Tree Green of Siberian Abies as a Raw Material to Manufacture Biologically Active Substances

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Abstract

The review systematizes the data from scientific publications, patents and Internet resources about the consumer products (preparations) made of the wood green of abies, their biological activity and areas of application. The group chemical composition of extractives from the tree green of abies and the technologies of obtaining them are characterized.

INTRODUCTION

An increase in timber felling that is taking shape in Russia demonstrates a noticeable contrast with the level of development of waste-free processing of the whole raw material resource in dendrochemical branch. Wood waste from wood-processing plants (bark, barking, sawdust etc.) account for 30 to 50 % of the mass of live wood; the negative disbalance “waste vs. processable waste” exceeds 100 mln m³/y [1]. The problem of utilization of cutting wastes – off-grade wood, stubs and wood green (WG) – is not less urgent from the position of ecology. The wastes remaining at the sites of continuous felling account for more than 20 % of the wood mass sent to processing.

At the same time, processing of GW in which unique biologically active compounds are concentrated has reasonable economical and ecological substantiation because it is able to solve many problems simultaneously: to increase the profitability of wood-processing works and to protect environments. The manufacture of human friendly products based on natural substances from GW – components of food and fragrance cosmetic, household chemical goods, means of immune and growth stimulation and protection in plant cultivation and cattle breeding, biologically active additions, curative and prophylactic means etc. – appears to be a powerful reserve of sustainable development of the branches of industry connected with the forest resources of Russia.

Forests of Russia are represented by coniferous species up to 75 % [2] but cedar laying in is limited in volume that of larch crows has only seasonal character, while that of pine is insignificant in comparison with the mass of the wood part. All-year-round, productive and available supplier of the green mass seems to be abies, including the Siberian species (Abies sibirica Ledeb.), which is concentrated and harvested on a large scale at the territory of the taiga zone of West and East Siberia, the Altay and Far East.

Folk medicine since old times knows the curative properties of abies green. Now it serves as a valuable raw material to obtain the components of curativ-prophylactic, wound healing and bactericide means in modern medicine, deodorant, aromatising and sanitary-hygienic additives to perfumery and cosmetics. However, the available review publications (for
example, see [3–6]) deal mainly with the
technologies of processing the WG of abies and
often contain incomplete data on the composition
of the prepared mixtures of native substances
and their biological activity. The information on
the use of extracted biologically active
substances (BAS) in consumer goods is presented
only fragmentarily. The present work is to fill
in the gap in systematizing and structuring the
information concerning these problems. In this
review, on the basis of the data from the
subject Internet sites, we characterize the group
chemical composition of extractive substances
(ES) of abies and the area of application of
the products manufactured by home industry,
and analyse the trends in developing the
technologies of processing the WG of abies.

MAJOR CHEMICAL COMPOSITION OF EXTRACTIVE
SUBSTANCES OF ABIES WG

Abies (WG, sprouts, bark, wood) is the
richest source of biologically active renewable
organic substances. The extractive components
of abies WG are usually divided into lipids
(including terpenoids), phenol compounds,
proteins (together with amino acids), vitamins
and carbohydrates.

Lipids

The lipid fraction is mainly (by 65–70 %)
represented by the group of so-called neutral
lipids that may be extracted from the abies WG
with organic low-polar extracting agents, for
example hydrocarbons (hexane, benzine), ethers
(MTBE, diethyl) and asters (ethylacetate). The
fraction of glycolipids in the total mass of lip-
id components of abies ES does not exceed 6 %;
only fragmentary data on them are available
[6, 7]. These data point to the presence of mo-
 nogalactosyldiacylglycerols, digalactosyldiacyl-
glycerols and ceramidoligohexosides. The phos-
pholipid content of abies WG varies from 0.4
to 1.4 % of the mass of absolutely dry raw
material (a.d.r.) These compounds are represent-
ed by glycerophospholipids, mainly phosphati-
dylcholines, phosphatidylethanolamines and
phosphatidylycerines [6, 8].

The most fully established composition is that
of neutral lipids isolated by means of

hydrodistillation (abies essential oil) or extraction
of WG with low-boiling organic extracting
agents, including liquid carbon dioxide. The
abies hydrodistillate (or CO$_2$ extract) includes
the groups of mono- and sesquiterpene
components at a ratio of about 10 : 1. These
groups, including hydrocarbons, alcohols and
alcohol acetates, comprise up to 6 % of the
mass of abies a.d.r., according to the data
reported in [9]. The major monoterpane
hydrocarbons are α-pinene, limonene, 3-car-
ene, camphene, β-phellandrene. In addition,
santhene, tricyclene, β-pinene, myrcene,
γ-terpinene, terpinolene, alcohols: borneol,
isoborneol, β-terpineol, geraniol, fenchol in the
free and bound state, and camphor were also
detected among the volatiles [10, 11]. Unlike
for other conifers, the volatile components of
abies are characterized by the high content of
bornylacetate: up to 40 % of the monoterpane
fraction [4, 6]. Sesquiterpene compounds are
represented by caryophyllene, humulene,
β-bisabolene, longifolene, β-bisabolol, nerolidol,
selina-6-ene-4-ol, sibirene, longiborneol,
caryophyllene and humulene oxides,
epicubenol, cubenol, epicubenol,
α-murolene, α-cadinene [5, 6].

Less volatile aliphatic and diterpene com-
ponents of lipids are represented by hydro-
carbons, alcohols and acids in the free and
bound states, that is, in the form of wax, gly-
cerides, esters of acids with lower alcohols.
Among them, identified compounds include
C$_{14}$–C$_{32}$ alkanes [5, 12], squalene, alcanols, the
major among which are nonacosanol-10 (C$_{29}$)
accounting for up to 1.5 % of the a.d.r. mass,
docosanol (C$_{22}$) and tetracosanol (C$_{24}$), as well
as other non-branched alcohols (C$_{21}$, C$_{26}$
and C$_{28}$) [5, 6, 12].

Neutral diterpenoids are represented mainly
by cis-abienol, epimanoil, epimanoyl oxide,
abitadiene, dehydroabitadiene, phytol,
geranylergeraniol, isopimarinal, abietinol,
dehydroabietinol, neoabietinol, 18-
norisopimarinal, 18-norabietinol, 18-
nordehydroabietinol, sandaracopimarinal,
anticopalol etc. This group also includes mono-
unsaturated alcohol phytol (C$_{29}$) which is a
component of chlorophyll and wax [5, 6, 12, 13]. Diterpene alcohols are present in the raw
material also mainly in the form of acetates.
Diterpene acids including isopimaric, abietic, dehydroabietic, palustric, neoabietic, sandracoabietic and levopimaric ones account not more than 10% of the mass of all the acid components of the ES of abies green [5, 6, 12, 14]. Genetically related aldehydes were also detected in trace amounts [5, 6].

Fatty acids [5, 6, 12, 14, 15] are represented both by saturated and by unsaturated acids (undecanolic, aluric, tridecanic, myristic, palmitic, palmitoleic, stearic, oleic, linolic, linolenic, behenic, lignoceric, arachidic, mainly in the bound form. Bound acids account for up to 30% of neutral weakly-polar extractives, that is, about 2% of the a.d.r. mass, while the free aliphatic and diterpene acids account for not more than 0.8% of the a.d.r. mass. Among them, aliphatic diacids may be present – hexadecane-1,16-diacid, octadecane-9-ene-1,18-diacid [15].

One of the distinguishing chemitaxonomic features of abies is relatively high triterpenoid content. Neutral triterpenoids including phytosterols common for plant raw material exhibit almost no differences from the set of the corresponding components from other conifers. In the group of triterpenoid alcohols, \( \beta \)-sitosterol, campesterol, cycloartenol, 24-methylenecycloartenol, citrostenol, obthusyfoliol were identified [5, 6, 12].

One more group of neutral triterpenoids includes lactones; the first compound isolated and identified [5, 6, 12, 15] was abieslactone \( \beta \)-lanosta-7,22,24-triene-26,23-olide and \( \beta \)-lanosta-8(9),22,24-triene-26,23-olide [4]; 3-hydroxy- and 3-keto analogues of abieslacin [5, 6] and native 3-acetate were isolated from bark and sprouts. Also 3-ketolactone with the saturated lacton cycle \((23R,25R)-3\text{-oxo}-\text{lanost}-7\text{-ene-26,23-olide}\) and spirospiran lacton (\(16R,23S\))-3-oxo-16,23-epoxylanosta-7,24-diene-26,23-olide were extracted from sprouts [6]. Ketone (22Z)-3\text{-hydroxy}-17,14-fridolanosta-7,14,22,24-tetraene-26,23-olide was discovered in the extract of needles [7].

The majority of triterpene acids present in needles, sprouts and turpentine of Siberian abies are biogenetically related to the identified lactones. As a total, more than 15 triterpene acids have been identified in the extracts of Siberian abies by present [6, 12, 15, 21–24]. The major ones of them have \( \beta \)-lanostane structure (in analogy with mariesic acid isolated from Abies mariesii Mast.) [25]. Firmanic, iso firmanic, mariesic, 23-oxomariesic acids were also detected in the turpentine of Siberian abies, along with 3,4-secoacids: abiesolidic, trans- and cis-abiesonic [21, 22]. Cis-sibiric and 4-methylene-3,4-seco-cycloart-4-(28)-ene-3-oic acids were isolated from the extract of needles [26, 27]. Some cis-isomers of triterpene acids may exist in two tautomer forms: free acid and cyclic lactol. Lactols are rather stable and can be isolated in the crystal state [21].

It is necessary to mention polyisoprenoids – isoprene oligomers (polyisoprenoids) which are regularly built linear cis- and trans-polyynes-1,5 with terminal hydroxyl group, and their 2,3-dihydro analogues – dolichols. Polypropenoids are present in the needles mainly in the form of acetates, in sprouts partially as esters of other aliphatic acids. In abies WG, \( C_{90} - C_{95} \) polypropenoids dominate: the components with 16–17 \( C_5 \)-isoprene units account for about 70% of the total number of polypropenoids. The content of dolichols in green plants is usually 100–1000 times less than that of polypropenoids, however, the fraction of dolichols in the needles of conifers is about 3% of the total amount of polyisoprenoids (while the content of polypropenol fraction is up to 1.2–2% of the a.d.r. mass) [5, 6, 12, 28, 29]. So, the abies WG may be considered as a rich source of polypropenoids and dolichols.

**Phenol compounds**

Phenol compounds are represented in the abies WG by lignan, flavonoids (up to 0.6% [6], including anthocyanins), esters of aromatic acids with the prevalence of alkyl ferulates, simple phenols (0.1–0.2% in the free form, up to 14% in the form of glycosides), phenol acids (0.05–0.07%, including \( p \)-oxybenzoic, vanillic, both free and in the form of glycosides; glycoside of protocathechuic acid; \( p \)-cumaric in the cis- and trans-forms in the free form and as glycosides) [6, 30]. Phenol aldehydes – coniferaldehyde, vanillic, veratric – are the same in the needles as those in wood. Acetophe-
nones from abies, similarly to those from other coniferous plants, are characterized by p-hydroxy-, 3,4-dihydroxy- and 3-methoxy-4-hydroxy substitution in the aromatic ring.

More than 20 simple phenols with the mass fraction up to 0.15 % were identified in the essential oil of abies; the major ones among them are 2,6-dimethylphenol, 2,4,6-trimethylphenol, m-cresol, 2,3- and 3,5-dimethylresorcinol, pyrocatechin, resorcinol, 2-methylresorcinol [31].

The major flavonoid components identified in Abies sibirica and Abies nephrolepis are kaempferol, quercetine, kaempferol-3-glucoside, quercetine-3-glucoside, isorhamnetine-3-glucoside, kaempferol-7-glucoside, as well as apigenine-8-C-β-D-glucopyranoside-α-L-rhamnopyranoside, which was called abietine after the source from which it was extracted for the first time [32]. Flavonoids in glycoside form are characteristic of the Canadian abies species: flavonol glycosides and C-glycosyl flavones, and a substantial amount of dihydroquercetine, which is more typical for larch [33]. This means that the content and assortment of flavonoids may serve as the chemitaxonomic sign for different abies species. Alkyl ferulates are present mainly in abies wood, so they are detected in the extracts of overall WG. As the alcohol components of ferulates, alkanols were identified, mainly docosanol and tetracosanol, as well as lignans with the prevalence of laryciresinol which was previously detected in larch raw material [34, 35]. In addition, secoisolaricresinol, 3,4-divanilyltetrahydrofuran, liouvill, olivel, pinoresinol, matairesinol, oxymatairesinol and their glycosides. Total lignin content of the abies WG is not more than 0.1 % of a.d.r. mass [6, 37]. At the same time, the needles of Siberian abies is distinguished by the high content (up to 2 % of a.d.r. mass) of maltol (2-methyl-3-oxo-γ-pyrole). Lignins comprise a substantial part of the abies raw material; they are represented mainly by the polymer of coniferyl alcohol (up to 32 %, in sprouts up to 44 % [6, 37]).

Proteins and amino acids

The abies wood green contains up to 12 % of raw protein calculated for a.d.r.; the protein content of needles is almost two times higher than that in sprouts [6, 37]. The amino acid composition, though representing rather wide variety (19 amino acids), is favourably distinguished by the high content of lysine, arginine, leucine, aspartic and glutamic acids. In native green, the contents of different amino acids differ significantly, while in the protein-vitamin concentrate the difference is only 4–5 times.

Vitamins

Wood green contains substantial amounts of vitamins, including carotenoids (up to 30 mg %), tocophersols (up to 25 mg %), vitamin K (up to 4 mg %), vitamin C (up to 400 mg %) [4, 6, 7, 37] and the vitamins of group B. In addition, phytosterols act as provitamin D [4, 6, 7, 37]. The content of chlorophyll in needles and in wood green is rather high (up to 900 mg %), while it is almost absent from the sprouts [6]. Water extractable microelements of abies WG (more than twenty) are important for animal and plant organisms.

Carbohydrates

The highest mass fraction belongs to the carbohydrate complex. Abies needles contain much cellulose (up to 28 %), easily and difficultly hydrolysable polysaccharides (12 and 29 %, respectively) [6, 37]. Carbohydrates also contain mono- and oligosaccharides; carbohydrate fragments serve as the component of numerous glycoside compounds [6].

METHODS OF PROCESSING THE ABIES WG AND EXTRACTION OF BIOLOGICALLY ACTIVE SUBSTANCES

Hydrodistillation

The first industrial technology of the extraction of biologically active substances from abies WG was steam- or hydrodistillation [38] resulting in the following products: essential oil (EO) of abies (the organic phase of the distillate) Florentine water (FW, the aqueous phase of the distillate), water condensate and non-volatile resinous substances (both these fractions get accumulated at the bottom of still reser-
The essential oil is a composition of well volatile low-polar mono- and sesquiterpene compounds; FW contains some relatively polar mono- and sesquiterpenoids in ES (concentration up to 1.5 %), mainly oxygenated, such as boras camphorbornyl acetate, camphor, verbenone, and hydrocarbons – caryophyllen and humulene [39]. Since FW is similar to ES in composition, it is often used repeatedly to make steam; thus the yield of ES increases [40, 41]. In addition to the compounds characteristic of FW, water condensate contains oligo- and polysaccharides [42], glycosides, polyphenol compounds and other water-soluble components washed with water from WG. The fraction of resinous substances is similar to tar in consistence and destination; the amount of this fraction depends on the ratio of needles and lignified sprouts in WG.

At present, abies EO is manufactures as the pharmacopeian preparation “Abies Oil” (AO), FS 42-3370–97 by more than 30 Russian plants registered in the State Register of Pharmaceutics [43]. In addition, a substantial amount of abies raw oil is manufactured at abies processing units located directly at cut areas. The concentration of bornyl acetate in it is often below the level of FS standard, so additional distillation is necessary to remove a part of monoterpene hydrocarbon fraction from EO in order to bring the product up to the standard level. This fraction is similar in composition to turpentine oil and colophony oil; these substances are used for hygienic indoor sanation [3]. In addition to the use as curative and hygienic means, abies oil is used as an extracting agent to isolate the BAS complex from plant raw material [44, 45].

Extraction based technologies

Technologies based on extraction became the foundation for modern methods of WG processing; they allow one to broaden the range and number of extractable native compounds. Implementation of these technologies started in 1931 when the battery counter-flow extraction of WG with hot water after evaporation of essential oil by live steam was introduced at the Tikhvin Wood Chemical Plant [46]. Water as an extracting agent extracts polar compounds mentioned above. A scheme of this kind of WG processing in installations of continuous action [47, 48] involving the system of closed FW circulation, utilization of the bottom water condensate and worked-out WG, was realized at the Chernogorsk Wood Working Plant and Lys’vales Plant [4]. At some plants (Tikhvin WCP, Irkutsk SSE Pinen), the production of Terpenoksamat preparation was launched [49]. It is indented for protection of humans and agricultural animals from blood-sucking insects. The products manufactured at the plants relying upon this technological scheme are AO, heavy abies oil (HAO) (FS 42659–73), extract coniferous natural (CE) (FS 42-2699–98), conifers forage flour (TU 2455-028-02068453–93) has conventional areas of application as curative, prophylactic and bactericide means, basic tonic additions in fragrant and cosmetic compositions and forage for agricultural animals and birds.

Within the framework of water extraction technology, broadening of the extractable compositions of BAS is achieved by modifying extraction conditions. For instance, abies WG processing involving preliminary steaming of abies branchlets with overheated water vapour (100–110 °C) under reduced pressure with the removal of vapour-gas mixture, its subsequent cooling and separation into AO and water extract was proposed in patent [50]. Thus obtained water extracts received the trade name of “Abisib”; according to the data of [51], the technology of its production was implemented at the plants: Delta JSC, Bioepl Scientific and Industrial Centre of the Research Institute of Biology and Biophysics, Biolit Co. in Tomsk. The description of the preparation declares its broad range of therapeutic action; the authors explain this fact by the presence of “biologically active substances, including polyvitamin complexes C, P, B, K, carotinoids, polyphenol complexes, saccharides, chlorophylline, phytoncides and various microelements”. It should be noted that the patented method of obtaining water extract coincides with the method of obtaining FW and excludes the presence of the majority of listed BAS that cannot occur in the vapour-
gas mixture due to their physicochemical properties. The presence of these compounds is characteristic of the bottom water condensate. One cannot exclude that the authors do not report reliable information as a now-how.

According to the data reported in [52–54], for alkali solution used as an extracting agent, a part of lipid fraction is additionally extracted from WG. This occurs due to saponification of lipids during extraction and accumulation of surface-active substances in water (salts of fatty, resin and triterpene acids) which promote the isolation of low-polarity and poorly soluble substances from the raw material. A concentrate of neutral lipids is isolated by treating of the formed emulsion with ethanol and light petroleum, while acid lipid components are isolated by extracting the acidified aqueous solution with diethyl ether. It is pointed out that the completeness of lipid extraction depends on the degree of grinding the wood green, on the method of pounding, and on the stability of the formed emulsion. In particular, pounding under the action of ultrasound causes an increase in the yield of lipids.

The treatment of WG with the extracting agents of organic nature is more efficient in the completeness of extraction (yield) and in the composition of ES than the treatment with water. It is the chemical nature of the extracting agent that essentially determines the chemical composition and yield of ES, so a great number of investigations is connected with broadening the range of extracting agents: revealing the differences in the composition of ES depending on the nature of extracting agents used (alkanes, alcohols, freons etc.) or their mixtures, and also on the sequence of their action of WG. Important characteristics of a potential extracting agent in the aspect of its possible use in production is profitability (availability and cost, possibility of regeneration) and ecological reasonableness (permissibility of the contact of living organisms with consumer products and wastes containing the residues of extracting agent, protection of labour in industry). It is evident that the most efficient technology is that combining extraction with water and with organic solvents.

The technology of water-benzene extraction allows one to isolate, in addition to the above-mentioned fractions, also liposoluble ones, containing mainly lipids, which broadens the assortment of products. Such a production of “Coniferous Chlorophyll Carotene Paste (CCCP) (GOST 21802–84) was organized in the Lisino Forestry in 1950 [9, 46] and later upgraded to increase the output and assortment of products. At present, similar works (Vyru Forestry Plant [55], Lisino Forestry [56, 57], Silava Enterprise[58], Tikhvin WCP, Lesokhimiya Co. etc. [59, 60]) produce various versions of essential oil, CCCP, Concentrate Provitamin Coniferous (CPC) (OST 56-33–85), Sodium Chlorophyllin Coniferous (OST 56-33–85), balsamic paste (OST 5658–83), Coniferous Wax (OST 56-65–82). The worked-out biomass is utilized as forage flour and the basis for compost [61].

A broad range of ES is extracted from WG with polar extracting agents, for example water-alcohol mixtures with variable concentration [1]. Their use promotes an increase in the yield of ES, first of all due to the fractions of phenols and saccharides, and decreases the selectivity towards lipids. On a laboratory scale, the possibilities of other organic extracting agents were studied: dichloromethane, trichloroethylene, ethylacetate, alcohol–benzene mixture, however these agents did not win wide application in the actual technologies due to toxicity and large expenses for regeneration.

Advance of extractive technologies is thought to be connected with the use of liquefied gases as extracting agents (CO₂, lower alkanes, freons). Rather low working temperature of extraction, low chemical aggressiveness, and specific extractive properties characteristic of each of the mentioned extracting agents provide high selectivity with respect to he lipid composition, with complete conservation of the extracted ES in the native state. The use of liquefied gases in tight apparatus is characterized by relatively small losses of extracting agents and low energy consumption for their regeneration, but this technology requires special equipment bearing elevated pressure. Nevertheless, due to the ecological reasonableness, practical absence of the residual amounts of extracting agents in ES and chemical inertness of extracting agents with respect to living organisms, as well as sparing extraction conditions, the technological
schemes of this kind are gradually spreading, especially for the recovery of expensive EO from various kinds of plant raw material. Compact and rather autonomous extraction installations are manufactured on the industrial scale.

The technology of WG extraction with liquefied carbon dioxide is actively developing [62–65]. The CO₂ extracts are much more expensive in production than other ones but their high consumer properties [11] ensure stable demand for them in food and fragrance cosmetic industry. It was reported in [66] that the residual amounts of CO₂ in concentrated extracts have a conserving action (prevent rancidification of fat and development of microflora), so the shelf live of extracts increases. The CO₂ extract of abies is manufactured at the Krasnoyarsk Mining and Chemical Combine and Siberian Plant of Extracts and Biotechnologies (Tomsk). Water-ethanol extracts obtained after CO₂ extraction are almost free from lower terpene hydrocarbons that exhibit resorptive action, so these extracts are used in manufacturing fodder for cattle breeding. The final stage of this technology may be, in particular, growing of mycelium of fungi (mushrooms) on worked-out WG, as a result of which it is transformed into a high-protein fodder product. The technological line involving the described sequence of operations was mounted at the Kansk Biochemical Plant JSC [63].

The authors of [67] proposed to use two-stage abies WG extraction with the agents of different polarity thus achieving increased yield of ES. At first, treatment of the raw material with liquid propane-butane mixture is performed, resulting in the extract close in composition to the abies EO. Then the raw material is extracted with 50–60% ethanol, the concentrated extract is settled, then the immiscible layers are separated from each other by decantation; a sum of water-soluble substances (CE) and the liposoluble fraction (CCCP) enriched with carotinoids and chlorophyll. The worked-out WG is processed into vitamin flour.

Improvement of extraction-based technologies is to a large extent determined by the use of the new equipment allowing one to intensify extraction processes. Among the works in this area, we are to mention the development of spiral (screw) extractors that allow one to perform the process in the continuous mode, rotary pulsating devices [1], disc extractors in which grinding is combined with extraction [68]. As a rule, intensification of extraction process causes an increase in the yield of ES and at the same time a decrease in selectivity.

Fractionating of extractive substances

In general, extraction technologies give multicomponent compositions of BAS with non-standardized composition. Simultaneously with improvements of these approaches, the methods of fractionating total extracts are under development. Fractionating implies more science-intensive technologies. The conjugated investigations of the chemical composition of fractions, structure and biological activity of components are also in progress. The comprehensive approach to WG processing includes also other methods along with extraction: rectification (including high-vacuum one), chromatography, separation of substances over their chemical features using acid and base reagents, and the simplest methods of chemical modification (saponification, interesterification). Investigations in this area in Russia are mainly carried out at the St. Petersburg State Forestry Technological Academy, Novosibirsk Institute of Organic Chemistry, SB RAS, Siberian State Technological University (Krasnoyarsk), Irkutsk Institute of Chemistry, SB RAS, Institute of Chemistry, UrB RAS (Syztykvkar), TsNILKhI (Nizhny Novgorod) and others. The information obtained in the investigations allows one to improve the methods of ES processing with the isolation of the groups uniform in chemical properties, or individual compounds with definite biological activity, and arrange the production of new preparations on this basis. Analytical estimations show [56, 57] that, in spite of additional financial investment, fractionating even of the known composites, for example CCCP, provides an increase in the economical efficiency of production. According to the data obtained by analysing the patent information, there are algorithms of processing WG both with diversification into 8–10 products and with obtaining one or two target products.
Examples of the first kind of processing are the methods [60, 70] of processing WG of coniferous species into a complex of products for pharmacology, cosmetics industry, and agriculture. In spite of the multistage character (about a dozen stages), this technology is worth attention because it provides complete separation of ES. The method includes extraction of ES from WG with an organic extracting agent followed by separation into components by means of the combined use of physical and chemical methods. Thus, the wax fraction is separated after keeping the cooled total extract for some time and then filtering it. The mother solution is treated with an excess of aqueous alkali, the fraction of acid ES soluble in the aqueous phase is separated in the form of free acids (by acidifying the aqueous phase), then separation into two fractions is performed: chlorophyllin acids and a sum of fatty and resin acids. Evaporation of the extracting agent, followed by vacuum distillation of the neutral part, is applied to separate the fractions of sesquiterpenoids and labdanum diterpenoids. The bottom residue is hydrolysed with a solution of alkali in alcohol, and then it is subjected to multi-stage extraction. As a result, the concentrates of sterols, di- and triterpenoids, polyproprenols are isolated. In patent [71], vacuum distillation in the mode of the turbulent film flow of solution over the heated surface is proposed for intensification of fractionating of neutral ES. Definite changes of the conditions of vacuum distillation, recrystallization and saponification described in [69, 70] allow one to increase the yield of labdanum diterpenoids and polyproprenols. According to the data reported in [12], a number of biologically active preparations were developed on the basis of the fractions obtained using the algorithm described in [69, 70]; the technological schemes of obtaining these preparations were implemented on a larger laboratory or experimental industrial scale. However, it should be noted that these methods of integrated processing of WG are not quite suitable for scaling with standard technological equipment and for forming profitable production on their basis.

The data described below are the examples of the use of the second method of WG processing implying isolation of a specific compound or a group of chemically related compounds from WG.

Maltol (E636) which is present, in particular, in the abies WG [72], is widely used in food and fragrance industry as taste amplifier and odour stabilizer. As a rule, Russian patents for the methods of obtaining maltol from the abies WG include CO2 extraction of the raw material [73–75] and isolation of the target product from the extract by sublimation and/or crystallization. To increase the yield and purity of maltol, the authors of [76] propose to supplement the CO2 treatment of WG with hot water and washing off the accompanying ES using diethyl ether before sublimation of the product. In addition to the target product maltol, other products of this method of WG processing are CO2 extract and forage flour. The technology of maltol production from the CO2 extract was implemented at the Siberian Plant of Extracts and Biotechnologies, experimental lots are manufactured at the Irkutsk Institute of Chemistry, SB RAS. There also is a foreign patent for the method of maltol extraction from the WG of Abies genus [77]. It is based on extraction with ethanol. Methods of obtaining synthetic maltol have been patented abroad, but they are multistage and inefficient in comparison with the extraction of native maltol from plant raw material.

One of the groups of BAS isolated from coniferous WG is polyprenols (PP). Their content in plants varies within the range $10^{-7}$–2%, however, the WG of conifers is the kind of raw material which is one of the richest ones in PP acetates and most available. The Kurarai Co. (Japan) patented [79] a method to isolate PP from needles using an organic extracting agent and complicated procedures for isolation/purification of the target product: chromatography, molecular distillation, distribution between two immiscible liquids etc. The PP concentrate can be obtained using the procedure described in [69–71], however, this approach is complicated and does not allow one to achieve a high yield. It should be stressed that the organic extracting agents used in the indicated works also extract low-molecular lipids, which brings complications into the purification of PP. A more reasonable method seems to be that described in patent [80]: needles are prepared for subsequent extraction of the PP fraction.
by means of carbon dioxide extraction. As a result of this operation, at first essential oil and some other lipid components are removed, then PP acetates are isolated by means of extraction with a hydrocarbon solvent. Such a sequence simplifies subsequent purification of the PP fraction. The PP with the main substance content \( \geq 95 \% \) are obtained by means of hydrolysis of acetates and single chromatographic purification. A technology of this kind was introduced at the Siberian Plant of Extracts and Biotechnologies. Phosphates of PP and dolichols exhibit essential biological activity, too [81]; the product based on them is used in veterinary.

Unlike other representatives of the Pinaceae family – fir, pine and larch – abies is distinguished by the high content of triterpenoids in needles, in particular triterpenic acids (TTA), while the concentration of diterpenic acids close to the former ones in polarity is insignificant [21, 24]. For this reason, TTA account for a substantial part of the acid fraction of the WG extract with organic extracting agents. Technologically reasonable methods for obtaining a mixture of TTA [82] or their salts [83] were developed; they imply WG extraction with a mixture of ethylacetate and light petroleum, followed by the treatment of the extracts with the aqueous solution of a basic agent (alkali or soda). The target product in the form of the sum of free TTA is isolated by neutralization of the water-alkali solution; evaporation results in obtaining a mixture of TTA salts. In patent [84], it is proposed to use a cheap and more readily available methyl-tert-butyl ether as an extracting agent. It was shown [85–87] that the preparation based on thus obtained sum of TTA (Novosil) exhibits phytoimmune correcting and fungicide activity. The simplicity of the technology of production of the sum of TTA and their high efficiency as the means of plant protection promote their popularity and an increase in the number of patents for the methods of obtaining these compounds. The authors of patent [88] propose to treat the abies WG preliminarily with live steam for 13–15 h (to remove the AO and thus to decrease the cytotoxic effect) and then extract the TTA mixture with methyl-tert-butyl ether (Silk preparation). The authors of patent [89] proposed to use a mixture of isopropanol or acetone with water as the extracting agent. They do not separate the total extract into the acidic and neutral parts (Biosil preparation). The method of TTA isolation by treating the ground raw material (with the humidity not more than 45 %) with the aqueous solution of alkali and extracting TTA with organic agents from the acidified aqueous part was patented [90]. There are patents describing the methods of obtaining solid watersoluble salts of TTA by means for the mechanochemical treatment of the plant raw material (bark or WG of abies) in mixture with other ingredients – sodium hydrocarbonate and a component containing protein [91] or cellulose [92]. The advantage of this method is that inflammable organic extracting agents are not involved in the technological process.

For the purpose of the integrated use of ES obtained according to the methods described in [82, 84], the authors of patent [93] proposed a method to isolate the sum of neutral isoprenoids from the neutral part of extract (which is a waste material from the production of TA) by distilling easily volatile components at decreased pressure; the biological activity of the product was revealed. According to the data of [93], the resulting product contains polypropenol acetates (up to 10 %), phytosterols (up to 30 %) and their esters (up to 40 %), chlorophyll and carotinoids (up to 5 %). The goal of [94] was to increase the functional possibilities of the method described in [89] due to the isolation of two biologically active preparations from the abies WG in one technological process. It is proposed to extract the raw material with an azeotropic mixture of isopropanol and water, to separate the extract by settling into two immiscible layers: the upper organic layer containing the sum of TTA, and the lower water-organic one containing from which the sum of the natural substances of phenol and carbohydrate nature is extracted after washing with a non-polar solvent.

It should be noted that the productions based on the technological approaches and schemes of WG abies processing, proposed in the patents, were arranged not in all the cases. One of the reasons is low profitability due to the narrow assortment of products and high production expenses. It follows from the data considered that in the majority of cases these products are multicomponent mixtures with non-
permanent (and not thoroughly studied) composition, with high concentrations of undesirable admixtures (for example, glycosides, tanning and tarry substances). These circumstances bring complications into the standardization of the composition and therefore certification of separate products, which finally limits their use in pharmacology and food industry. On the other hand, low cost of the production of composite products of abies WG processing ensures their use in the preparations for household chemical goods, fragrance industry, cosmetics, agricultural production and veterinary.

PRODUCTS OF ABIES WG PROCESSING IN CONSUMER GOODS

The fractions of extractive substances isolated from the abies WG find wide application in perfumery and cosmetics and phytotherapeutic means due to the high biological activity, absence of clearly expressed side effects, and good compatibility with other components of consumer goods. The useful properties of the preparations are due to the presence of natural BAS: vitamins (E, group K, provitamins D, carotenoids), phytosterols, polyrenols, chlorophyll, amino acids, phytosteroids, microelements etc. (see above). The range of the biological action of the ES of abies is extremely broad: anti-inflammatory, regenerative, wound-healing activity, bactericidal, antiviral, antifungal properties; biogenic and immunostimulating, adaptogenic, tonic, and deodorant action. It should be noted that the combination of anti-inflammatory and regenerative effects is characteristic of the complex remedies of plant origin because synthetic preparations suppressing inflammation at the same time inhibit proliferation. The combined anti-inflammatory, wound-healing, regenerative action of the components of WG provides high efficiency of the skin care means based on them. These preparations have a positive effect on inflamed skin, cure microfissures, abrasion, burns etc. Due to the pronounced wound-healing action normalizing the capillary circulation and removing spasms of minute vessels, as well as due to the improvement of metabolism and tissue regeneration, the abies ES are used in the prophylactics and combined treatment of varicose dermatitis, arthritis, osteochondrosis, injuries, sprain and other diseases. Such a characteristic feature of the preparations of plant origin is the soft antimicrobial effect is important in perfumery and cosmetics and prophylactic preparations. A broad range of bactericidal and fungicidal activity allows one to scotch the growth of various pathogenic microorganisms but does not kill the natural flora. The absence of side effects in applying the abies phytopreparations allows one to use them for treatment and prophylactics of skin diseases (fungal infections, dermatosis, furunculosis, seborrhea. It is known that the components of WG ES are efficient in curing the diseases caused by infections stable to antibiotics, in particular complications arising as a consequence of the antibacterial therapy. General corroborative, immunomodulating, tonic action of the preparations made of the abies WG is the basis of antistress and adaptogenic agents increasing the stability of an organism against hazardous action. These preparations decrease the intoxication syndrome caused by antibiotics, have cardioprotecting and hypotensive effect, increase tolerance to physical stress, resistibility to the diseases of gastrointestinal tract.

Examples of the cosmetic, fragrance and phytotherapeutic preparations based on the abies WG and manufactured by Russian plants are presented in Table 1. It should be noted that pine and fir WG is used along with the abies WG for the production of some preparations in the European part of Russia.

AO is the most frequent ingredient of consumer products. As a preparation included in pharmacopoeia, AO is used for compresses and embrocations efficient against toothache, parodontosis, rheumatism, diseases of the musculoskeletal system and upper air passages. AO is used in sports medicine as a heating massage agent, to cure sprain of tendons and muscles. For instance, AO is included into cream balms for massage with the heating effect [95, 96]. Tonic, deodorant and antimicrobial effects of the components of AO are used in aromatizing agents for use indoor. Bactericidal, anti-inflammatory [97] and antimicrobial [98]
properties of AO are used in bath preparations [99]. The authors of [100] developed a preparation to cure drowse; it contains EO of conifers and caffeine. On the basis of AO, balsams intended for skin and hair care are manufactured [101–103]; they have nutritive and tonic action, improve the metabolic functions of cells, granulation and epithelization of tissues.

Along with AO, the CO$_2$ extract of Siberian abies is widely used as a component of hygienic and fragrance cosmetic means. Among the products containing AO and CO$_2$ extracts of abies, there are cream balsams intended for tegraded treatment and prophylactics of skin diseases [104], nervous and bronchial-lung system, musculoskeletal system, skin tonics, deodorant creams for feet with antifungal action, creams for sick skin, gels for antiseptic treatment of hands, creams against mosquitos and midges, anticellulitic creams etc. The CO$_2$ extract of abies as an efficient agent of disinfection and deodorization is used in manufacturing bath preparations [105], air fresheners [106], foamy cleaning means [107], shaving preparations [108], shampoos with antimicrobial action, gels for feet [109] etc.

Abies oil and the CO$_2$ extract of Siberian abies along with other plant extracts are included into food balsams and concentrates [110, 111]. These products are used as taste additives in various drinks and phytococktails increasing the protective forces of an organism and improving metabolism. Soft drinks and biologically active additions are manufactured on the basis of he aqueous fraction of the CO$_2$ extract.

A series of curative and prophylactic preparations of generally tonic action based on the aqueous extract of Siberian abies is manufactured at the Bioepl Centre in Tomsk dealing with the system investigation of abies (see [50]). The Abisib preparation was clinically tested and registered in the State Register of Medical Products. According to the data of patent [50], Abisib stimulates hematology, cures inflammatory diseases of upper air passages, is efficient in the combined treatment of tuberculosis as an agent removing the intoxication syndrome and normalizing the blood characteristics [112]. The preparations has cardioprotecting and hypotensive action, increases tolerance to physical stress [113] and resistibility to the diseases of the gastrointestinal tract [50]. The anti-tumour activity of preparation “Abisib” was reported [114]. A broad range of therapeutic action and the absence of side effects are declared for similar preparations and biologically active additions (see Table 1). According to the data reported in [115, 116], the action of the Abisil preparation manufactured using the abies turpentine is similar to that of Abisib. Abisil is used as a curative and prophylactic agent in surgery, dermatology, stomatology and oto-laryngology. Creams containing the aqueous extract of abies and WG exhibit wound healing, bactericide, antifungal activity. The aqueous extract of Siberian abies is included into hygienic preparations for oral cavity care.

The derivatives of chlorophyll (CCCP, sodium chlorophyllin, coniferous wax) have been used for more than 50 years as a bactericide, deodorant additive in fragrance and cosmetic products. They are ingredients of toothpastes preventing parodontosis, of soap, bath extracts. A copper-containing derivative of chlorophyllin has a more pronounced bactericide action; it is used as a disinfectant in footwear deodorants, to accelerate hair dyeing, and as a food dye. The CPC preparation is used in shampoos and special hygienic preparations for nails.

As we have already mentioned, a number of biologically active preparations was developed on the basis of the strategy of complex processing of the WG of coniferous species, patented in [69, 70, 117]. On the basis of the concentrate of chlorophyllin acids (with the content of chlorophyllin derivatives ≤30 %), a biologically active addition was developed [118]; it broadens the assortment of the means used, in particular, for the prophylactics of adiposity. An insecticide preparation is obtained from the concentrate of resin acids and higher fatty acids after neutralization with soda [119]; the sesquiterpene fraction incorporating murolenes and cardinens is used as a repellent against blood-sucking insects. A mixture of di- and tri-terpenoids may be used as a biologically active emulsifier in fragrance and cosmetic means.

On the basis of the fraction of labdanum alcohols obtained in processing the coniferous WG, a curative and prophylactic preparation “Silbiol” was developed [12]. It contains isoabi-
<table>
<thead>
<tr>
<th><strong>WG</strong></th>
<th><strong>Commercial product</strong></th>
<th><strong>Normative document</strong></th>
<th><strong>Manufacturer</strong></th>
<th><strong>References</strong></th>
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<td>Gel for antiseptic treatment of hands “Asepton”</td>
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<td>&quot;Abitel&quot; Florenta drink</td>
<td>RU 004335S.P:643.06.2002</td>
<td>Biolit Co. [97]</td>
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<td>BAA</td>
<td>&quot;Dry concentrate of mineral water from Lake Shira with the extract of Siberian abies&quot; Oral cavity care preparation &quot;Argodent-khvoya&quot; Foamy cleanser &quot;Pikhta&quot; Shampoo &quot;Pikhta sibirskaya&quot;</td>
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<tr>
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enol, cis-abienol, epimanool as the major components. The fungicide activity of the preparation is comparable with the activity of nystatin, while the degree of inhibition of viral reproduction (influenza viruses of A and B types, and parainfluenza) is close to that of reman-thadine [120]. High efficiency of preparation “Silbiol” as a component of local pharmaceutical forms in therapy of nonspecific colpitis and dysbacteriosis arising as a consequence of the antibacterial therapy was demonstrated [121]. The antiseptic and antiviral action of Silbiol is used in curativ prophylactic toothpastes. A number of veterinary remedies of antimycotic, antimicrobial, anti-inflammatory and wound-healing action is manufactured on the basis of “Silbiol”. The major components of the fraction of labdanum alcohols are also extremely valuable raw material for the synthesis of fragrance compounds, for example ambroxide.

In addition to the conventional use in food industry (E636), maltol is intensively investigated during the recent time for biological activity. Its antioxidant and antiradical activity was demonstrated [122], which explains the promising character of its use as a bioantioxidant in fragrance-cosmetic and pharmaceutical preparations. According to the data of [123], the bactericidal and fungicidal activity of maltol, exhibited in the inhibition of the growth of yeast-like fungi, Gram-positive and Gram-negative bacteria, is only slightly smaller in comparison with modern antibiotics. Taking into account the natural origin, very low toxicity, and weaker skin-irritating action, Maltol can serve as a valuable bactericide component of prophylactic cosmetics and cleansers.

Polyprenol concentrate exhibits a broad range of biological activity. Antiulcerogenic activity of PP exceeds the known anti-ulcer effect of the oil of sea buckthorn [12]. The possibility to use PP to cure disorders of immune functions connected both with immunodeficiency and with hyperimmune states was demonstrated [124]. Taking into account extremely low toxicity, PP are used as prophylactic means with anti-stress and adaptogenic properties. Polyprenols are the active substance of Ropren preparation which possesses hepatoprotecting properties and is used to stimulate natural regeneration of liver cells [125–127]. The action of the preparation for prophylactics of respiratory viral infections is based on the antiviral and immunomodulating properties of PP [128].

On the basis of physiologically active phosphates of PP and dolichols, the specialists of N. F. Gamalei NIIEM, RAMS, together with N. D. Zelinskiy Institute of Organic Chemistry and Caprito Chemical Co. developed an antiviral medical preparation “Fosprenil”. It possesses the direct antiviral activity, enhances the natural stability of an organism towards infections, accelerates regeneration of tissues and organs affected by viruses, normalizes their functioning [81]. “Fosprenil” is registered as a veterinary preparation to treat carnivore plague, viral enteritis and infectious hepatitis in dogs, as well as panleukopenia, infectious peritonitis and rhinotracheitis in cats. Fosprenil preparation is used for prophylactics and treatment of a number of viral infections of young cattle and pigs.

The traditional area of application of the WG products is agricultural forage production. The action of ES of the abies WG on the animal organism is determined by the natural antioxidants – inhibitors of the oxidation of various unsaturated compounds in the organism (tocopherols, carotinoids, phenol compounds, unsaturated fatty acids and many others); substances with the bactericide and antiscirrhal activity; adaptogens and immunomodulators; surfactants (salts of resin acids, triterpenic and fatty acids) promoting emulsification and absorption of forage components in the digestive tract.

Forage coniferous flour made of the extracted WG is much cheaper than the vitamin grass flour but the production of combined forage products from coniferous WG seems more promising. A number of patents was dedicated to various methods of enriching the extracted WG with vitamins, microelements and nutrition substances using some fractions of ES. During extraction, WG gets free from resin substances and essential oil having a negative effect on the quality of forage, while the addition of ES to flour increases the relative mass content of useful substances: proteins, carotene, calcium, phosphorus, saccharides etc. Such a strategy was realized in obtaining biologically active forage additions for animals and birds [129], vitamin flour [130] etc.
Due to the high protein content, WG can be used to manufacture the protein-vitamin concentrate enriched with protein up to 55%, including up to 11% fat and up to 12 mg % carotene [6, 37]. It was mentioned above that a complex of liposoluble substances from WG is used as the vitamin additives: CCCP, PVK, sodium chlorophyllin, possessing growth-stimulating and sanation effects, improving the physiological state and productivity of animals and birds. In addition, CCCP is used in veterinary as wound-healing agent, to cure gastrointestinal diseases of young animals and to fight against cow barrenness [11]. The copper derivative of chlorophyllin is used as the forage addition to the food for domestic animals to increase the milk yield and as the deodorant agent [12]. The PP concentrate is used as a forage addition [13]; its efficiency is notable even at the background of the decreased protein and vitamin content of the basic ration of agricultural animals [12]. On the basis of PP, a veterinary preparation used for prophylactics of bronchopneumonia in animals is manufactured [134].

The extractive substances of abies are used as the means of crop protection. According to the data of tests [85–87], the extract of the sum of abies TTA exhibits the high biological activity of this kind. The basis of its action is the stimulation of the immune system of plants and seeds (phytoimmune correction) which promotes acceleration of growth and development, brings about complex stability against the diseases (especially those of fungal and bacterial origin) and unfavourable environmental factors. A substantial advantage of the use of phyto-preparations in comparison with the synthetic ones is the polyfunctional action of the former on the plants, which allows not only to increase crop capacity, improve the quality of fruitage, and decrease the losses of the crop but also to decrease the level of pesticide load for obtaining ecologically safe products. Preparations based on the abies TTA (see Table 1) are included into the list of pesticides and agricultural chemicals allowed for application at the territory of RF [135].

The high efficiency of composites made of the abies ES as the means for plant protection promotes the development of new preparations. Among the most recent ones, the powdered composite increasing the plant productivity should be mentioned; it contains water-soluble TTA salts together with protein- or cellulose-containing product. According to the data of [91, 92], the use of this preparation for wheat seed encrustation increases their germinating capacity, forms strong, well-rooted germs.

In addition to plant-protection means based on the TA sum, preparations were developed that contain the sum of neutral isoprenoids [93], the sum of polar substances of phenol nature, and the substances of carbohydrate nature [94]. These means are intended for enhancement of growth processes and the crop productivity of agricultural species.

**CONCLUSION**

So, the analysis of literature data shows that along with mastering the traditional technologies of the production of composite products, science-intensive methods of the isolation of chemically relative groups from the abies WG are developed; so are the methods of isolating separate compounds exhibiting specific biological activity. In turn, the advance of the new products to the market is determined by the balance between the economical expediency of their production and the practical significance of their consumer properties.

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