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Triterpenoids Inherent in the Coniferous Plants of Pinaceae Family

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Abstract

An attempt is made to systematize the data from scientific publications, patents and the internet resources concerning triterpene components in the plants of Pinaceae family those could be considered as chemotaxonomic markers and as the active principle of biologically active preparations. Examples are given for the major structural groups of triterpenoids inherent in conifers and data concerning the presence of these compounds in total extractive substances of the plants of different genera of the family. A problem connected with the examination of bioactivity of triterpenoids inherent in coniferous plants is assessed.

Key words: triterpenoids, Pinaceae family, lanostanoids, serratanes

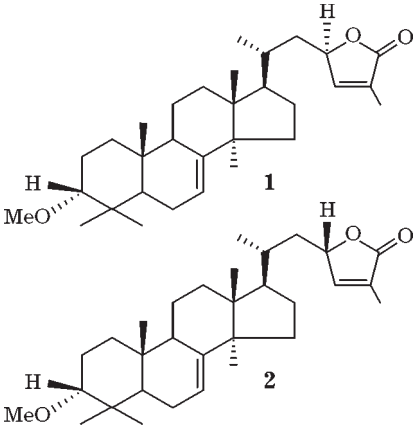
INTRODUCTION

Coniferous trees in the territory of Russia are presented predominantly by the plants of family Pinaceae those are the main forest-forming species of the Siberian region. The Novosibirsk, Tomsk, Kemerovo Regions, the Altai and Krasnoyarsk Territories are considered the natural habitat of the *Siberian abies* (Siberian fir) *Abies sibirica*, spruce fir *Picea obovata*, pine (Archangel fir) *Pinus sylvestris*, cedar pine *Pinus sibirica*, Siberian larch *Larix sibirica* [1]. In the case of continuous cutting down the storing of felling debris (wood green, bark) as raw materials for industrial and semi-industrial processing should be carried out taking into account its purpose and chemical composition.

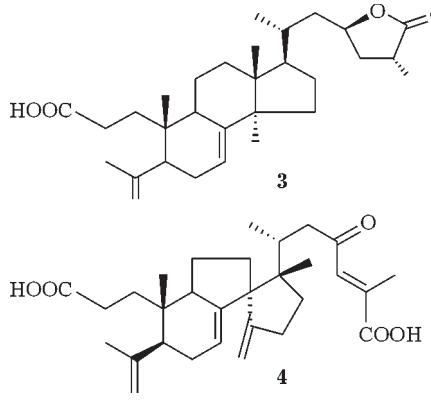
The greatest differences between various conifer species can be observed in the set of triterpene compounds those are positioned in the literature as chemotaxonomic markers [2]. At the same time, it is known about a wide range of the physiological activity of triterpenoids belonging to lanostan, serratane, dammarane, gopane series, the most inherent in the chemical composition of wood green and bark of conifers [3–12]. Most widely, triterpenoids are presented in different species of abies trees. Over the territory of Russia, there are seven species of abies spread from more than 50 species growing in Asia, North America, North Africa and some European countries. In the literature there are details available concerning the components of 20 abies species. The abies species are characterized mainly by lanostan-type compounds, the composition of bark and spruce needles is presented by serratane-type triterpenoids [2], whereas the content of triterpenoids in the needles, spears and bark of pine and larch is insignificant. From the seven species of abies spread over the territory of Russia, the most extensive natural habitat of growth is inherent in the *Abies sibirica* [1]. The chemical composition of different parts of this plant was widely studied. The information concerning the composition and the ratio between biologically active components formed the basis of the complex processing of large-scale felling debris those serve as a raw material for obtaining commercial products with a wide range of consumer properties [11].

TRITERPENOIDS INHERENT IN ABIES

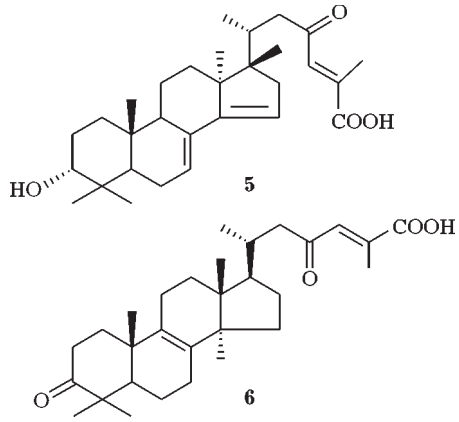
The investigation of triterpenoids inherent in different abies species began in 1938, when abieslakton was isolated from *Abies mariesii* **1**, a triterpene lactone with lanostan skeleton [3]. Its structure was proved once and for all by means of XRD structure analysis [3] and NMR spectroscopy [13]. Later, this compound was revealed in other abies species [3, 14, 15]. Abieslakton is isomeric with respect to grandisolid **2** which was isolated from *Abies grandis* which growing in the North America. The difference of the structure consists in the orientation of the hydrogen atom at C23 carbon atom. Both compounds belong to Δ^7-lanostanoids those are most inherent in different abies species.



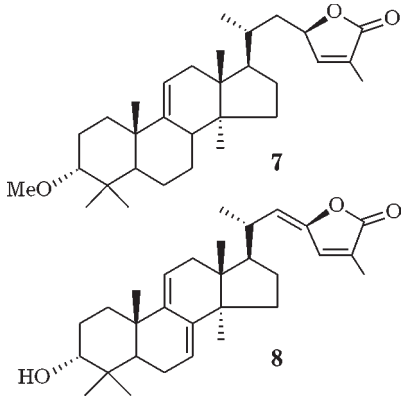
The compounds with hydroxyl, acetoxyl or keto group at the third carbon atom with different structure of the side chain of the lactone ring belong to the same series. 3,4-Secolanostanoids first isolated from the gum of the *Abies siberica* and characterized by the researchers of the NIOCh of the SB RAS (Novosibirsk), abiesolidic **3** and abiesonic **4** acids are structurally related to them [16, 17].



$\Delta^{7,14}$ -Lanostanoids, such as 23-oxomariesioic acid A **5** are to a most prevailing extent inherent in abies needles [18]. A detailed study of various abies species resulted in identifying the compounds of Δ^8 series, structurally similar to (24*E*)-3.23-dioxolanosta-8,24-diene-26-oic acid **6** [19].

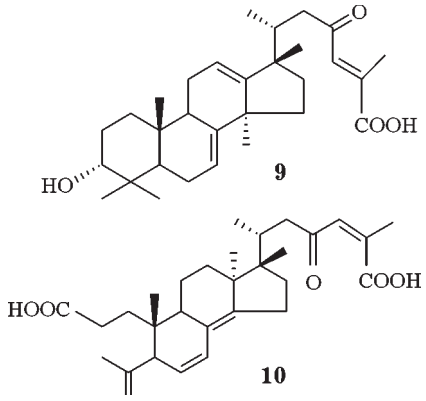


There were isolated and characterized lanostanoids of Δ^9 (*e. g.*, veytchiolid **7** [3]) and $\Delta^{7,9}$ series (pindrolakton) **8** [3], but they were not detected in *Abies sibirica*.

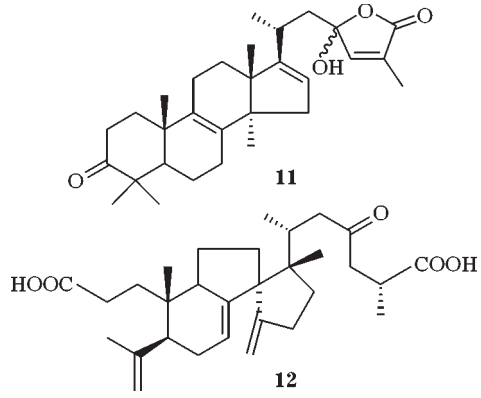


Lanostanoids of $\Delta^{7,12}$ series, such as 23-oxomariesiic acid B **9**, were for the first time discovered in *Abies mariesii* [20] and later in *Abies sibirica*. Among secolanostanoids there were $\Delta^{6,8}$ compounds detected such as *cis*-sibiroic acid **10** [21].

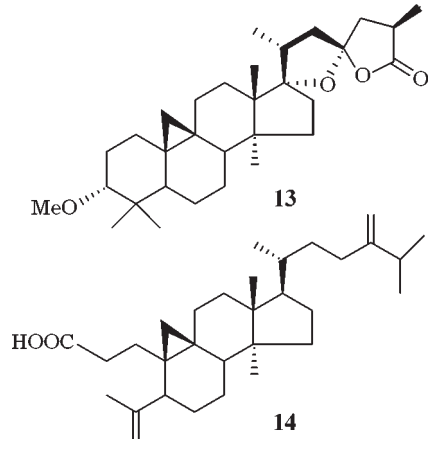
In recent years, under more detailed studying *Abies chensiensis* there were $\Delta^{8,16}$-lanostanoids revealed therein **11** [22]. Abies species are also characterized by the presence spiro compounds, in addition to the mentioned



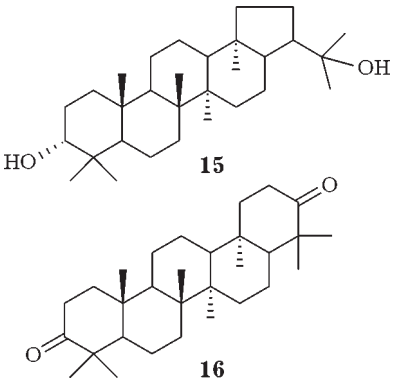
abiesonic acid. So, from different abies species, there were isolated 25 spiro compounds including (25R)-23-oxo-3,4-*seco*-abiesa-4(28),7,14(30)-trien-3,26-dioic acid from *Abies alba* **12** [23].



In addition, more than 10 cycloartanoids were identified (*e. g.*, **13**) including *seco*-cycloartanoids. For one of them, 24-methylene-3,4-*seco*-cycloart-4(28)en-3-oic acid **14**, was for the first time synthesized from 24-methylenecycloartanol isolated from sea buckthorn fruit [24].



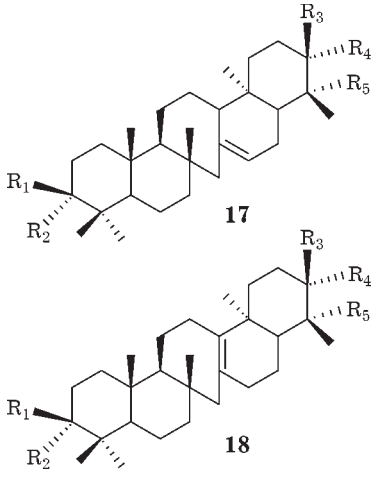
In the raw material from *Abies veitchii* and *Abies mariesii* species there was detected gopane and gammacerane triterpenoids, such as 3α,22-gopandiol, gammaceran-3,21-dione **15**, **16** [3].



In addition, in one of abies species *Abies spectabilis*, there were found small amounts of dimethyl ether of 21-episerratanediol as well as of isoserratanedione [25].

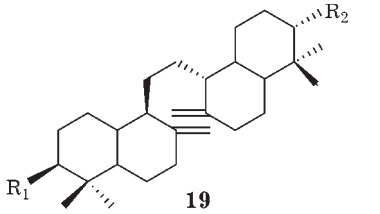
TRITERPENOIDS INHERENT IN PINE AND SPRUCE

Lanostanoids were isolated also from pine *Pinus monticola* Dougl. and *Pinus armandii*, whereby all the selected compounds belong to Δ^9 series [26, 27]. As far as the domestic species of pines *Pinus sylvestris* and *Pinus sibirica* are concerned, lanostanoids were not revealed therein. From the bark of *Pinus sylvestris* and *Pinus sibirica*, there were triterpene compound isolated those belong to serratane series relative to Δ^{14}-serratenes [28]. Triterpenoids with such a skeleton (**17**) were revealed in *Pinus banksiana* Lamb., *Pinus lambertiana* Dougl., *Pinus taeda* L., *Pinus palustris* Mill., *Pinus radiata*, *Pinus armandii* [26, 27, 29, 30]. Δ^{14}-Serratenes were also revealed in different



spruce species including common spruce *Picea obovata* L., Ajan spruce *Picea jezoensis* and Norway spruce *Picea abies* Kor. Besides Δ^{14}-serratanes, in and common spruce there were Δ^{13} serratanes **18** identified.

In the bark of common spruce there were onoseranes **19** found, whereas in the Ajan spruce there were abeoserratanes and epoxyserratanes **20–22** revealed [31–33]. In the plants of *Pinus* species there were no such triterpenoids found.



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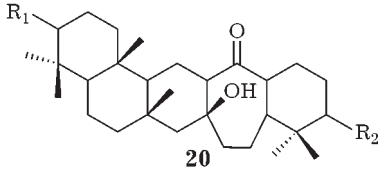

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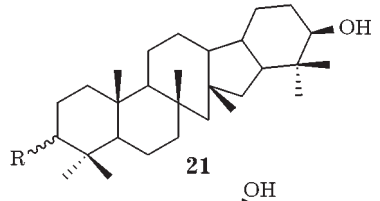

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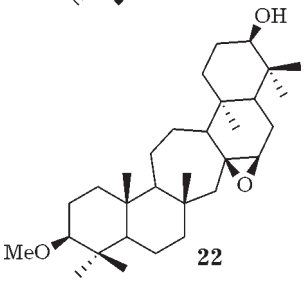

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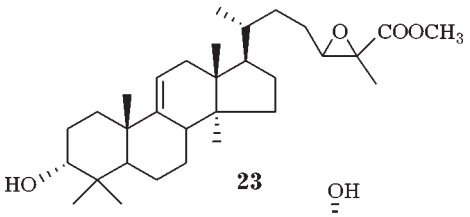
TRITERPENOIDS INHERENT IN LARCH

According to the data available from the literature, the lanostanoids such as methyl (24S,25R)-epoxy-3α-hydroxylanost-9(11)-en-27-oic acid methyl ester **23** [34] lanost-9(11)-ene-3α,24S,25-triol **24** [31, 35] isolated from larch *Larix sibirica* and *Larix kaempferi* also belong to Δ^9 series.



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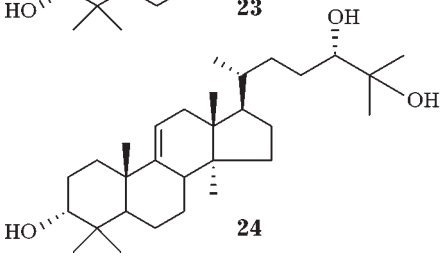

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CONCLUSION

Thus, the generalized information can serve the chemotaxonomic and pharmacognostic purposes for the identification of raw material, for determining the quality of raw material, its processing schemes and for the prediction of bioactivity of the extracts obtained in the technological view. To date, from the plants of family Pinaceae there are isolated more than 110 lanostanoids, more than 30 serratenes and biogenetically close to them onoseranes, abeoserratanes and epoxyserratanes isolated. It should be noted that a large contribution was made by research workers of the NIOCh of the SB RAS (Novosibirsk), who isolated more than 50 triterpene components from the domestic species of conifers to characterize by means of modern spectral methods. According to the studies performed they published more than 50 scientific articles, patented various methods for obtaining growth-promoting preparations with fungicidal action for agriculture (the most part of this information is presented in the reviews [3, 11, 31, 35, 36]). Taking into account a rapid accumulation of data concerning different types of physiological activity for lanostan and serratane based triterpenoids from conifers, including the suppression of α-glycosidase, NO suppression effect [10], enhancing the adaptive capacity of a living organism [37] as well as a structural analogy between the components of conifer and triterpenoids from Shisandraceae and medicinal fungi [38], it is reasonable to

continue the active investigation of the triterpenoids of conifers.

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