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TRITERPENOIDS OF PLANTS OF THE GENUS Abies HILL

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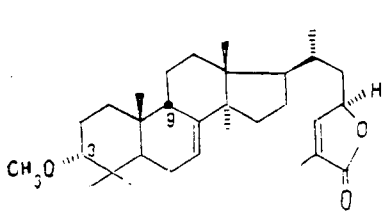
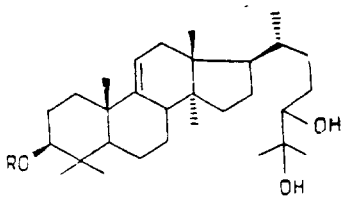
UDC 547.595.9:547.914.4

A review is given for the first time of the results of investigations of Soviet and foreign authors on the isolation of triterpenoids from the bark, needles, oleoresin, and seeds of various species of Abies (fir) and the determination of their structures and properties. Features of the PMR, mass, UV, and CD spectra of the compounds under consideration are discussed specially and information is given on their classification, distribution in firs, and biological activities.

In recent years, investigations connected with the study of the composition of the extractive substances of coniferous plants of the genus Abies Hill (fir) have been developed intensively. In a review published in 1972, Norin [1] reported that the bark of three species of fir contained "a triterpenoid of a unique type" – abieslactone (I). This compound has the well-known lanostane carbon skeleton, and its uniqueness consists in the β-configuration of the hydrogen atom at C-9 and the α-configuration of the oxygen-containing substituent at C-3. Triterpenoids have also been found in other conifers of the Pinaceae family, but they belong to different structural types (for example, serratane derivatives from the bark of species of Pinus [2] and Picea [3]) or are assigned to widely distributed triterpenols or 4,4-dimethylsterols [4-6]. The closest to abieslactone are the lanost-9(11)-enetriol (II) and the methoxydiol (III), which have been detected in the bark of Pinus monticola Dougl. [7].



I



II R = H

III R = CH_3

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 443-455, July-August, 1990. Original article submitted January 10, 1989.

TABLE 1. Triterpene Compounds Isolated from Plants of the Genus Abies Hill (in the case of carboxylic acids information for the corresponding methyl esters is given in columns 3-5)

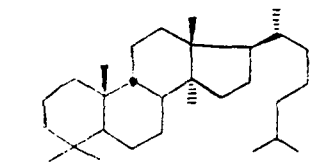
Number of the compound	Trivial name	Empirical formula	$[\alpha]_D$, deg	mp °C	Literature
1	2	3	4	5	6
		9β -Lanost-7-enoids			
I	Abieslactone	$C_{31}H_{48}O_3$	−113	252—253	8—13
IV	—	$C_{30}H_{46}O_3$	−70,9	243—245	11, 13
V	—	$C_{30}H_{44}O_3$	+22,9	224—228	11, 13
VI	Firmanoic acid	$C_{31}H_{46}O_4$	+23	110—111	14—16
VII	—	$C_{31}H_{46}O_4$			14, 16
VIII	Isofirminoic acid	$C_{31}H_{46}O_4$	+36,8	142—144	17
			+24	163—164	15
IX	Firmanolide	$C_{30}H_{42}O_4$	− 8	193—195	15
X	Isofirmanolide	$C_{31}H_{42}O_4$	+24	193—195	15
XI	—	$C_{31}H_{42}O_3$	−51,4	218—220	18
XII	—	$C_{30}H_{44}O_4$	+34,9	177—181	18
XIII	24,25-Dihydroabieslactone	$C_{31}H_{50}O_3$	−66,6	195—197	13
		3,4-Seco-9β -lanost-7-enoids			
XIV	Abiesolidic acid	$C_{31}H_{46}O_4$	+10,3	154—155	19,20
		Lanost-8-enoids			
XV	—	$C_{31}H_{46}O_4$	+45,5	132—134	17
XVI	—	$C_{30}H_{42}O_3$	−62,3	247—248	18
		Lanost-9(11)-enoids			
XVII	—	$C_{30}H_{48}O_3$	+47	239—240	21
		13,17-Friedo-9 β -lanostanoids			
XVIII	Mariesiic acid B	—	—	—	22
XIX	23-Oxomariesiic acid B	—	—	—	22
		Mariesianoids			
XX	Mariesiic acid A	$C_{30}H_{46}O_4$	+116	197—200	23
XXI	23-Oxomariesiic acid A	$C_{31}H_{46}O_4$	+53,2	—	22,24
XXII	—	$C_{31}H_{46}O_4$	+19,9	192—194	24
XXIII	—	—	—	—	24
XXIV	—	—	—	—	24
XXV	—	$C_{32}H_{48}O_4$	−6	Oil	25
		3,4-Secomariesianoids			
XXVI	cis-Sibiric acid	$C_{32}H_{46}O_5$	−115	Oil	25
XXVII	Anhydrosibiric acid	$C_{31}H_{42}O_4$	−297	Oil	25
		Abiesanoids			
XXVIII	Mariesiic acid C	$C_{31}H_{44}O_4$	−33,6	Oil	22
XXIX	Isomariesiic acid C	$C_{31}H_{44}O_4$	−154	Oil	22
		3,4-Secoabiesanoids			
XXX	Abiesonic acid	$C_{32}H_{46}O_5$	−37,3	93—94	24,26
XXXI	cis-Abiesonic acid	$C_{32}H_{46}O_5$	—	Oil	24,26
		Cycloartanoids			
XXXII	Abietospiran	$C_{30}H_{48}O_3$	−16,8	219—221	27
XXXIII	Cyclograndisolide	$C_{31}H_{48}O_3$	—	191—193	28
XXXIV	Epicyclograndisolide	$C_{31}H_{48}O_3$	—	193—194	28
		3,4-Secocycloartanoids			
XXXV	—	$C_{32}H_{52}O_2$	+61	31—32	29

Today, it is known that abieslactone is a representative of ubiquitous group of triterpenoids that is characteristic for Abies species. Work on the isolation of these compounds is being pursued by several groups of researchers, but complete clarity has not yet been achieved on the distribution of the triterpenoids of lanostane and related types in firs, and a fairly large number of questions have arisen on the interrelationship of the compounds of different structural types even within these groups.

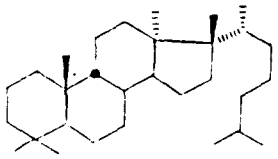
The aim of our review is to generalize literature information on fir triterpenoids, the study of which is becoming an independent field of the chemistry of the terpene compounds of coniferous plants. Its urgency is due not only to the novelty and exotypical nature of the structure of the compounds that are being isolated but also to the high content of the latter in the natural raw material (the bark, needles, seeds, and oleoresin of various species of fir) and the biological activity of individual representatives of this group of compounds.

STRUCTURAL TYPES AND NOTATION

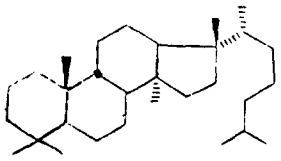
At the present time, 35 triterpenoids isolated from eight species of fir are known (Table 1). They are classified according to the type of carbon skeleton, and the main ones are 5α-lanostane (A), 17,14-friedo-5α,9β-lanostane (B), 17,13-friedo-5α,9β-lanostane (C), 8(14 → 13)-abeo-17,13-friedo-5α,9β-lanostane (D), and cycloartane (E).



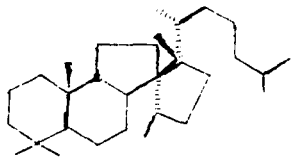
A



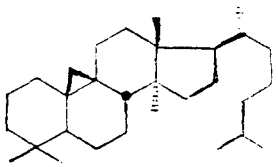
B



C



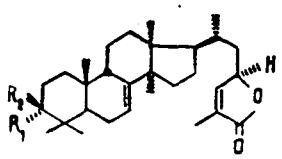
D



E

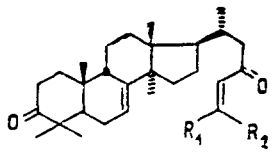
The name "mariesiane" has been proposed for the carbon skeleton B [24], and for D it is desirable to use "abiesane." The numbering of the carbon atoms in skeletons B, C, and D is kept the same as in lanostane in the light of the postulated scheme for the biogenesis of the corresponding triterpenoids [22, 23, 26]. Thus, abiesonic acid (XXX) may be called 3,4-secoabiesa-4(28),7,14(30),24E-tetraen-23-on-26-oic acid.

In a more detailed consideration, type A can be divided into four groups — 9β-lanost-7-enoids, 3,4-seco-9β-lanost-7-enoids, lanost-8-enoids, and lanost-9(11)-enoids, as has been done in Table 1. From the compounds belonging to type B it is possible to single out separately the group of 3,4-secomariesianoids, while type E can be divided into cycloartanoids proper and 3,4-secocycloartanoids. The same relates to the abiesane type (D). Thus, all known triterpene compounds of the fir are divided into 10 structural groups.



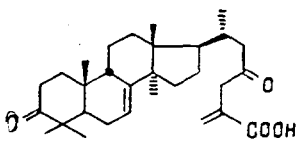
IV. R_1=OH, R_2=H

V. R_1+R_2=O

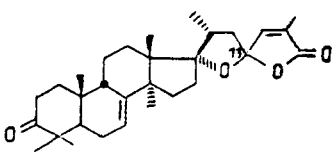


VI. R_1=COOH, R_2=CH_3

VII. R_1=CH_3, R_2=COOH

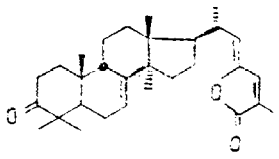


VIII

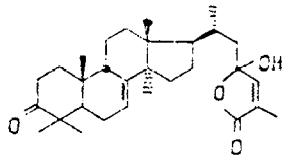


IX. 13S

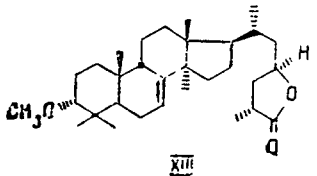
X. 13R



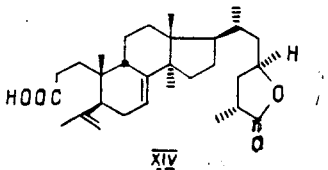
XI



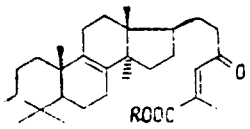
XII



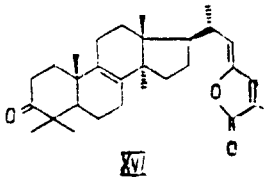
XIII



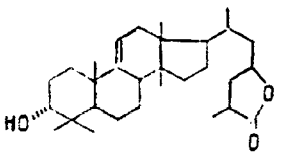
XIV



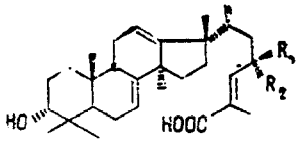
XV



XVI

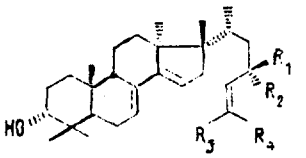


XVII



XVIII $R_1 = OH$, $R_2 = H$

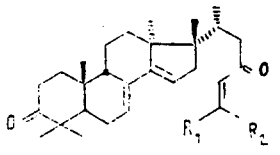
XIX $R_1 + R_2 = O$



XX $R_1 = OH$, $R_2 = H$, $R_3 = COOH$, $R_4 = CH_3$

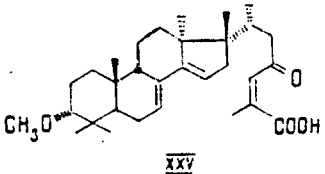
XXI. $R_1 + R_2 = O$, $R_3 = COOH$, $R_4 = CH_3$

XXII. $R_1 + R_2 = O$, $R_3 = CH_3$, $R_4 = COOH$

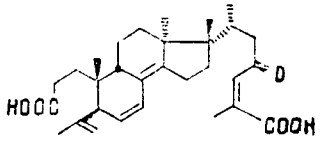


XXIII $R_1 = COOH$, $R_2 = CH_3$

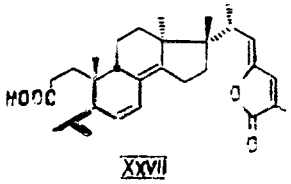
XXIV $R_1 = CH_3$, $R_2 = COOH$



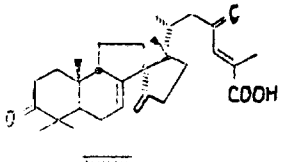
XXV



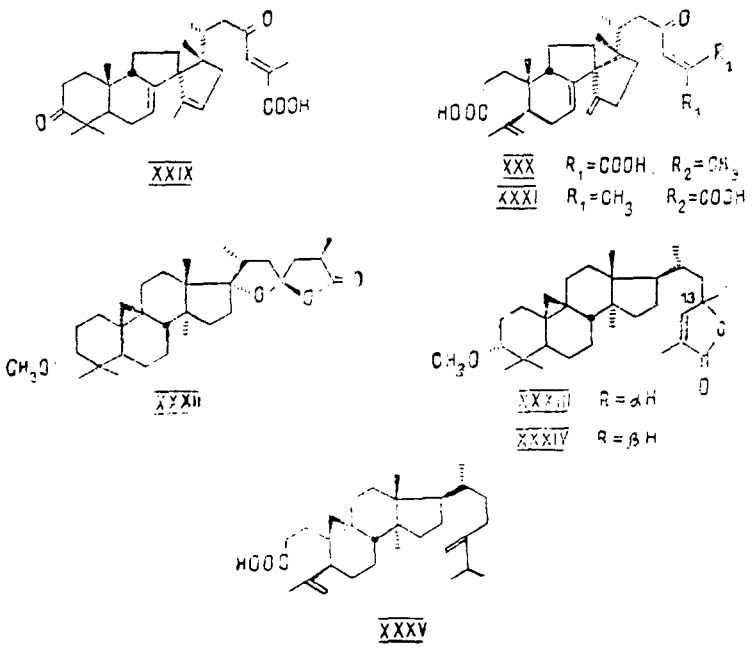
XXVI



XXVII



XXVIII



DISTRIBUTION OF TRITERPENOIDS IN Abies SPECIES

The investigation of triterpenoids of the fir has practically only just begun, since of the approximately 50 species of Abies growing on the planet [30], only eight have been partially studied. These compounds are components of the oleoresin [20] and make up a considerable part of the extractive substances of the bark, the needles, and seeds. Thus, abietospiran (XXXII) has been obtained with a yield of 14% from the raw material taken [27]. Whether the triterpenoids are necessary products of the metabolism in all species of fir is unknown, as yet, but the available information permits the assumption that this is in fact the case in view of the high content of triterpenoids in the material already studied.

The distribution of the triterpenoids known at the present time over the species of fir studied is as follows:

1. Abies alba Mill.: XXXII (bark), XVII (needles), XIV (deoresin);
2. Abies amabilis (Dougl.) Forbes: I, IV, V (bark);
3. Abies firma Sieb. et Zucc.: VI, VII, IX, X, XIX, XXI (seeds);
4. Abies grandis (Dougl.) Lindl.: XXXIII, XXXIV (bark);
5. Abies mariesii Mast.: I (bark, needles), XVIII, XX, XXVIII, XXIX (seeds);
6. Abies mayriana Maybe et Kudo: XIV (deoresin);
7. Abies procera Rehd.: I (bark);
8. Abies sibirica Ledb.: I, IV, V, XIII (bark), XIV, XXX (deoresin), VI-VIII, XI, XII, XV, XVI, XXI-XXVII, XXX, XXXI, XXXV (needles).

Any serious generalization whatever of these facts is still difficult, since only three materials have been investigated relatively fully – the needles of the Siberian fir (Abies sibirica) and the seeds of two Japanese species of fir (A. firma and A. mariesii). It is possible to draw the preliminary conclusion from the results of the investigations of the Siberian fir that the biosynthesis of 9β-lanostanoids from mariesianoids is pronounced in its needles. In their turn, mariesianoids have not yet been found in the oleoresin, for which the presence of 3,4-seco derivatives of the 9β-lanostane and abiesane series is characteristic [19, 26].

Cycloartanoids with oxygen-containing substituents in the side chain are apparently present only in individual species of fir, and their distribution may be elucidated in subsequent investigations.

It is impossible not to mention the high degree of oxidation of the molecules of the compounds under consideration. In this connection, the search for simple triterpenoids of the 9β-lanostane series, which are possibly biogenetic precursors of the more oxidized derivatives, appears promising.

METHODS OF ISOLATION AND SOME FEATURES OF THE CHEMICAL PROPERTIES OF THE COMPOUNDS

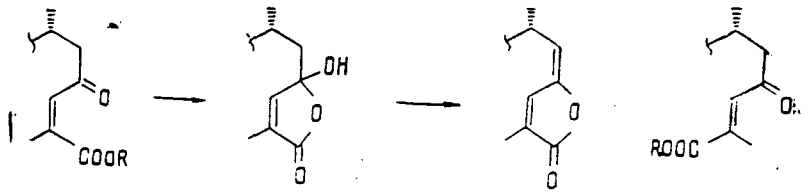
Various known methods are used for isolating triterpenoids, the choice of them being determined by the nature of the raw materials and the properties of the desired compounds. For the neutral lactones, the presence of which in extracts is high, it is possible to manage without chromatographic separation. Thus, abieslactone (I) and abietospiran (XXXII) have been isolated by simple crystallization of a total extract of the bark [10, 27], while the sum of the lanostane lactones of the bark of the Siberian fir crystallizes almost quantitatively from a petroleum ether solution of the neutral fraction of a gasoline extract [13].

As a rule, the triterpene acids are found in the raw material in the form of a complex mixture, and it proves to be most effective to separate them in the form of methyl esters by absorption chromatography on silica gel [17, 22, 24]. The HPLC method has not yet been used for the triterpene acids from the fir.

A number of triterpene acids considered have a β-acylacrylic acid fragment in their molecule [for example, abiesonic acid (XXX)], which makes possible their selective separation from the sum of all the other acids, including resin acids, by extracting an ethereal solution of the mixture to be analyzed (oleoresin, extract of the bark or of the needles) with an aqueous solution of sodium bicarbonate [20, 24].

The most interesting chemical properties of the fir triterpenoids that must be taken into account in the isolation and purification of these compounds are connected with the above-mentioned grouping. Thus, the ease of cis-trans isomerization of the Δ^{24} double bond taking place even under the action of sunlight [24] and also on the alkaline saponification of the methyl esters [24] must be specially mentioned.

When the acids are methylated with an ethereal solution of diazomethane it is necessary to use a low temperature [22] or bring to a minimum the time of contact of the substance with the diazomethane [24], which is due to the known tendency of diazomethane to add to an activated double bond [31].



Acids with the fragment F (R = H) in the molecule can be converted into the hemiketal form (G), the dehydration of which leads to the alkylidenebutenolide (H) [18]. These transformations, which are known for β-acetylacrylic acid [32], are apparently common for all fir triterpenoids having fragment F (R = H) in their molecules. It is interesting to note that a tautomer with fragment G [compound (XII)] has been isolated in the chromatographic separation of an extract of Siberian fir needles [18]. The tautomeric transformation F → G takes place on acid catalysis [18], which must be borne in mind in the analysis of mixtures of triterpene acids.

As one more feature of the chemical properties of the fir triterpenoids we must mention the stereospecificity of the catalytic hydrogenation of abieslactone, leading to a 24,25-dihydro derivative with the "unnatural" configuration at C-25 [13]. In view of this, it is natural to assume that the biosynthesis of abiesolidic acid (XIV) takes place not through a saturated lactone of the type of 24,25-dihydroabieslactone but with the reduction of the Δ^{24} double bond in an earlier stage, before the formation of the lactone ring.

So far as concerns hydrogenation processes, it is necessary to mention the stability of the conjugated dienic system in the molecule of the methyl ester of the 3,4-secomariesanoid (XXVI) [25] and in the 3-O-acetate of the methyl ester of mariesanoid (XXII) (unpublished results of the author) on catalytic hydrogenation over $Pd/CaCO_3$ in ethyl actetate. In the first case, this is due to steric screening of the dienic system by other fragments of the molecule [25], and in the second case the noncoplanarity of the dienic system itself, which has been shown by x-ray structural analysis of two derivatives of the mariesiane series [23, 24].

Finally, we must mention the relative ease of isomerization of 9β-lanost-7-ene derivatives into lanost-8-ene derivatives under the action of strong acids [11, 32]. The delayed detection of this fact was responsible for the erroneousness of the first conclusions concerning the structure of abieslactone [10].

STRUCTURE DETERMINATION

In view of the complexity of the chemical structure of the fir triterpenoids, the most reliable method is the use of x-ray structural analysis (XSA), which is necessary in the investigations of the structures of compounds with new carbon skeletons. Thus, it has been used to demonstrate the structures of abieslactone (I) [11], abietospiran (XXXII) [27], mariesiic acid A (XX) [23], mariesiic acid C (XXVIII) [22], abiesonic acid (XXX) [26], and the acid (XXII) [24].

The revelation of the structural features of the molecules with the structures shown will in future permit their use to establish the structures of related triterpenoids, as has been done in the deduction of the structures of the 3,4-secomariesanoids (XXVI) and (XXVII) [25], 24,25-dihydroabieslactone (XIII) [13], and others.

A successful expedient is a combination of the analysis of spectral characteristics and chemical correlation with substances the structures of which have been shown by the XSA method [22, 24].

SPECTRAL PROPERTIES

In this section a brief account is given of the described features of spectra which, in particular, permit the determination of the inclusion of a compound under investigation into some of the known groups of fir triterpenoids.

PMR Spectra. The PMR spectra recorded in an instrument with a working frequency of not less than 200 MHz are informative for consideration. The usual solvent employed is deuterochloroform.

Δ^7-9β-Lanostenoids can easily be recognized from the characteristic position of the signal for the H-7 proton (5.50-5.65 ppm) [11, 16]. It does not depend appreciably on the type of substitution at the C-3 atom (keto, methoxy, or other group), but changes sharply on the opening of ring A (5.29 ppm in methyl abiesolidate [19]).

For mariesianoids [22, 24], 3,4-secomariesianoids [25], and 17,13-friedo-lanostanoids [22], the protons of the exocyclic double bonds give signals of characteristic form with definite values of the chemical shifts, which makes it possible to use them for the preliminary recognition of compounds of these structural groups.

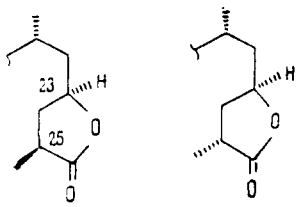
Features of the PMR spectra of these cycloartenoids have been discussed previously in a review by Isaev et al. [33] and we shall not dwell upon them here.

Continuing a consideration of the signals in the PMR spectra of fir triterpenoids, it is impossible not to mention the almost coincident chemical shifts of the signals for the 2 H-2 protons in the spectra of 3-keto-9β-lanost-7-ene derivatives [16]. These protons [for the methyl esters of the acids (VI-VIII) and for the lactone (V, XI, and XIII)] appear as a doublet of doublets of characteristic form at 2.4-2.5 ppm with J = 8.0 and 6.5 Hz (working frequency of the instrument 200.13 MHz).

Other features of the PMR spectra relate to the signals of the protons of the side chains of the molecules. In the first place we must mention the characteristic nature of the magnitudes of the chemical shifts of the signals due to the H-24 and the 3 H-26 signals of methyl β-acrylacrylate groupings (fragments F and I, R = CH_3) [14, 26]. Regardless of the structure of the cyclic framework, they permit the determination of the configuration of the Δ^{24} double bond in a molecule with such a grouping.

PMR spectroscopy will apparently prove useful in the identification of fragments J and K from the positions of the signals for H-23 and H-25 protons, and also from the shape of the signal of the latter [13, 16] (see scheme on following page).

It must be mentioned that for mariesiane derivatives an instrument with a working frequency of 200.13 MHz has proved inadequate for revealing all the signals of the methyl groups, because of their overlapping [24].



J K

^{13}C NMR results have been given for triterpenoids in four papers [13, 15, 19, 22], but they are still insufficient for any generalizations whatever. There are disputed questions on the assignment of the signals for the C-4 and C-10 atoms for spectra of abieslactone and other compounds [13].

Mass Spectrometry. The mass-spectrometric fragmentation of the molecules of the methyl esters of abiesolidic acid (XIV) and its derivatives under the action of electron impact has been analyzed in detail [19].

For 3,23-diketolanostenoids with a Δ^7 or Δ^8 double bond the characteristic nature has been established of an ion with m/z 325, which is the main one in the mass spectrum and is formed as the result of the occurrence of a McLafferty rearrangement in the side chain with the subsequent ejection of methyl group [16].

The use of a series of derivatives at C-3 has permitted a scheme to be given for the fragmentation of mariesiane and 3,4-secomarieasiane esters, in the molecules of which a McLafferty rearrangement is impossible because of the absence of a hydrogen atom at C-17 [25]. The results already available at the present time will undoubtedly prove useful in the chromato-mass spectrometric analysis of natural mixtures of fir triterpenoids.

UV Spectroscopy. Three types of chromophores of interest from the point of view of UV spectroscopy are present in the molecules of the triterpenoids under investigation – a conjugated dienic system in the cyclic part of mariesianoid and 3,4-secomariesianoid molecules, a β-acylacrylic acid fragment, and an alkylidenebutenolide chromophore in the side chain.

In the mariesianoids [compounds (XX) and (XXI)], the $\Delta^{7,14}$-dienic system is nonplanar [23, 24], and the band of the long-wave $\pi \rightarrow \pi^*$ transition is found at 225 nm, but, since it is superposed on other absorption bands, this transition can be detected reliably only in circular dichroism spectra [25].

In the 3,4-secomariesianoids [compounds (XXVI) and (XXVII)], the $\Delta^{6,8(14)}$-dienic chromophore appears in the form of an intense maximum in the UV spectrum at 253 nm [for (XXVI)] or 260 nm [for (XXVII)] with values of $\log \varepsilon$ of 4.37 and 4.29, which correspond to what is expected for $\Delta^{6,8(14)}$ dienes of the steroid series [34]. When a β-acylacrylic acid fragment (fragment F or I) is present in the molecule of a triterpenoid, a maximum or a shoulder is observed in the UV spectrum at 230-240 nm with $\varepsilon \sim 4$ [14, 24, 26].

Extremely characteristic is an absorption maximum due to an alkylidenebutenolide chromophore [compounds (XI), (XVI), and (XXVII)]. It is found in the UV spectra at 280 nm and has a high intensity ($\varepsilon \sim 22{,}000$), like the analogous maximum in the UV spectrum of the simplest lactone of this type – protoanemonin [35].

Circular Dichroism. The circular dichroism (CD) method has proved very useful in the investigation of the fir triterpenoids, and possibilities of its use have apparently not yet been exhausted. So far it is possible to mention only the following observations.

A Δ^7 double bond in the molecule of a 9β-lanost-7-ene derivative leads to a strong negative Cotton effect (CE) with the position of the extremum below 205 nm [32]. For a $\Delta^{9(11)}$-lanostene derivative, the analogous effect has a positive sign.

The $n \rightarrow \pi^*$ transition corresponding to the keto group in a 3-keto-9β-lanost-7-ene derivative appears in the form of a positive CE at 270-280 nm. For the 3-ketomariesianoids, the analogous effect is negative [16]. It must be mentioned that for 3-keto-9α-lanosta-7,24-diene the corresponding CE has a negative sign [36]. The reversal of the sign of the CE on passing to 3-keto-9β-lanost-7-enoids is due to the nature of the conformation of the A rings in the molecules of the latter, which has been confirmed by PMR spectra [16].

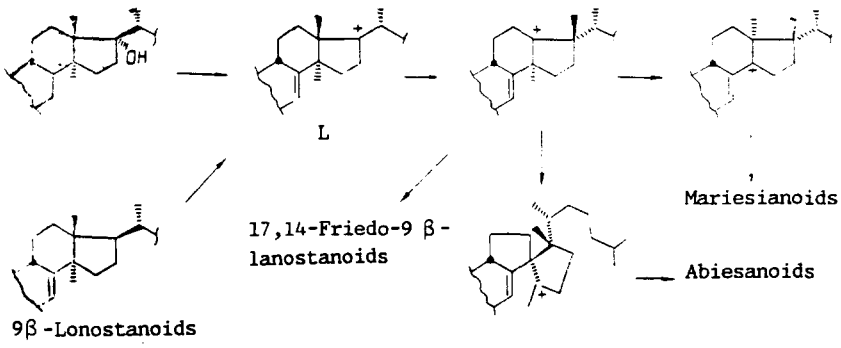
The long-wave $\pi \rightarrow \pi^*$ transition in the $\Delta^{7,14}$-dienic system of the molecule of the mariesianoid (XXV) appears in the form of a very strong positive CE at 225 nm [25], while the

analogous transition in the $\Delta^{6,8(14)}$-dienic system of the 3,4-secomariesianoid (XXVI) (cis-sibiric acid) is responsible for the appearance of a negative CE corresponding to the maximum in the UV spectrum observed for this transition [25].

Any compound having a methyl β-acylacrylate chromophore (fragments F and I) in its molecule gives a negative CE for the $n \rightarrow \pi^*$ transition in the C(23)-carbonyl group, while for the Z-isomers it is located in the 330-340 nm region and for the E-isomers at 350-360 nm [16, 25]. A shorter-wave transition ($\pi \rightarrow \pi^*$) in the enonic system, corresponding to the maximum at 230-240 nm in the UV spectra has not been analyzed specially, but its appearance has been reported in one case [14].

BIOGENETIC INTERRELATIONSHIP

The close biogenetic affinity of the triterpenoids under consideration appears fairly obvious, and their carbon skeletons (apart from the cycloartane skeleton) can be formed as the result of the isomerization of a hypothetical carbocation with the fragment L, as shown in the scheme given below [22, 23, 26].



The cleavage of ring A in the molecules of the triterpenoids during the processes of biosynthesis is encountered very frequently, and a special review has been devoted to the 3,4-secotriterpenoids [37]. For the fir triterpenoids the most interesting question appears to be at what stage of biosynthesis the cleavage of ring A takes place in the precursor molecule – before or after isomerization (according to the scheme shown above) of the main carbon skeleton. It has been suggested [25] that the direct biogenetic precursors of the 3,4-secomariesianoids (XXVI) and (XXVII) are not mariesianoids but 3,4-seco-9β-lanost-7-enoids.

The question of the unusual (α) configuration of the methoxy group at C-3 in the molecule of abieslactone (I) and of the hydroxy group in the same position in other triterpenoids, has not been considered at all in the literature. The absence of experimental facts has not yet permitted an unambiguous explanation of the formation of 3α-substituted derivatives to be given. It is likely that squalene itself, and not its terminal epoxide, is involved in the biosynthesis of the fir triterpenoids, and the introduction of hydroxy groups is ensured already in the cyclic intermediate by the enzyme 3α-hydroxylase. Two alternative routes may also be considered – the participation of (R)-epoxysqualene in the cyclization stage or the formation of 3α-hydroxy derivatives from their 3β-epimers through the stage of 3-keto derivatives.

Information on the biological activity of the fir triterpenoids is still sparse. Abieslactone (I) does not exhibit antitumoral activity, is inactive in relation to yeasts and other fungi, and possesses weak activity in relation to certain Gram-positive and Gram-negative microorganisms [10].

Interesting results have been obtained by Japanese workers [22]. Thus, mariesiic acids A (XX), B (XVIII), and C (XXVIII), 23-oxomariesiic acids A (XXI) and B (XIX), and firmanoic acid (VI) suppressed the growth of a Gram-positive bacterium (Bacillus subtilis) and of the two actinomycetes used (Micrococcus luteus and Nocardia corallina). All these acids, and also their methyl esters, proved to be inactive with respect to Gram-negative bacteria and yeast fungi. Assuming that the activity of the acids investigated is connected with the structures of the side chains in the molecules, the authors tested model compounds – 2-methyl-4-hydroxypent-2E-enoic and 2-methyl-4-oxopent-2E-enoic acids, which, however, proved to be inactive. From this the importance of the cyclic part of the molecules of the triterpenoids investigated for the manifestation of biological activity was deduced.

In conclusion it must be mentioned that antimicrobial activity is well known for fir oleoresin obtained both by tapping and by extraction [38].

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