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Increase of pine acerose leaves application efficacy

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ABSTRACT
In this work, we conducted investigations aimed at intensification of the methods of obtaining of pine needles essential oils and the depth of oil extraction.

Keywords: Picea, *Pinus sylvestris* L., trees, buds, resin (hedge), essential oil, tannins, galipot, colophony, terebenthene.

1. Introduction

In Ukraine, pine trees and their parts appear to be the main fine wood in forestry engineering. Among the numerous pine species, in Ukraine only one species, Scotch pine (*Pinus sylvestris* L.) – an evergreen tree reaching up to 30-40 m in height and 1.5 m in trunk diameter – is widely spread.

In Ukraine there also grows one more species of Pinus genus, namely common spruce (Picea).

These plants occur all over forest and forest-steppe regions as well as in the Carpathian Mountains and in the Crimea.

Besides, virtually in all the regions there are man-made plantations in the form of woods.

Major pine wood consumers are woodworking industry, building industry, as well as paper and cellulose manufacturing.

In medicine, pharmacy and chemistry, pine tree and spruce are of great interest as a raw material source of major organic compounds, therapeutic and biologically active substances.

With this aim, pine buds, resin (galipot) and occasionally acerose leaves are used. Annually, 30 tons of buds are gathered while improvement felling of recent plantations.

While timber felling, there are waste products in the form of branches whose resources of acerose leaves are estimated at hundreds of tons.

Besides, each year more than 3 million young trees are cut down during New Year holidays. Christmas trees, after realization of their role, could be a source of pine needles on conditions that special fir tree receiving and utilization centres would be organized.

Thus, pine needles constitute easily available and renewable raw product resource deserving more attention.

Nevertheless, the attitude towards pine needles results in a bit of shock because of major part of pine acerose leaves being burnt in power installations, kiln burners and spontaneous sites for coniferous waste product burning. Meanwhile, all valuable substances of pine needles turn into combustion products.

Pine and spruce are like natural factories, where biologically active carbohydrates (mainly of cyclic structure, hexane and hexene derivatives) accumulate in various parts of the plant as a result of biochemical processes [1].

Some of organic compounds may serve as therapeutic agents. For instance, pine bud extracts and tinctures have traditionally been used for curative purpose.

Buds contain resin, essential oil (containing bornyl acetate, pinene, limonene), bitter substance pino - picrin, tannins, vitamin C, etc.

Common turpentine ("turpentine oil") and terebenthene, tar and dry distillation products, balsam of fir, etc. are obtained from galipot. Pine and spruce are labeled as medicinal plants of Ukraine [2].

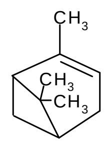
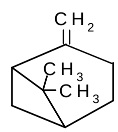
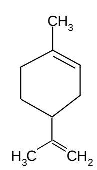
In comparison with buds, pine needles have a broader range of organic substances. Pine acerose leaves contain ascorbic acid, about 5% of tannin, alkaloids, essential oils comprising pinene, limonene, boras camphor, bornyl acetate, cadinene, anthocyanic compounds; they have traditionally been used in preparing vitamin beverages as well as chlorophyll (vitamin paste used in burns, wounds and dermatologic disorders).

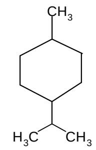
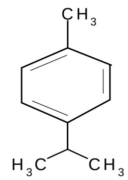
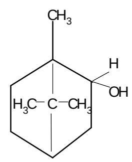
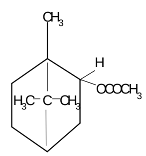
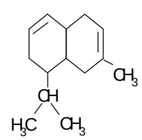
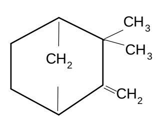
Nowadays, Scotch pine is an indispensable source of valuable organic products:

1) Galipot is secreted in the form of resin in artificially or spontaneously produced damages in the bark of pine tree trunk. In the air, the resin evaporates and hardens. Resin is a yellow viscous fluid with turpentine odour; it is miscible with ether, alcohol, acetone, but is insoluble in water. Turpentine and colophony are obtained from it.
2) Colophony is a resin obtained from pine galipot; it is either yellow or red hard vitriform substance with the density of 1007–1085 kg/m^3. It is softened at temperature about 70 °C. It is used in varnish and paper manufacturing and as a metal brazing flux.
3) Terebenthene is a mobile fluid with a characteristic odour. It is obtained from galipot with the help of method of partial hydrodistillation. It is used as a solvent, applied in pharmaceutical industry and it enters into the composition of various cosmetic and medicinal substances.
4) Essential oil is a complex mixture of terpenoids, tannins, alkaloids and anthocyanins. It is used in pharmaceutical industry and cosmetics. It is obtained from pine needles by means of hydrodistillation method. It is the most valuable product.

2. Material and Methods: chart 1 contains data concerning the main individual compounds being a part of pine acerose leaves essential oil.

Chart 1: Main individual compounds which constitute a part of pine needles essential oil.

Name	Gross formula	Molecularweight	Structuralformula	Melting temperature°C	Boiling temperature °C	Solubility in solvents	Note
α-pinene	$C_{10}H_{16}$	136.23		-75.5	156.2	Miscible with alcohol, ethanol InsolubleinH$_2$O	α-pinene and β-pinene are the main components of "turpentine oils", which are obtained with the help of water vapour distillation of some parts of Scotch pine galipot. α-pinene prevails; it occurs in dextrorotatory, laevorotatory and latent forms. It is the main substance of terebenthene.
β-pinene	$C_{10}H_{16}$	136.23		-62.2	164	Miscible with alcohol, ethanol InsolubleinH$_2$O	
Limonene	$C_{10}H_{16}$	136.23		-96.9	175.5	Miscible with diethyl ether, ethanol InsolubleinH$_2$O	It occurs in optically active form. Latent L-limonene appears in pine needles oil. Terebenthene contains large quantities of racemate, named dipentene.

p-terpane (1-Methyl-4-isopropyl-cyclohexane)	$C_{10}H_{20}$	140.27		–	170	Miscible with alcohol, ethanol InsolubleinH$_2$O	It is a product of limonene disproportionation. It is an ancestor of terpenes and camphors.
p-Cymene (1-Methyl-4-(1-methyl-ethyl)benzene	$C_{10}H_{14}$	134.21		-67.94	177.1	Miscible with alcohol, ethanol InsolubleinH$_2$O	It is a product of limonene disproportionation.
Borneol (Borneo camphor)	$C_{10}H_{17}OH$	154.26		208-209	212	Miscible with ether, petroleum-ether, ethanol, benzol Insoluble in H_2O	It is a product of camphor reduction produced from pinene.
Bornylacetate (Borneol,acetate)	$C_{12}H_{20}O_2$	196.29		29	223-226	Miscible with ethanol, organic solvents InsolubleinH$_2$O	It is formed as a result of biochemical reaction of borneol acetylation.
β-cadinene	$C_{15}H_{24}$	204.35		–	101.3–275	–	It is a bicyclic sesquiterpene.
Camphene	$C_{10}H_{16}$	136.23		50	159-160	Miscible with diethyl ether, benzol, ethanol Insoluble in H_2O	It is a parent substance for industrial synthesis of camphor.

3. Results and discussion

Indeed, pine needles oils are a complex multicomponent product.

For instance, acerose leaves of Canadian pine tree contain 38 compounds: bornyl acetate, camphene, α-pinene, cadinene to name but a few [4].

Essential oil of Siberian cedar has been identified to have 54 components among which α-pinene, limonene, cadinene and α-bisabolol prevail [5].

In Ukraine pine woods rank the first place in area extent (36.2%).

Pine needles supply is very large (15–20% of all the biomass) and constitutes a great renewable source of raw products. In spite of the fact that the products obtained from these raw materials have long been in use, extraction and processing technologies lag behind of the present needs.

Pine acerose leaves contain much more biologically active and energy substances than wood.

In this work, we conducted investigations aimed at intensification of the methods of obtaining of pine needles essential oils and the depth of oil extraction.

The process of distillation with water vapour of immiscible with water fluid is submitted to the following dependence [3]:

$$Y = \frac{Y_п \cdot M \cdot P_{пж} \cdot \varphi}{18(P - P_{нас})} , \quad (1)$$

In which Y – the quantity of the distilled fluid,

$Y_п$ – the quantity of the water vapour,
M – the molecular weight of the fluid,
P – general pressure in the system,
φ – coefficient of water vapour saturation,
$P_{нас}$ – fluid vapour resilience at the temperature of water vapour.

As we can see in the mentioned above dependence, the intensification of the process can be achieved by means of either general pressure lowering or the process temperature increase leading to the increase of $P_{нас}$ and reduction of the pressure difference $P – P_{нас}$.

Pine needles essential oil extraction is based on the application of the traditional methods of hydrodistillation, the main drawbacks of which are long duration and insufficient extent of oil extraction because of strong links with subcellular deposits.

With the aim of the process intensification taking into account the dependence [1] we have conducted a series of experiments concerning the pine needles essential oil extraction at higher temperatures (115 °C) at the expense of superheated water vapour application.

On the assumption of temperature rise having negative influence on the distillate quantity and composition, we have minimized the process duration.

As a result of the conducted experiments, we have determined the optimum duration of the process at 180±5 minutes and 55±5 minutes by means of the traditional method at higher temperatures.

Generalized results of the experiments are supplied in Chart 2.

Chart 2: Yield and physicochemical indices of essential oil in a specimen of Scotch pineace rose leaves.

Indices	Essential oil of a specimen of Scotch pine needles	
	At temperature of superheated water vapour	At temperature of saturated water vapour
Duration, minutes	55±5	180±5
Oil yield, %	1.62±0.06*	1.43±0.05*
Density ρ^{20}, g/cm^3	0.8793	0.8793
Refraction index, n_4^{20}	1.4819	1.4819
Acidity index, mg KOH/g	0.39	0.38
Esterification number, mgKOH/g	104.63	105.87

*(in terms of fresh raw materials (57.3% humidity).

4. Conclusions

Essential oil quantity depends to a large extent on the content of components. Component content of the derived oils has been identified by means of the method of chromatography-mass spectrometry with the help of a partition gas chromatograph«Varian 1200L», ionization by electron impact, ionizing energy70 eV. We have used capillary column DB-5HT (Agilent Technologies), phase – 5% phenylpolysiloxane, 95% methylpolysiloxane. Temperature programme: isotherm for 1 minute at 30 °C, stepwise temperature rise: up to 60 °C at a rate of 3° C/min, then up to 200 °C at a rate of 20 °C/min, after that up to 300 °C at a rate of 30 °C/min and holding during 3 minutes at the final temperature. Input sample volume is 1 microliter, injector temperature is 250 °C. Mixture component content has been identified by means of internal normalization technique. Peak rating has been conducted by means of the derived mass spectra matching with the data of mass spectral library NIST/06 Mass Spectral Library.

While analyzing the component content of the essential oils derived under different conditions (Chart 2), identity has been ascertained.

None of the samples had additional compounds characteristic of either kind of oil.

Thus, rise of essential oil distillation temperature by 15 °C and the process duration reduction does not result in any changes in component content of essential oils and does not impair their quality.

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