. For example, inversion of the cellulose hydrolyzate gives the inverted solutions characterized by the glucose content of ~70% on the average, i.e., the glucose yield is 35–45% of a.d.w. weight. These are transparent, pale yellow glucose syrups with a high purity quotient (85–90% and above). For comparison, hydrolysis of the lignocellulosic residue with con-

centrated acid (the first hydrolysis route) gives glucose in the yield of 23–25% of a.d.w. weight.

Thus, there exists a possibility in principle to carry out conversion (saccharification) of lignocellulosic residue with the aim to produce crystalline glucose.

Pectic Substances in the Larch Bark

Twelve per cent pectin contained in larch bark [55] makes it suitable as a raw material for preparation of this product. It was shown that larch bark-derived pectin is capable for removing cesium-137 from body and inhibiting Sarcoma 180 cancer cell growth [56]. Also, it is a useful gelation agent in marmalade manufacture [57]. Pectins recovered from larch were applied in preparation of Pektosorbin veterinary drug intended for treatment of gastroenteritis in calves and chickens [58]. The membrane tropic activity and ability to stabilize membrane structures opens prospects for medicinal and biological applications of pectin [59]. Larch bark-derived pectin exhibits reducing and stabilizing properties in reactions with noble and transition metal ions, run in aqueous alkaline solutions, which give nanobiocomposites [60].

With a view to adopting adequate technological solutions, the parameters of pectin recovery from larch bark were examined with the use of the classical procedure [61]. The latter includes the following stages: pretreatment to remove impurities, hydrolysis of protopectin, extraction of pectin, and isolation of pectin from the extract by precipitation.

Pretreatment of the raw material by sequential extraction with ethyl acetate and hot water promotes deactivation of enzymes and removal of low-molecular-weight impurities of carbohydrate nature. It should be noted that the extractable components are not waste products; they can be used for preparation of practically significant products for medicine [62] and leather industry [49].

It was shown that, with increasing temperature in the hydrolysis and extraction stages, the yield of pectic substances tends to increase and passes through a maximum at 80°C. These results are in good agreement with the data from [63] concerning the behavior of pectins in traditional isolation processes: An increase in temperature causes partial hydrolysis of protopectin, and the yield of the product increases, but above 80°C the superstructure of pectic substances is destroyed. This is also suggested by a sharp decrease in the molecular weight of pectins with extraction temperature increasing from 80 to 90°C [61]. The bulk of pectic substances passes to extract within 1 h of extraction; further prolongation of the extraction process does not significantly affect the product yield.

Compared to acetone, ethanol is a more selective precipitating agent for pectic substances, and precipitation with alcohol gives purer products, as suggested by the residual content of uronic acid in pectic substances: 78.12% in the case of ethanol against 69.77% for acetone.

The revealed characteristics of the process of extraction of pectic substances from larch bark will be used for development of their production technology of part of the integrated larch biomass processing scheme.

Utilization of wood processing waste is an important economic task. In this context, the above-presented eco-friendly technologies which possess high technical and economic characteristics hold much practical relevance.

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