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TRITERPENOIDS FROM *Abies* SPECIES.

IV. NEW TRITERPENE ACIDS FROM THE NEEDLES OF *Abies sibirica*

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UDC 547.914.2+539.26

Four new triterpene acids of the mariesiic acid series have been isolated from an extract of the needles of the Siberian fir in the form of their methyl esters, and their structures have been established on the basis of chemical transformations, spectral characteristics, and x-ray structural analysis.

Continuing an investigation of the triterpenoids of *Abies sibirica* Ledeb. (Siberian fir) [1-4], we found that an ethereal extract of it (yield 9%) contained 51% of acids the bulk of which were triterpene acids. The acids were separated by a known method [5] into "strong" (21% of the total amount of acids) and "weak." The 24-methylene-3,4-secocycloart-4(28)-en-3-oic acid described previously [3] and also all the resin and fatty acids, which were present in a ratio of 91:9 (GLC), passed into the weak-acid fraction. According to the GLC of their methyl esters, the diterpene (resin) acids consisted of dehydroabietic (38.3%), abietic (24.4%), palustric (20.2%), neoabietic (14.2%), and sandaracopimamic (2.8%) acids.

We have previously [4] described two new triterpene acids present in the strong-acid fraction for which structures (I) and (II) were suggested on the basis of spectral characteristics. In a further analysis of its composition, we isolated in the form of methyl esters four other new acids with the carbon skeleton of mariesiic acid A (III) — a component of an extract of the weeds of the fir *Abies mariesii* Mast. [6]. (See following page.)

Chromatography of the strong acids on silica gel gave a number of fractions which were methylated with diazomethane and chromatographed on the same sorbent. In this way, four methyl esters corresponding to the main components of the initial mixture were isolated (see the Experimental part). Two of them — the esters (IV) and (V) — had been described previously [4], while the other two were new compounds having the structures expressed by formulas (VI) and (VII). The latter was isolated in the form of the acetate (VIII), crystallized

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Translated from Khimiya Prirodykh Soedinenii, No. 6, pp. 824-831, November-December, 1987.
Original article submitted April 17, 1987.

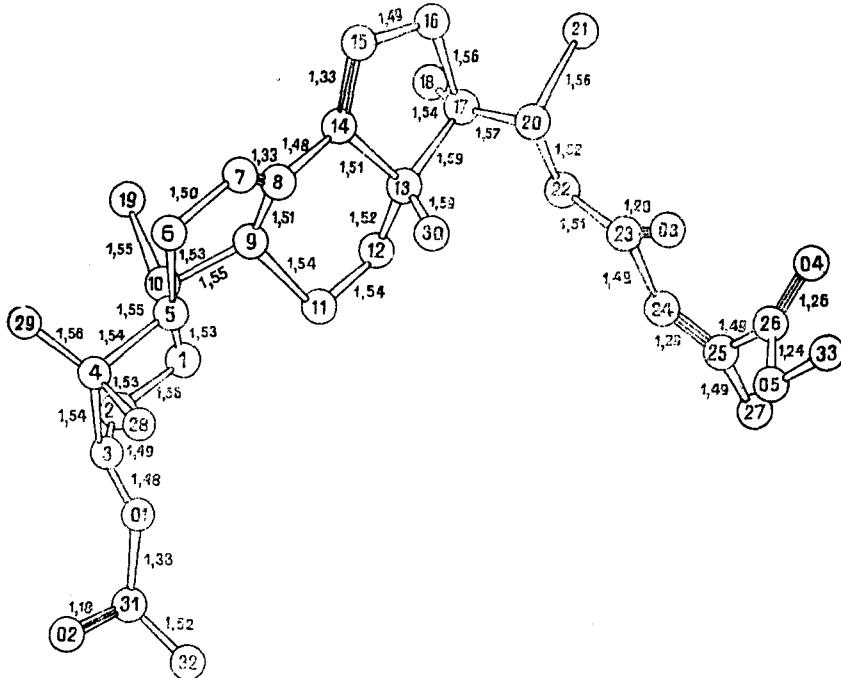
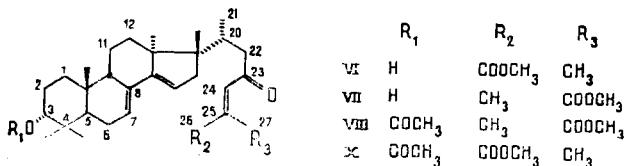
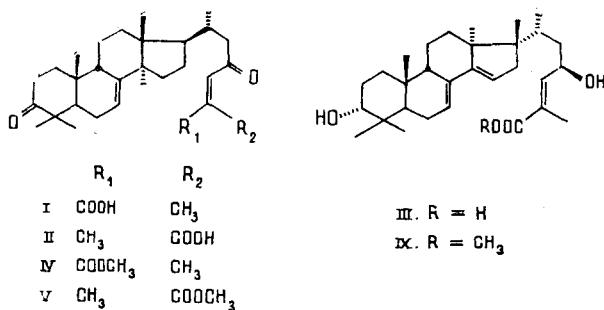


Fig. 1. Molecular structure of the acetate (VIII). The probable errors in the bond lengths amount to 0.01-0.02 Å.



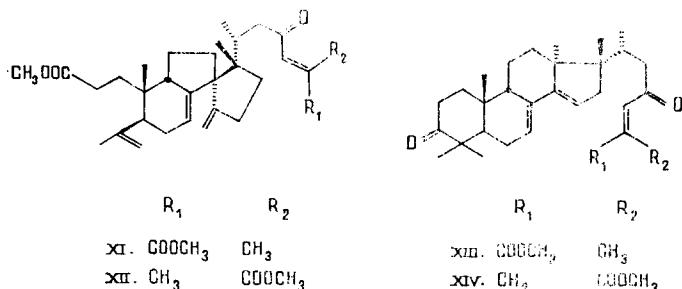
ing well from methanol. The structure of this acetate was established by x-ray structural analysis.

The spatial structure of the molecule of ester (VIII) is shown in Fig. 1. All the rings are present in the usual conformations - chair, half-chair, flattened chair, and envelope for rings A, B, C, and D, respectively. Judging from [6], the same forms of the rings, one also found for the mariesic acid A molecule. The two endocyclic double bonds in the molecule of (VIII) are nonconjugated, the C7=C8-C14=C15 torsional angle being 51.7°. The C24=C25 double bond is present in the same plane as the keto group and C-23, and the ester group is completely free from conjugation with the neighboring double bond (the C24=C25-C26=O torsional angle is 86.5°).

The structure and absolute configuration of the second ester (VI) were shown by its chemical correlation with methyl mariesiate A (IX). The treatment of an ethanolic solution of the ester (VI) with sodium tetrahydroborate followed by chromatography of the mixture of products gave approximately equal amounts of ethyl mariesiate A, methyl mariesiate A, and methyl 23-epimariesiate. The PMR spectrum of the ester (IX) obtained agreed with that

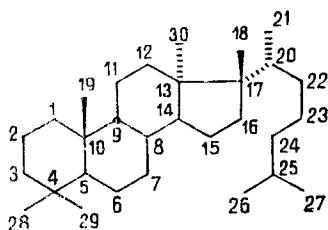
given in the literature [6], while the spectrum of its ethyl analogue differed from the latter only by the presence of the signals of the protons of an ethoxycarbonyl group in place of the singlet signal of the protons of a methoxycarbonyl group. Mariesiic acid A obtained by the saponification of its methyl ester had an optical rotation corresponding to that of the natural product.

When an ethereal solution of the acetate (VIII) was irradiated with the light of a high-pressure mercury lamp, a photoequilibrium mixture (monitoring of TLC of the initial compound and the acetate (X), identical in its spectral characteristics and optical properties with the product of the acetylation of the ester (VI)) was formed after ~2 h. This showed the absolute configuration of the molecule of the acetate (VIII), which corresponds to the formula given.



We have described a similar isomerization previously for dimethyl abiesonate (XI) and its 24E-isomer (XII) [1]. As was established, it is reversible and, just as for the esters (IV) and (V), takes place according to TLC, even when ethereal solutions of either of the above mentioned compounds are allowed to stand in sunlight. Cis-trans isomerization also takes place in the alkaline saponification of the acetate (VIII) in ethanol – in addition to the expected keto acid its 24E-isomer (isolated in the form of the methyl esters) and also unidentified degradation product the amount of which rises with an increase in the time of the reaction, are formed.

The presence among the acids investigated of the 3-oxolanostane derivatives (I) and (II) permitted the assumption that the 3-oxo analogues of the acids corresponding to the methyl esters (VI) and (VII) were also present. In order to find and identify them, we obtained samples of the keto esters (XIII) and (XIV) by the oxidation of the methyl esters (VI) and (VII), respectively, with pyridinium chlorochromate in methylene chloride. Analysis by TLC using the keto esters (XIII) and (XIV) as markers showed that the compounds sought were actually present in the fractions isolated in the process of separating the methylated strong acids. Samples of these acids were then successfully isolated by chromatography, and their IR and PMR spectra and their circular dichromism (CD) curves coincided with those for the synthetic samples.



The amounts of the acids corresponding to the methyl esters (IV, V, VI, VII, XII, XIII, and XIV) in the strong-acid fraction were, according to the results of chromatography, approximately 7, 12, 21, 15, 1, 1, and 4%, respectively.

The composition of the weak-acid fraction was not studied in detail, but it was established by TLC that it did not contain the acids described above with the trans configuration of the C24=C25 double bond, and the main components (~70%) were the acids corresponding to the methyl esters (V) and (VII).

EXPERIMENTAL

Except where specially mentioned, the instruments and the conditions for chromatography and for recording spectra have been described in [1]. Abbreviations in the descriptions of the PMR spectra: s - singlet; d - doublet; q - quartet; m - multiplet. The interpretation of the mass spectra was confirmed by the calculation of the elementary compositions of the corresponding ions. Empirical formulas were determined by mass spectrometry.

Needles of the Siberian fir gathered in February, 1986, in the environs of Novosibirsk were separated from shoots and dried in the air. To determine the yield of extract, a portion of the air-dry needles was dried in vacuum over phosphorus pentoxide. Extraction was performed in a Soxhlet apparatus. The strong-acid fractions were methylated by the addition of an excess of an ethereal solution of diazomethane to an ethereal solution of the fraction under investigation followed by the rapid elimination of the solvent and the excess of diazomethane in a rotary evaporator. Unless otherwise mentioned, the estimates of the compositions of the unseparated fractions are given on the basis of TLC.

Primary Separation of the Extract. The ethereal extract obtained from 65.00 g of absolutely dry needles was treated as described for a solution of the oleoresin in [1, 5]. This gave a total of 0.63 g of strong acids, a total of 2.37 g of weak acids, and 2.86 g of a neutral fraction. The same fractions were obtained similarly from the air-dry needles.

The chromatography of 2.37 g of the mixture of weak acids gave 0.12 g of a mixture of nonpolar acids and 2.25 g of polar triterpene acids (the eluents being petroleum ether containing 20% of diethyl ether, and diethyl ether, respectively). The mixture of nonpolar acids was treated with 40 ml of a saturated ethereal solution of diazomethane and the mixture was evaporated to dryness. The methyl ester of 24-methylene-3,4-secocycloart-4(28)-en-3-oic acid isolated from the resulting mixture of esters has been described in [3]. The analysis of the methyl esters of the resin and fatty acids (the latter were not identified quantitatively) was performed on a Chrom-4 instrument (with a 0.3 mm × 20 m glass capillary column coated with PMS; $t_{col} = 200^\circ\text{C}$).

The chromatography of 14.00 g of the combined strong acids gave fractions 1-7 with yields of 0.13, 1.14, 1.33, 4.20, 0.93, 4.92, and 0.25 g, respectively (a total of 12.90 g) (the eluent was petroleum ether containing gradually increasing amounts, from 20 to 100%, of diethyl ether).

Isolation of Individual Methyl Esters. The crystallization of fraction 2 (1.14 g) from diethyl ether yielded 0.19 g of the acid (I), which has been described in [4]. The methylation of the mother liquor followed by chromatography gave 0.38 g of the ester (IV) and 0.50 g of a mixture of it with unidentified compounds (~1:1).

Chromatography of the methylated fraction 3 (1.33 g) gave 0.32 g of a mixture of the esters (IV) and (XIII) (~1:1), 0.20 g of unidentified substances, and 0.80 g of the ester (VI) containing trace amounts of compounds (V) and (XIV). The rechromatography of the 0.32 g fraction yielded 0.01 g of the keto ester (XIII) and 0.31 g of a mixture of it with the ester (IV). The 0.80 g fraction was acetylated with acetic anhydride in pyridine (20°C, 12 h).

After the usual working up and chromatography of the product, 0.55 g of the ester (X) and 0.20 g of a mixture of the esters (V) and (XIV) (~1:1) was obtained.

Crystallization of fraction 4 (4.20 g) from diethyl ether gave 1.00 g of the acid (II) [4], which was methylated with diazomethane. Chromatography of the methylated mother solution gave, successively, 0.05 g of a mixture of substances containing the ester (XI) (TLC), 0.10 g of the ester (XII), 0.44 g of the ester (V), 1.90 g of a mixture of (V, VI, and XIV), and 0.17 g of the ester (VI). The 1.90 g fraction was acetylated as described above. Chromatography of the product yielded 1.61 g of the acetate (X), 0.08 g of the ester (V), and 0.16 g

of a mixture of substances (V) and (XIV) (~1:1). Rechromatography of the latter yielded 0.08 g of the pure keto ester (XIV).

Chromatography of the methylated fraction 5 (0.93 g) yielded 0.05 g of a mixture of (XIV) and (V) (~1:1), 0.66 g of a mixture of substances containing the ester (VI) as one of the main components, and 0.02 g of unidentified compounds.

The chromatography of the methylated fraction 6 (4.92 g) gave 0.61 g of a mixture of (VI) and two unidentified esters (TLC), 3.85 g of a mixture containing 50% of the ester (VII), and 0.30 g of unidentified substances. The 3.85 g fraction was acetylated as described above. Chromatography of the product gave 3.70 g of combined acetates, two crystallizations of which from methanol yielded 1.42 g of the acetate (VIII).

The methylated fraction 7 (0.25 g) was a mixture of the ester (VII) (~50%) and unidentified substances (according to TLC).

Methyl (3R,24Z)-3-acetoxy-23-oxomariesia-7,14,24-trien-26-oate (VIII) was isolated in the form of crystals with mp 192-194°C, $[\alpha]_D^{25} +19.9^\circ$ (c 2.5; chloroform). UV spectrum: $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 227 nm ($\log \epsilon$ 4.25). IR spectrum $\nu_{\text{max}}^{\text{KBr}}$, cm^{-1} : 1630 (C=C), 1720 and 1740 (C=O). Mass spectrum m/z (%): 524 (M^+ , 15); 506 (5); 382 (75), ($M - 15 - \text{COCH}=\text{C}(\text{CH}_3)\text{COOCH}_3$) $^+$; 355 (55), ($M - \text{side chains}$) $^+$; 295 (83), ($M - \text{side chain} - 60$) $^+$; 169 (100), ($\text{CH}_3\text{CHC(O)CH}=\text{C}(\text{CH}_3)\text{COOCH}_3$) $^+$; 127 (24), ($\text{COCH}=\text{C}(\text{CH}_3)\text{COOCH}_3$) $^+$. PMR spectrum: 0.82-0.98 (6 CH_3), 2.01 (3 H, d, $J = 1.5$ Hz, Me-225), 2.05 (3 H, s, OCOCH_3), 3.77 (3 H, s, COOCH_3), 4.65 (1 H, d, $J \approx 2$ Hz, H-3), 5.17 and 5.55 (1 H each, m, with $W_{1/2} = 6$ and 10 Hz; H-15 and H-7, respectively); 6.15 ppm (1 H, q, $J = 1.5$ Hz, H-24).

The x-ray structural experiment for the acetate (VIII) was performed on a Syntex P2₁ diffractometer using Mo radiation with a graphite monochromator. Crystals in the monoclinic system, $a = 7.379(3)$, $b = 12.184(5)$, $c = 17.406(5)$ Å, $\beta = 101.77(3)^\circ$; space group P2₁; $d_{\text{calc}} = 1.14$ g/cm³). Using the 2 θ /ω scanning method in the interval $2\theta < 55^\circ$, the intensities of 2287 independent reflections were measured, and the 1516 of these with $I > 2\sigma$ were used in the calculations. The structure was interpreted by the direct method using the RANTAN procedure [7]. The final refinement of the structure by the method of least squares in the anisotropic-isotropic block-diagonal approximation led to $R = 0.083$ and $R_w = 0.068$, where $w^{-1} = (\sigma_F^2 + 0.000172F^2)$. The positions of the hydrogen atoms with fixed B_{iso} values were calculated geometrically in each cycle of refinement. The coordinates of the nonhydrogen atoms obtained are given in Table 1. A considerable anisotropy of the vibrations of the terminal atoms of the side chain may be noted, since B_{33} is 2-3 times higher than B_{11} and B_{22} .

Methyl (3R,24E)-3-hydroxy-23-oxomariesia-7,14,24-trien-26-oate (VI). Crystals with mp 58-60°C (from a mixture of petroleum ether and diethyl ether). UV spectrum: $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 237 nm ($\log \epsilon$ 4.25). IR spectrum, $\nu_{\text{max}}^{\text{CCl}_4}$, cm^{-1} : 1630 (C=C), 1705, 1740 (C=O), 3640 (OH). PMR spectrum, ppm: 0.82-0.96 (6 Me), 2.19 (3 H, d, $J = 1.5$ Hz, Me-27), 3.44 (1 H, d, $J \approx 2.5$ Hz, H-3), 3.78 (3 H, s, COOCH_3), 5.16 and 5.55 (1 H each, $W_{1/2} = 6$ and 10 Hz, respectively, H-15 and H-7, 7.06 (1 H, q, $J = 1.5$ Hz, H-24).

The 3-O-Acetate (X) of the Ester (VI). Oil with $[\alpha]_D 0^\circ$ (c 9.7; chloroform). UV spectrum: $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 237 nm ($\log \epsilon$ 4.26). Mass spectrum, m/z (%): 524 (M^+ , 22), 504 (7), 382 (84), 355 (65), 295 (100), 169 (90), 127 (37). The PMR spectrum differed appreciably from that for (VI) only by the presence of a signal at 2.03 ppm (3 H, s, OOCCH_3) and by the position of the H-3 signal at 3.78 ppm.

Photoisomerization of the Acetate (VIII). This was carried out as described in [1] for dimethyl abiesonate (XI). Chromatography of the product obtained from 0.3 g of the acetate (VIII) yielded 0.1 g of compound (X) and 0.2 g of the initial substance. The CD curve and the PMR spectrum of the ester (X) obtained were identical with those of a sample synthesized by the acetylation of the ester (VI) with acetic anhydride in pyridine.

Reduction of the Ester (VI). With stirring, 0.05 g of sodium tetrahydroborate was added to a solution of 0.060 g of the ester (VI) in 5 ml of ethanol, and the mixture was left at room temperature for 1 h. After the usual working up and chromatography, 0.005 g of ethyl mariesiate A, 0.014 g of a mixture of ethyl and methyl mariesiates A, 0.013 g of methyl mariesiate A (oil, the PMR spectrum coincided with that given in the literature [6]), 0.019 g of a mixture of (IX) and 23-epi-(IX), and 0.006 g of 23-epi-(IX) were obtained.

TABLE 1. Coordinates (in fractions of the cell, $\times 10^4$) of the Nonhydrogen Atoms in the Molecule of the Acetate (VIII)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C (1)	5986 (12)	1168 (8)	4226 (5)	C (2)	6792 (13)	0443 (8)	4957 (5)
C (3)	8312 (15)	1050 (8)	5480 (5)	C (4)	9319 (14)	1407 (8)	5092 (6)
C (5)	9130 (11)	2000 (7)	4311 (5)	C (6)	10655 (12)	2246 (10)	3853 (6)
C (7)	9906 (13)	2826 (9)	3096 (6)	C (8)	8130 (12)	2827 (7)	2750 (5)
C (9)	6633 (11)	2271 (7)	3088 (5)	C (10)	7455 (11)	1460 (8)	3756 (5)
C (11)	5337 (11)	3192 (7)	3256 (5)	C (12)	4451 (11)	3788 (7)	2492 (5)
C (13)	5821 (10)	4238 (7)	2029 (4)	C (14)	7435 (10)	3477 (8)	2032 (5)
C (15)	8031 (12)	3506 (8)	1360 (5)	C (16)	6936 (12)	4301 (8)	6795 (5)
C (17)	5134 (12)	4477 (8)	1119 (5)	C (18)	3771 (12)	3602 (7)	0758 (5)
C (19)	7979 (13)	0422 (7)	3333 (5)	C (20)	4333 (11)	5658 (7)	0920 (4)
C (21)	4052 (12)	5918 (9)	0026 (5)	C (22)	2540 (11)	5882 (7)	1191 (5)
C (23)	2090 (14)	7079 (8)	1272 (5)	C (24)	0198 (12)	7312 (16)	1411 (5)
C (25)	-0514 (12)	8271 (9)	1459 (5)	C (26)	0520 (18)	9293 (13)	1354 (13)
C (27)	-2353 (12)	8479 (8)	1653 (6)	C (28)	11202 (14)	2171 (9)	5650 (6)
C (29)	11035 (11)	0332 (8)	5036 (6)	C (30)	6749 (12)	5290 (7)	2482 (5)
C (31)	7034 (14)	2093 (11)	6430 (6)	C (32)	6213 (6)	3195 (10)	6582 (7)
C (33)	1959 (22)	10879 (19)	1467 (14)	O (1)	7533 (9)	2077 (6)	5735 (4)
O (2)	7256 (13)	1340 (8)	6861 (5)	O (3)	3183 (8)	7802 (6)	1241 (4)
O (4)	0433 (12)	9668 (9)	0671 (7)	O (5)	1335 (13)	9794 (9)	1944 (7)

Methyl 23-epimariesiate A formed crystals with mp 169-171°C (from acetonitrile) with the empirical formula $C_{31}H_{48}O_4$. IR spectrum, $\nu_{\text{max}}^{\text{CCl}_4}$, cm^{-1} : 1650 (C=C), 1715 (C=O), 3600 (OH). PMR spectrum, ppm: 0.77, 0.85, 0.90, 0.93, and 0.96 (3 H each, singlets of angular Me groups); 0.89 (3 H, d, $J = 7$ Hz, CH_3 -21); 1.89 (3 H, d, $J = 1.5$ Hz, CH_3 -27); 3.44, 5.12, and 5.52 (1 H each, multiplet with $W_{1/2} = 6$, 6, and 10 Hz, H-3, H-15, and H-7, respectively); 4.55 (1 H, ddd, $J = 4.6$, 9.0, and 9.0 Hz, H-23); and 6.59 (1 H, dq, $J = 9.0$ and 1.5 Hz, H-24).

Ethyl mariesiate A formed an oil the PMR spectrum of which differed from that of (IX) only by the presence of the signal of the protons of the ethyl group (4.18 ppm, 2 H, q, $J = 7.0$ Hz, and 1.28 ppm, 3 H, t, $J = 7.0$ Hz) in place of the singlets of the protons of methoxycarbonyl group.

Saponification of Methyl Mariesiate A. A solution of 0.013 g of methyl mariesiate A in 5 ml of methanol containing 0.05 g of NaOH was kept at room temperature for 5 h. After the usual working up procedure, 0.010 g of mariesic acid A was obtained with $[\alpha]_D^{20} + 100^\circ$ (c 0.22; acetone) (according to the literature [6]: $[\alpha]_D + 116^\circ$ (c 1.73; acetone)).

Saponification of the Acetate (VIII). At 50°C, 0.65 g of the acetate (VIII) was dissolved in 20 ml of 10% ethanolic KOH, and the solution was left at the same temperature for 1.5 h. Then it was diluted with 50 ml of water and extracted with 50 ml of diethyl ether. The aqueous phase was separated off, acidified with hydrochloric acid to pH 2, and extracted with diethyl ether (100 ml). The ethereal extract was washed with water to neutrality, and an ethereal solution of diazomethane was added to it until a permanent yellow coloration appeared. After the solvent had been driven off and the combined products had been chromatographed, 0.18 g of the ester (VI), 0.23 g of a mixture of unidentified products, and 0.18 g of the ester (VII) in the form of an oil were obtained. PMR spectrum, ppm: 0.83 (3 H, d, $J = 7$ Hz, Me-20); 0.85 (6 H); 0.91, 0.94, 0.96 (3 H each, tertiary methyl groups); 2.00 (3 H, d, $J = 1.5$ Hz, Me-26); and 3.43 ppm (1 H, m, $W_{1/2} = 6$ Hz, H-3). The signals of protons of the 3.45-6.20 region were the same as in the spectrum of the ester (VIII).

Methyl (24E)-3,23-Dioxomariesia-7,14,24-trien-26-oate (XIII). Oil, UV spectrum: $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 234 nm ($\log \epsilon = 4.09$). IR spectrum: $\nu_{\text{max}}^{\text{CCl}_4}$, cm^{-1} : 1630 (C=C), 1700 (shoulder), 1722, 1733 (C=O). PMR spectrum, ppm: 0.83-1.11 (18 H, s, tertiary methyl groups); 2.19 (3 H, d, $J = 1.5$ Hz, Me-27); 2.72 (1 H, ddd, $J = 5.0$, 14.0, and 14.0 Hz, H-2); 3.78 (3 H, s, COOCH_3); and 5.21, 5.59, and 7.05 (1 H each, multiplets with $W_{1/2} = 6$ and 10 Hz and quartet with $J = 1.5$ Hz, respectively; H-15, H-7, H-24). CD curve (c $7.3 \cdot 10^{-3}$ M; methanol); $\Delta\epsilon = -1.50$ (299 nm), -0.98 (345 nm) (minima).

Methyl (24Z)-3,23-Dioxomariesia-7,14,24-trien-26-oate (XIV). Oil, UV spectrum: $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 230 nm ($\log \epsilon = 3.97$). IR spectrum: $\nu_{\text{max}}^{\text{CCl}_4}$, cm^{-1} : 1635 (C=C), 1720, 1750 (C=O). PMR spectrum: 0.83-1.11 (18 H, s, tertiary methyl groups); 2.00 (3 H, d, $J = 1.5$ Hz, Me-27); 2.72 (1 H, ddd, $J = 5.0$, 14.0, and 14.0 Hz, H-2); 3.76 (3 H, s, COOCH_3); and 5.20, 5.58, and 6.14 (1 H each, multiplets with $W_{1/2} = 6$ and 10 Hz, and quartet with $J = 1.5$ Hz, respectively; H-15,

H7, and H-24). CD curve ($c 8.7 \cdot 10^{-3}$ M; methanol): $\Delta\epsilon = -2.0$ (297 nm), -1.14 (330 nm) (minimum and inflection, respectively).

Synthesis of the Keto Esters (XIII) and (XIV). To a suspension of 0.30 g of pyridinium chlorochromate [8] in 10 ml of methylene chloride were added 0.07 g of sodium acetate and a solution of 0.09 g of the ester (VI) in 10 ml of methylene chloride. After being stirred at room temperature for 1.5 h, the reaction mixture was deposited on a column containing 5.0 g of silica gel. Elution with diethyl ether led to the isolation of 0.09 g of combined products the chromatography of which on silica gel yielded 0.06 g of the keto ester (XIII).

Analogously, 0.030 g of the ester (VII) yielded 0.022 g of the keto ester (XIV).

SUMMARY

1. Seven triterpene acids belonging to three structural types have been isolated in the form of methyl esters from Siberian fir needles.

2. The structures of the four new acids have been established on the basis of spectral characteristics, chemical transformations, and x-ray structural analysis.

3. Natural 24-cis-abiesonic acid has been detected for the first time.

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