TRITERPENOIDS FROM Abies SPECIES.

VIII. A NEW METHOXYMARIESIONOID AND TWO 3,4-SECOMARIESIANOIDS FROM Abies sibirica NEEDLES

S. A. Shevtsov and V. A. Raldugin

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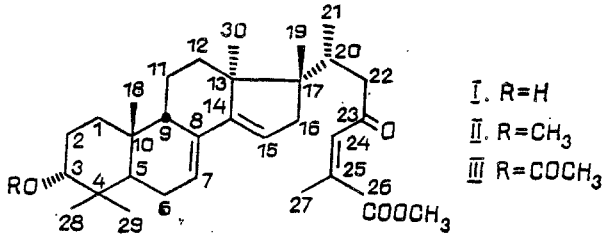
Three new triterpenoid acids have been isolated from an ethereal extract of Siberian fir needles, and the structures of their methyl esters have been established on the basis of spectral characteristics.

Continuing a study of the composition of the complex mixture of acids in an ethereal extract of Siberian fir needles, we have investigated the components of the methylated fraction 6 described in communication [1]. It consisted of the known ester (I) with a mariesiane carbon skeleton and a number of other, accompanying, unidentified methyl esters. As described in the paper cited, when this fraction was rechromatographed on silica gel the mixture of these esters was eluted first, and its components have been the object of the present work. After additional chromatographic separation it was possible to isolate three new compounds from this mixture in the form of viscous oils the IR spectra of which contained no absorption bands of hydroxy groups.



The structures and stereochemistries of the first of them, which are shown by formula (II) were established on the basis of the results of a comparison of its PMR, mass, and CD spectra with those for the known acetate (III) [1]. The PMR spectrum of the ester (II) differed from that of compound (III) only by the presence of a singlet signal at 3.26 ppm (the protons of a methoxy group), by the absence of the signal of the protons of the acetyl groups, and by a shift (with no change in shape) of the signal of the H-3 proton into the 2.80 ppm position expected for a H-3 proton in the spectra of 3α-methoxytriterpenoids [2, 3]. In the spectrum of the compound under investigation, the signals of the H-7, H-14, and H-24 olefinic protons coincided in shape and position with those for the acetate (III), and the chemical shift of the signal for the H-24 proton (1 H, 6.15 ppm) showed the (24Z) configuration of the molecule of the ester (II). The singlet signals of the angular methyl groups (see the Experimental part) differed only slightly in position from the analogous signals for the acetate (III). Using a solution in benzene-d_6 it was possible to record the positions of both components of the doublet signal due to the protons of the secondary methyl group (CH_3-20), which for a solution in deuterochloroform were superposed on the signals of the tertiary methyl groups.

The mass-spectrometric fragmentations of the molecules of compounds (II) and (III) took place identically, as is illustrated by the figures in Table 1. The most notable feature is the formation in both spectra of an intense peak of ions with m/z 295 corresponding to the removal of the side chain and the elimination of a molecule of methanol (II) or of acetic acid (for III). Neither spectrum contained the peak of the ion corresponding to a McLafferty rearrangement in the side chain of the molecule. This is impossible for a 23-ketomariesianoid because of the absence of a hydrogen atom at C-17 [4].

Novosibirsk Institute of Organic Chemistry, Siberian Branch, USSR Academy of Sciences.
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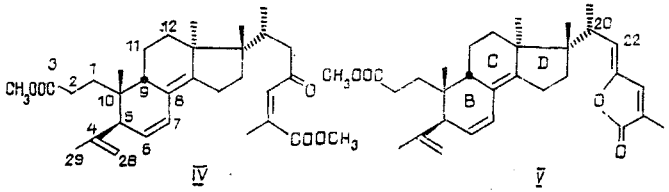
TABLE 1. Intensities of the Peaks and Elementary Composition of the Ions in the Mass Spectra of Compounds (II) and (III)*

Ion	II			III		
	m/z	%	composition	m/z	%	composition
1. M^+	496	29	$C_{32}H_{48}O_4$	524	15	$C_{33}H_{48}O_5$
2. $(M-15-A)^+$	354	100	$C_{25}H_{38}O$	382	75	$C_{26}H_{38}O_2$
3. $(M-15-A-15)^+$	339	18	$C_{24}H_{35}O$	367	13	—
4. $(M-B)^+$	327	98	$C_{23}H_{35}O$	355	55	$C_{24}H_{35}O_2$
5. $(M-15-A-15-ROH)^+$	307	15	—	307	11	—
6. $(M-B-ROH)^+$	295	96	$C_{22}H_{31}$	295	83	$C_{22}H_{31}$
7. B^+	169	59	—	169	100	$C_9H_{13}O_3$
8. A^+	127	53	—	127	24	—

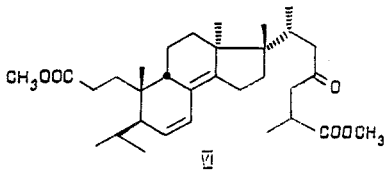
*Arbitrary designations: A – $C(O)CH=C(CH_3)COOCH_3$; B – $CH(CH_3)-CH_2C(O)CH=C(CH_3)COOCH_3$; ROH – CH_3OH for (II), CH_3COOH for (III). The elementary compositions given in the Table were determined from the accurate values of the masses of the corresponding ions.

On the circular dichroism (CD) curve for the ester (II) it was possible to observe two pronounced Cotton effects (CEs) – negative at 330 nm and positive at 225 nm, corresponding to a $n \rightarrow \pi^*$ transition in the C(23)=O group [5] and to a $\pi \rightarrow \pi^*$ transition in the conjugated dienic system. The same effects (at 330 and 225 nm) are observed on the CD curve of the acetate (III), which serves as proof of the structure of the ester (II) and an indication of its absolute configuration, as expressed in formula (II). The correctness of the assignment of the CE at 225 nm to a $\pi \rightarrow \pi^*$ transition in the dienic system was confirmed by the observation of the same effect on the CD curve of the product obtained by reducing the acetate (III) with lithium tetrahydroaluminate in diethyl ether. Thus, the acid (II), isolated in the form of its methyl ester, was (3R)-3-methoxy-23-oxomariesia-7,14,24Z-trien-26-oic acid. As was established on the basis of the facts given below, the other two methyl esters had the structures expressed by formulas (IV) and (V), respectively. The catalytic hydrogenation of ester (IV) over $Pd/CaCO_3$ in ethyl acetate gave the tetrahydro derivative (VI), which was also used to establish the structure of the substances isolated.



IV

V



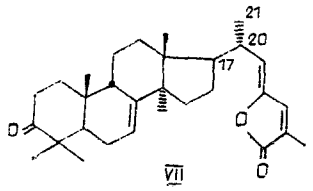
VI

The PMR spectra of compounds (IV) and (V) differed appreciably by the signals of the protons present at the atoms from C-20 to C-27. In each of them (see the Experimental part) three singlets were observed (for the tertiary methyl groups CH_3-10, CH_3-13, and CH_3-17) and one doublet due to the CH_3-20 group. Some of the signals were identical in form and position for the two spectra. They related to the protons of the isopropenyl and the unconjugated carbonyl groups, to the protons of the cis-disubstituted double bond (H-6 and H-7), and to the doubly allyl H-5 proton. The spin-spin coupling between H5 and H6 and between H6 and H7, and also between the protons of the CH_3-4 group and the 2H-28 protons was established with the aid of double resonance.

In the PMR spectra of the ester (IV) and (V) the signals of the H-5 protons were present at 2.59 ppm (doublet with $J_{5,6}$ = 5.5 Hz) and shifted to 1.9 ppm in the spectrum of the

derivative (VI) (established by using double resonance). This observation is a proof of the assignment of the signal mentioned to the H-5 proton.

The signals of the protons preent in the side chains of the molecules of esters (IV) and (V) were similar to those in the PMR spectra of the methoxymariesianoid (II) and the lactone (VII) [6]. In contrast to the latter, the signal of the H-20 proton in the PMR



VII

spectrum of compound (V) had the form of a doublet of quartets with $J_{20,22}$ = 10 Hz, $J_{20,21}$ = 7 Hz (the existence of spin-spin coupling just between H-22 and CH_3-20 was established with the use of double resonance). Consequently, in its molecule there was no hydrogen atom at C-17, as in the mariesiane triterpenoids. The absence from the mass spectra of the esters (IV) and (VI) of the peaks of ions connected with a McLafferty rearrangement in the side chain permits the same conclusion to be drawn concerning the nature of the substitution at C-17 in their molecules.

The signals due to the H-24, CH_3-25, and CH_3OOC protons in the PMR spectrum of the ester (IV) coincided in form and position with those for the methoxy ester (II) which permits the double bond in the side chain to be ascribed the (Z)-configuration. This was also confirmed by the formation of the ester (IV) when the lactone (V) was treated with an ethanolic solution of alkali followed by acidification and the methylation of the acid fraction of the product formed. This transformation was analogous to that used in establishing the structure of the lactone (VII) [6] and is a chemical correlation of the structures of compounds (IV) and (V).

In the molecules of substances (IV)-(VI), the cis-disubstituted double bond forms part of a conjugated dienic system the second double bond of which is tetrasubstituted, while the dienic system itself is a heteroannular transoid system. These conclusions are based, in the first place, on the absence from the PMR spectra of the compounds under consideration or any other signals of olefinic protons whatever, apart from those identified, and, in the second place, on the presence of a maximum at 253 nm (log ε 4.25) in the UV spectrum of the tetrahydro derivative VI. Similarly the maximum is in the UV spectrum of the lactone (V) and that of the ester (IV), although in the former it is shifted somewhat (λ_{max} 260 nm) because of superposition on the maximum due to the alkylidenebutenolide chromophor (λ_{max} 280 nm) [6]. The position of the absorption maximum in the UV spectrum of compound (VI) corresponds to that expected just for $\Delta^{6,8(14)}$-dienes of the steroid series (248-253 nm) [7, 8]. In the case of a $\Delta^{6,8(9)}$-diene (homoannular cisoid system) an absorption maximum should be located at 275 nm [8].

Again, one side chain of each of the molecules (IV) and (V) includes a fragment with an unconjugated carboxymethyl group the signal of the protons of which in the PMR spectra coincides with that for known methyl esters of 3,4-secotriterpene acids [9-11]. This chain has the structure $CH_2CH_2COOCH_3$ and is located on a quaternary carbon, as was established on the basis of the observation in the mass spectrum of the ester (IV) of a characteristic [12] peak of $(M - 87)^+$ ions (22%) corresponding to the splitting out of this chain from the molecular ion. This interpretation was confirmed by the elementary composition of the $(M - 87)^+$ ions. In the mass spectrum of the lactone (V), the peak of the analogous ions (m/z 391, 11%) was also observed. It must be mentioned that these ions cannot be formed in the fragmentation of the ester (IV) through any cleavage whatever in the side chain containing the α-enone grouping, and this peak does not appear in the mass spectrum of the ester (III), the molecule of which contains an unopened ring A. In the mass spectrum of the ester (IV), strong peaks of three other ions were also observed, with m/z 368, 341, and 127, which, according to their elementary compositions, corresponded to established fragmentation pathways of the side chain in mariesianoid molecules (see Table 1).

The combination in the molecules of the compounds under investigation of an isopropenyl group and the fragment $CH_2CH_2COOCH_3$ shows that they belonged to the 3,4-secotriterpenoid series, representatives of which are widespread in plants [13] and are components of the

needles [1, 11] and oleoresin [9, 10] of the fir species being studied. The spectral characteristics of compounds (IV) and (V) that were discussed above and the conversion of lactone (V) into ester (IV) permit the proposal of the structures shown for these substances. The stereochemistries of the (IV) and (V) molecules are suggested on the basis of biogenetic considerations (the degree of expression of the biosynthesis of mariesianoids in the needles under investigation). The correctness of the proposed structures was confirmed in an analysis of the optical properties of the substances under consideration.

The CD curve of ester (IV) showed two negative CEs, at 250 and 330 nm. The latter ($n \rightarrow \pi^*$ transition in the α-enone system of the side chain) coincided accurately in sign and position with that for (24Z)-mariesiene derivatives [5]. In the tetrahydro derivative (VI), as was to be expected, this effect underwent a hypsochromic shift and appeared at 280 nm, although with the same sign. The retention of the sign in this case confirmed our hypothesis [5] concerning a definite influence on its configuration of an asymmetric center at C-20 and its lack of dependence on the structure and configuration of the remainder of the side chain in the series of 23-keto derivatives of mariesianoids and lanostanoids under consideration.

The second CE observed on the CD curve under consideration is present, as on the CD curve for the ester (VI), at 250 nm, which permitted its unambiguous assignment to a $\pi \rightarrow \pi^*$ transition in the conjugated dienone system. The negative sign of this effect indicates the left-handed spirality of the dienic chromophore [14] (see also reference 20 in [15]), which, according to Dreiding models, is realized in the structure of (IV) only if two conditions are satisfied – the β-configuration of the H-9 atom and the α-configuration of the methyl group located at C-13.

The negative sign of the observed CE corresponds to the structure and stereochemistry of the cyclic parts of the molecules of compounds (IV-VI) from the point of view of a different approach to the interpretation of the CE for the dienone chromophore based on an analysis of the contribution of the allyl axial and pseudoaxial substituents [15, 16]. For this purpose it is necessary to consider first the orientation of the pseudoaxial substituent at C-5. According to Dreiding models, a ring with a cis-disubstituted double bond in the molecules of these compounds can be present in two conformations – boat and flattened half-chair. In each of them, the C(9)–H bond is pseudoaxial, and for the boat an α-substituent has the pseudoaxial position at C-5, and for the half-chair a β-substituent has it.

In both cases, the conjugated dienic system is levospiral, but for the boat conformation it is strongly bent [the C(6)...C(14) dihedral angle is of the order of 40°], which must lead to a disturbance of conjugation, as in known mariesiane compounds [1, 17]. The position of the maximum in the UV spectrum of the derivative (VI) corresponds to that expected [8], and this variant of the conformation must be rejected. In the second conformation, it is just with a β-conformation (pseudoaxial) of the isopropenyl group that good agreement is obtained between the observed value of the constant $J_{5,6}$ (5.5 Hz) in the PMR spectra with those calculated (according to Dreiding models, the H(5)C(5)C(6)H(6) dihedral angle amounts of 35-40°, from which we obtain $J_{5,6}$ = 5-6 Hz [18]). In the conformation substantiated in this way, the three pseudoaxial substituents – the isopropenyl group, the H-9 atom, and the CH_3-13 group – will give negative contributions to the CE, and only one – the α-hydrogen atom at C-15, will make a positive contribution. Thus, in the light of the axial substituents, for the $\pi \rightarrow \pi^*$ transition in the dienic system of each of the molecules (IV)-(VI) one must expect a negative CE, which agrees with experiment.

The diaxial arrangement of the isopropenyl group and the $CH_2CH_2COOCH_3$ fragment in the conformation deduced apparently also explains the observed inertness of the conjugated dienic system in the molecules of the esters (IV) and (VI) on catalytic hydrogenation, preventing the contact of this system with the surface of the catalyst both from the α- and from the β-side.

For the natural acids corresponding to the dimethyl ester (IV) and to the monomethyl ester (V) we propose the trivial names cis-sibiric and anhydrosibiric acids, respectively.

The biogenetic precursors of the 3,4-secomariesianoids isolated are, most probably, 3,4-seco-Δ^7-lanostene derivatives. The formation of a Δ^6- (and not a Δ^{14}-) -double bond after the migration of the CH_3-13 and CH_3-14 groups [9], as can be assumed, is due to the difference in the conformation of ring B in the molecules of the lanost-7-ene and 3,4-secolanost-7-ene precursors, as can be seen from Dreiding models.

EXPERIMENTAL

IR spectra were recorded for solutions in CCl_4 on a UR-20 instrument, and UV spectra for solutions in ethanol on a Specord UV-Vis, while the specific optical rotations and CD curves were obtained on a Spectropol 1 spectropolarimeter for solutions in chloroform and methanol, respectively. High-resolution mass spectra were recorded on a Finnigan MAT 8200 instrument. PMR spectrum were obtained for solutions in $CDCl_3$ on a Bruker WP-200 SY instrument (200.13 MHz; internal standard: chloroform, the signal of which was taken as 7.24 ppm, δ scale).

For chromatography we used type KSK silica gel (0.07-0.10 mm) with, as eluent, petroleum ether containing increasing (from 10 to 50%) amounts of diethyl ether.

Isolation of Compounds (II), (IV), and (V). The head fraction (0.61 g) obtained on the chromatography of fraction 6 (4.92 g) [1] was rechromatographed on silica gel using a ratio of substance to sorbent of ~1:50. This led to the successive elution of the methoxyester (II) (0.08 g), the ester (V) (0.08 g), and the ester (IV) (0.16 g).

Methyl Ester of (3R,20R)-3-Methoxy-23-oxomariesia-7,14,24Z-trien-26-oic Acid (II). Colorless oil with $[\alpha]_D^{20}$ −6° (c 0.3). IR spectrum, cm^{-1}: 1705 (C=O); 1740 (α-butenolide). The mass spectrum is given in Table 1; CD spectrum: $\Delta\varepsilon_{330} = -1$, $\Delta\varepsilon_{225} \approx +40$ ($c = 1.7 \cdot 10^{-4}$ M). PMR spectrum, ppm: 0.80-0.92 (18 H, the protons of six methyl groups); 1.75 (3 H, d, J = 1 Hz, CH_3-4); 2.00 (3 H, d, J = 1.5 Hz, CH_3-25); 2.79 (1 H, narrow m, H-3); 2.48 (1 H, d with broadened components, J = 15 Hz, H-22a); 3.26 and 3.77 (3 H each, singlets, OCH_3 and $COOCH_3$, respectively); 5.13, 5.52, and 6.15 (1 H each, multiplets, H-15, H-7, and H-24, respectively, coinciding in form with the analogous signals in the spectrum of the ester (III) [1]).

PMR spectrum for a solution in C_6D_6, ppm: 0.85, 0.87, 0.96, 1.03, and 1.06 (3 H each, singlets, angular methyl groups); 0.90 (3 H, d, J = 6.6 Hz, CH_3-20); 1.67 (3 H, d, J = 1.7 Hz, CH_3-25); 2.68 (1 H, distorted triplet with a splitting of 2 Hz, H-3); 3.12 and 3.47 (3 H each, singlets, OCH_3 and $COOCH_3$, respectively); 5.31 and 5.68 (1 H each, multiplets, H-15 and H-7); 6.16 (1 H, q, J = 1.7 Hz, H-25).

Product of the Exhaustive Reduction of the Acetate (III). A solution of 0.10 g of the acetate (III) in 10 ml of diethyl ether was treated with 0.1 g of lithium tetrahydroaluminate and the mixture was left at room temperature for 1 h. After the usual working up, an oily liquid was obtained (0.08 g) (a mixture of substances according to TLC), the IR spectrum of which contained no absorption of carbonyl groups (in the 1670-1800 cm^{-1} region). CD spectrum: positive CE at 225 nm, $\Delta\varepsilon \approx 40$ ($c = 1.6 \cdot 10^{-4}$ M).

Methyl Ester of 3,4-Secomariesia-4(28),6,8(14),22,24-pentaen-26,23-olid-3-oic (anhydrosibiric) Acid (V). Oil, with $[\alpha]_D^{20}$ −297° (c 0.13). Empirical formula $C_{31}H_{42}O_4$ (m/z 478.3080; calculated 478.3079). UV spectrum, λ_{max}, nm: 260 (log ε 4.29); 280 (log ε 4.26). IR spectrum, cm^{-1}: 900, 1645, 3080 (C=CH_2); 1745 ($COOCH_3$); 1780 (γ-lactone). PMR spectrum, ppm: 0.72, 0.76, 0.94 (each 3 H, s, CH_3-10, CH_3-13, CH_3-17), 0.97 (3 H, d, J = 7.0 Hz, CH_3-20), 1.68 (3 H, d, J = 1 Hz, CH_3-4), 1.98 (3 H, d, J = 1.5 Hz, CH_3-25), 2.59 (1 H, d, $J_{5,6}$ = 5.5 Hz, H-5), 3.12 (1 H, dq, $J_{20,21}$ = 7.0 Hz, $J_{20,22}$ = 10.5 Hz, H-20), 3.64 (3 H, s, $COOCH_3$), 4.62 (1 H, d, $J_{28a,28b}$ = 2 Hz, H = 28a), 4.93 (1 H, dq, $J_{28b,28a}$ = 2 Hz, $J_{28b,29}$ = 1 Hz, H-28b), 5.16 (1 H, d, $J_{22,20}$ = 10.5 Hz, H-22), 5.33 (1 H, dd, $J_{6,5}$ = 5.5 Hz, $J_{6,7}$ = 10 Hz, H-6), 6.17 (1 H, d, $J_{7,6}$ = 10 Hz, H-7) and 6.98 (1 H, q, $J_{24,27}$ = 1.5 Hz, H-24). Mass spectrum (m/z %): 478 (55) − M^+, 391 (13) − $(M - CH_2CH_2CO - OCH_3)^+$, 341 (70) − $(M - 137)^+$, 83 (100).

Conversion of the Lactone V into the Ester (IV). A solution of 0.023 g of lactone (V) in 10 ml of methanol was treated with 5 ml of a 10% ethanolic solution of sodium hydroxide, and the mixture was heated in the water bath at 60-70°C until the initial substance had disappeared (monitoring by TLC). After being cooled to room temperature, the solution was diluted with 30 ml of water and was acidified with 5% hydrochloric acid to pH 2, and, after the addition of 20 ml of a saturated aqueous solution of sodium chloride, the product was extracted with diethyl ether (3 × 30 ml). The ethereal extract was treated with an excess of an ethereal solution of diazomethane (~10 ml), and the diazomethane and the solvent were rapidly driven off in a rotary evaporator. This gave 0.020 g of a product the chromatography of which yielded 0.007 g of an unidentified compound and 0.004 g of the ester (IV), identical with an authentic sample according to TLC and to PMR and CD spectra.

Dimethyl Ester of 23-Oxo-3,4-secomariesia-4(28),6,8(14),24Z-tetraen-3,26-oic (cis-sibiric) Acid (IV). Colorless oil with $[\alpha]_D^{20}$ −175° (c 0.099). UV spectrum, λ_{max}, nm: 253

(log ε 4.37). IR spectrum, cm^{-1}: 900, 1645, 3080 (C=CH_2), 1740 ($COOCH_3$), 1635, 1705 (α-enone). Mass spectrum (m/z, %). 510 (73) – M^+, 423 (18) – $(M - CH_2CH_2COOCH_3)^+$, 368 (19) – (M – 15 – $C(CO(=C(CH_3)COOCH_3)^+$, 341 (32) – (M – side chain)$^+$, 169 (30) – (side chain)$^+$, 127 (49) – $(C(O) - CH=C(CH_3)COOCH_3)^+$. The results of elementary analysis for the ions with m/z 510, 423, 368, and 341 corresponded to those calculated for the empirical formulas $C_{32}H_{46}O_5$, $C_{28}H_{39}O_3$, $C_{25}H_{36}O_2$, and $C_{23}H_{33}O_2$, respectively. PMR spectrum, ppm: 0.64, 0.81, 1.01 (each 3 H, singlets, methyl groups at C-10, C-13, and C-17); 0.82 (3 H, d, J = 6.0 Hz, CH_3-20); 1.75 (3 H, d, J = 1.0 Hz, CH_3-4); 3.63 and 3.78 (each 3 H, singlets, C(3)$OOCH_3$ and CH_3OOC-25, respectively); 2.00 (3 H, d, J = 1.5 Hz, CH_3-25), 2.60 (1 H, d, H-5, $J_{5,6}$ = 5.5 Hz), 4.71 (1 H, d, H-28a, $J_{28a,28b}$ = 2.0 Hz), 4.92 (1 H, dq, H-28b, $J_{28b,28a}$ = 2.0 Hz, $J_{28b,29}$ = 1 Hz), 5.33 (1 H, dd, H-6, $J_{6,5}$ = 5.5 Hz, $H_{6,7}$ = 10.0 Hz), 6.15 (1 H, q, H-24, $J_{24,27}$ = 1.5 Hz), 6.18 (1 H, d, H-7, $J_{7,6}$ = 10.0 Hz).

The Tetrahydro Derivative (VI). A solution of 0.05 g of the ester (IV) in 20 ml of ethyl acetate was stirred in an atmosphere of hydrogen in the presence of 0.05 g of Pd/$CaCO_3$ for 12 h, after which the reaction mixture was filtered through a layer of silica gel, the solvent was driven off, and the product was purified by chromatography. This gave 0.04 g of compound (VI) in the form of a colorless oil. UV spectrum, λ_{max} 253 nm (log ε 4.25). Mass spectrum (m/z, %): 514 (18) – M^+; 427 (10) – $(M - CH_2CH_2COOCH_3)^+$. PMR spectrum: 0.66, 0.93, 1.03 (each 3 H, singlets, methyl groups at C-10, C-13, and C-17); 0.82 and 0.84 (each 3 H, doublets, J = 6.7 Hz each, $(CH_3)_2CH$–); 1.00 (3 H, d, J = 6.7 Hz, CH_3-20); 1.19 (3 H, d, J = 6.8 Hz, CH_3-25); 2.74-3.04 (2 H, m); 3.64 and 3.68 (each 3 H, singlets, C(3)$OOCH_3$ and CH_3OOC-25, respectively); 5.51 (1 H, dd, $J_{6,5}$ = 5.0 Hz, $J_{6,7}$ = 10.0 Hz, H-6); 6.25 (1 H, d, $J_{7,6}$ = 10.0 Hz, H-7).

SUMMARY

Three new triterpene acids have been isolated in the form of their methyl esters from an extract of fir needles, and for them the structures of (3R)-3-methoxy-23-oxomariesia-7,14,24Z-trien-26-oic, 3,4-secomariesia-4(28),6,8(14),22,24-pentaen-26,23-olid-3-oic, and 23-oxo-3,4-secomariesia-4(28),6,8(14),24Z-tetraene-3,26-dioic acids, respectively, have been established on the basis of spectral and chemical characteristics.

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