Petroleum ether—diethyl ether (97:3) eluted the combined aldehydes (0.54 g), which were reduced to alcohols [4], and the latter, in the form of their acetates, were analyzed by GLC (Table 2).

Petroleum ether—diethyl ether (95:5) eluted epimanool (0.29 g) and then the total primary alcohols (0.23 g), which were acetylated and identified by GLC (Table 2).

Petroleum ether—diethyl ether (85:15) led to the isolation of larixyl acetate (1.59 g) with bp 80°C, identical in physical and spectral characteristics with an authentic sample.

Diethyl ether eluted larixol (0.32 g) with mp 97-98°C, giving no depression of the melting point with an authentic sample.

CONCLUSIONS

1. The composition of the neutral diterpenoids of the oleoresins of five species of conifers growing in Transcarpthia has been studied. Features of the distribution of the diterpenoids according to species have been revealed.

2. It has been established that for each type of oleoresin the predominance of one or a few diterpenoids is characteristic. In Pinus mugo the main compounds are diterpene aldehydes, in A. alba the main components is cis-abienal, in Picea abies and P. excelsa it is isocembrol, and in the oleoresin of Larix decidua it is larixyl acetate.

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TRITERPENOIDS FROM Abies SPP.

VI. "ISOFIRMANIC" AND (24E)-LANOSTA-8,24-DIENE-3,23-DION-26-OIC ACIDS FROM SIBERIAN FIR NEEDLES

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UDC 547.595,9:547.914.4

Two triterpene acids have been isolated in the form of methyl esters from an extract of Siberian fir needles, and their structures have been established as 9β-lanosta-7,25-diene-3,23-dion-26-oic and (24E)-lanosta-8,24-dien-3,23-dion-26-oic acids, respectively.

It has been shown previously that the main lanostane acids in an extract of needles of the Siberian fir Abies sibirica Ledb. are the diketo acids (I) and (II), the structures of the corresponding methyl esters of which (III) and (IV) have been established [1, 2]. Acid (I) was recently described by Hasegawa et al. under the name of "firmanoic" [3]. They isolated it in the form of the methyl ester from an extract of the seeds of the fir Abies firma Sieb. et Zucc. A second acid ("isofirmanoic") was isolated from the same extract, and the structure expressed by formula (V) was established for its methyl ester on the basis of spectral characteristics.

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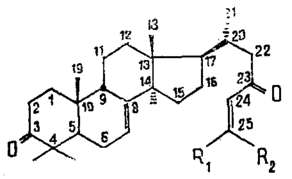
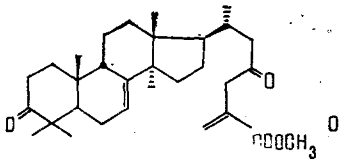
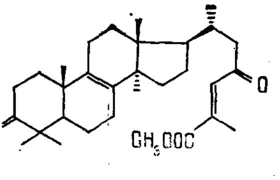


	R_1	R_2
I.	COOH	CH_3
II.	CH_3	COOH
III.	$COOCH_3$	CH_3
IV.	CH_3	$COOCH_3$

Continuing a study of the triterpenoids of the Siberian fir, we have obtained methyl esters of two new components of an extract of the needles one of which has the same structure as methyl isofirmanoate (V). Since our deduction of the formula (V), and also some experimental results used in this deduction differ from those given by Hasegawa et al. [3], in the present paper we give our derivation in the present paper and also a description of the determination of the structure of the methyl ester of another new acid from the needles under investigation – methyl (24E)-lanosta-8,4-diene-3,23-dion-26-oate (VI).



V



VI

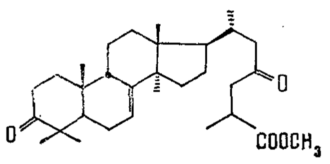
The esters (V) and (VI) were isolated by chromatography and crystallization of the mother liquors formed in the isolation of compounds (III) and (IV) [4]. The spectral characteristics of our sample of the ester (V) corresponded to those given in the literature [3], with the exception of two important points – the presence of a maximum in the UV spectrum (λ_{max} 290 nm, log ε = 2.33) and the appearance of the signal of a 2H-24 group in the PMR spectrum in the form of an almost degenerate AB system with J_{AB} = 17 Hz, and not as a singlet.

A maximum in the UV spectrum corresponding to the n → π* transition in the C(23)=O group is expected for structure (V) and, judging from the value of the molar extinction, indicates the presence of a β-enone grouping in the molecule of the ester (V) [5]. According to Hasegawa et al. [3], there is no such maximum in the UV spectrum of the methyl ester (V).

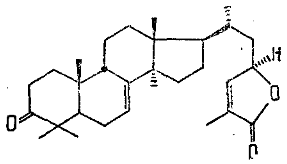
The components of the AB system for the 2H-24 protons in the PMR spectrum of the ester (V) are somewhat broadened through the allyl spin-spin coupling of these protons with the protons of an exomethylene group (established by double-resonance experiments), while the distance between the single lines amounted to 2 Hz (the working frequency of the instrument was 200.13 MHz). Hasegawa et al., using an instrument with a higher working frequency (400 MHz) recorded the signals under discussion in the form of a two-proton singlet.

An important feature of the PMR spectrum of the ester (V) is the presence in it of the signals of two methylene groups (2H-2 and 2H-22) which are apparently typical for 3,23-diketolanostanoids. A doublet of doublets due to the 2H-2 protons coincides completely in form and position with that for the esters (III) and (IV), while a doublet of doublets for the 2H-22 protons (H-22a – 2.22 ppm, J = 16 and 10 Hz; H-22b – 2.52 ppm, J = 16 and 2 Hz) are analogous to the corresponding signals in the PMR spectra of esters (III) and (IV) and of 23-ketomariesanic derivatives [2].

The catalytic hydrogenation of the ester (V) gave a product identical according to TLC and PMR spectroscopy with the 24,25-dihydro derivative (VII) of the ester (IV) that we had synthesized previously [2]. This chemical correlation, together with the spectral characteristics, permits the unambiguous deduction of structure (V) for the ester under investigation ("methyl isofirmanoate").



VII



VIII

To establish the absolute configuration of the molecule of the ester (V) we recorded the circular dichroism (CD) spectrum of this compound. The curve obtained, which had an

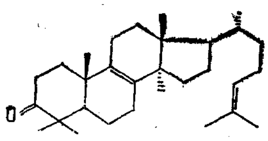
TABLE 1. Chemical Shifts (ppm) of Some Signals and Spin-Spin Coupling Constants (Hz, shown in parentheses) in the PMR Spectra of Compounds (VI), (IX), and (III)

Atom	VI	IX	III
$2CH_3$-4	0,74 s	0,69 s	
CH_3-10	0,87 s	0,86 s	—
CH_3-13	1,05 s	1,05 s	—
CH_3-14	1,07 s	1,07 s	—
	1,10 s	1,10 s	—
2H-2	2,39 ddd (15,5; 5,6; 3,0) 2,56 ddd (15,5; 11,0; 5,0)	2,39 ddd (15,5; 5,6; 3,0) 2,56 ddd (15,5; 11,0; 5,0)	—
CH_3-20	0,90 d (6 5)	0,89 d (6 5)	0,88 d (6,5)
H-22 a	2,27 dd (16,0; 10,0)	—	2 27 dd (16,0; 10,0)
H-22 b	2,61 dd (16,0; 2,0)	—	2,61 dd (16,0; 2,0)
H-24	7,05 q (1,5)	—	7,05 q (1,5)
CH_3-24	2,20 q (1 5)	—	2,20 d (1,5)
$COOCH_3$	3.79 s	—	3,79 s

asymmetric form, showed a negative Cotton effect (CE) with a minimum at 277 nm and a magnitude of the dichroic absorption $\Delta\varepsilon = -5.1$. The situation here is not simple, since molecule of the ester (V) contains two keto groups the absorption maxima of which for the $n \rightarrow \pi^*$ transition practically coincide. This conclusion is based, in the first place, on the observed absorption maximum of the ester (V) in the UV spectrum (290 nm) and, in the second place, on the characteristics of a known model compound — the ketolactone (VIII) [5]. On its CD curve, a positive CE at 290 nm with a value $\Delta\varepsilon = +2.45$ is observed for the $n \rightarrow \Delta\varepsilon$ transition in the C(3)=O group. The value of $\Delta\varepsilon$ for the ester (V) is twice as great and, in view of the asymmetry of its CD curve, it may be assumed that the observed CE is the algebraic sum of a positive CE due to the C(3)=O group and a more intense and broader negative CE for the C(23)=O group. In actual fact, if the signs of the two CEs coincided, the position of the extremum on the observed curve should coincide with the position of the maximum in the UV spectrum, while the second possible variant, with opposite signs of the CEs for its components is unsatisfactory because of the value of the observed dichroic absorption ($\Delta\varepsilon = -5.1$), twice as great as that for the model compound (VIII).

Thus, the absolute configuration of the molecule of the ester (V) is the same as that of molecules (I-IV). The negative sign of the CE for $n \rightarrow \pi^*$ transition in the C(23)=O group can hardly be connected with the chirality of the β-enone system [6, 7] since it is retained for other 23-ketolanostanoids [2]. Its considerable independence of the structure of the aliphatic moiety of the molecule of the series of compounds under consideration permits the conclusion that the CE is due only to the asymmetric induction of the chiral center at C-20.

The structure and stereochemistry of the molecule of the ester (VI) were established on the basis of its spectral and optical characteristics. According to the results of mass spectrometry, it is an isomer of the esters (III)-(V), while in its PMR spectrum it is possible to single out two groups of signals one of which coincides with that for the protons of the side chain of the ester (III) [1] and the second (the signals of angular methyl groups and the signals of the two H-2 protons) corresponds to the signals of the cyclic moiety of the molecules of a model compound — 20R-lanosta-8,24-dien-3-one (IX) [8] (see Table 1). Particularly characteristic is the coincidence of the form and position of the signals for the 2H-2 protons, which in both spectra give doublets of doublets at 2.39 and 2.56 ppm.



The main (100%) peak in the mass spectrum of (VI) has m/z 325.2541 ($C_{23}H_{33}O$), as in the mass spectrum of the esters (III-V). The fragment corresponding to this peak is formed as the result of the occurrence in a McLafferty rearrangement in the side chain of the molecule [9] with the subsequent (or preceding) elimination of the methyl group from its cyclic moiety. This interpretation is based on results discussed previously for the hexadeuterodihydro derivative of the ester (IV) and in the absence of this ion peak in the mass spectra of 3,23-diketomariesianic derivatives [2]. The latter cannot undergo a McLafferty rearrangement because of the presence of their molecules of a methyl group at C-17 in place of a hydrogen atom. The interpretation of the ion with m/z 325 (100%) as $(M - 2Me - \text{side chain})^+$ with cleavage at C-22—C-23 given by Hasegawa et al. [3] is incorrect.

Two Cotton effects are observed on the CD curve for the ester (VI) — a negative one at 350 nm ($\Delta\varepsilon = -0.87$) and a positive one at 285 nm ($\Delta\varepsilon = +1.48$), corresponding to $n \rightarrow \pi^*$ transitions in the C(23)=O and C(3)=O groups, respectively. The sign of the first CE shows the R configuration of the asymmetric center at C-20 [2], while the second confirms the presence of 3-ketolanost-8-ene fragment in the molecule of the ester under investigation [10]. These facts show that formula (6) expresses the absolute configuration of the molecule.

The acid corresponding to the methyl ester (VI) is so far the only representative of lanost-8-ene derivatives from Abies species.

It may be assumed that the minor components of the acid fraction of diethyl ether extracts of Siberian fir needles are optional constituents. Their presence is undoubtedly connected with as yet uninvestigated regional and seasonal differences in the composition of the needles used. Thus, we have obtained isofirmanic acid, in the form of a methyl ester, only from an extract of fir needles collected in Perm province. It was not detected in two samples of needles collected in Novosibirsk province and in the Altai (region of Lake Teletskoe).

EXPERIMENTAL

CD curves were recorded on a Spektropol I spectropolarimeter for solutions in methanol, the concentrations of the substances being $2.77 \cdot 10^{-3}$ and $5.60 \cdot 10^{-3}$ M for the esters (V) and (VI), respectively. Melting points were determined on a Kofler stage. The other instruments used and the conditions for recording the spectra and for performing chromatography have been described in [2].

Methyl 9β-Lanosta-7,25(26)-diene-3,23-dion-26-oate (V). An extract of Siberian fir needles collected in Perm province was worked up and separated as described in [4]. This gave a fraction of (5.07 g) of "strong" acids similar in polarity to fraction "4" described in [4]. The bulk of the acid (II) was removed from it by crystallization from diethyl ether. The mother liquor was methylated with an ethereal solution of diazomethane and was chromatographed, which led to the isolation of 0.50 g of a mixture of the esters (IV) and (V) with a predominance of the latter (TLC). Crystallization from diethyl ether gave 0.25 g of the ester (V) with mp 142-144°C, $[\alpha]_D^{20}$ +36.8° (c 1.90; chloroform) (according to the literature [3]: mp 163-164°C (from hexane), $[\alpha]_D$ +24° (chloroform)). UV spectrum (in ethanol): λ_{max} 290 nm (log ε 2.38); (in methanol) λ_{max} 290 nm (log ε 2.45). CD (λ_{max}, nm (Δε)): 277 (−5.1), 270 (−4.6), 260 (−3.2), 250 (−1.70), 280 (−4.6), 290 (−3.1), 300 (−1.2), 310 (−0.5), 320 (−0.4).

Methyl (24E)-Lanosta-8,24-diene-3,23-dion-26-oate (VI). For the isolation of the ester (VI) we used the mother liquor from the crystallization of the methyl ester (III) obtained as described in [4]. Its (0.5 g) recrystallization from a mixture of petroleum ether and diethyl ether (1:1) gave 0.2 g of compound (VI) with mp 132-134°C; $[\alpha]_D^{20}$ +45.5 (c 0.22; chloroform), empirical formula $C_{31}H_{46}O_4$ (found: m/z 482.3429; calculated: 482.3396). UV spectrum (in ethanol): λ_{max} 239 nm (log ε 4.17). IR spectrum (in chloroform), cm^{-1}: 1695, 1725 (C=O). Mass spectrum (m/z, %): 482 (M^+, 24), 467 (41), 340 (10), 325 (100), 313 (10), 311 (12), 127 (23). For the PMR spectrum, see Table 1. CD [λ_{max} , nm (Δε)]: 285 (+1.48), 350 (−0.87).

The ester (V) was hydrogenated as described for the ester (IV) [2]. From 0.15 g of the ester (V), after the working up and chromatography of the products on silica gel, 0.10 g of the dihydro derivative (VII) was obtained; its PMR spectrum coincided with that for an authentic sample of compound (VII).

CONCLUSIONS

Two lanostane acids have been isolated in the form of methyl esters from an extract of Siberian fir needles; the structure of one of them corresponds to the known isofirmanoic acid, while for the other the structure of (24E)-lanosta-8,24-diene-3,23-dion-26-oic acid has been established.

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GLYCOSYLATION OF TRITERPENOIDS OF THE DAMMARANE SERIES.

IX. β-D-GLUCOPYRANOSIDES OF 20(S),24(R)-EPOXYDAMMARANE-3α,12β,17α,25-TETRAOL

L. M. Atopkina, N. F. Samoshina, V. A. Denisenko, and N. I. Uvarova

UDC 547.917+547.918+547.597

Glycosides have been synthesized from 20(S),24(R)-epoxy-dammarane-3α,12β,17α,25-tetraol, which was isolated from the leaves of Betula costata. Exhaustive glycosylation of betulafolienetetraol oxide with α-acetobromoglucose in the presence of mercury cyanide gave an acetylated 3,12,25-triglucoside (yield 61%), while glycosylation in the presence of insoluble silver compounds led to the formation of 3- and 12-mono- and 3,12- and 12,25-diglucopyranosides (total yield 57-82%). The structures of the glucosides obtained have been established on the basis of the results of IR and ^{1}H and ^{13}C NMR spectroscopy.

Intensive investigations being made of the composition of the saponins of Panax ginseng C. S. Meyer and plants related to it have shown that, in addition to the known ginsenosides R_{g1}, R_e, R_{b1}, R_{b3}, and R_d, they contain saponins of the ocotillol type which have been called pseudoginsenosides [1, 2].

In order to study the structure-activity interrelationship, we have carried out the synthesis of glucosides from 20(S),24(R)-epoxydammarane-3α,12β,17α,25-tetraol (1), which differs from the genin of the pseudoginsenosides – 20(S),24(R)-epoxydammarane-3β,6α,12β,25-tetraol – by the position of one of the hydroxy groups and the configuration of the hydroxy group at C-3.

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