TRITERPENOIDS FROM Abies SPECIES

XII. (24Z)- and (24E)-8(14 → 13)-ABEO-17,13-FRIEDO-LANOSTA-8,14(30),24-TRIENE-3,23-DION-26-OIC ACIDS – NEW TRITERPENOIDS FROM THE NEEDLES OF THE SIBERIAN FIR

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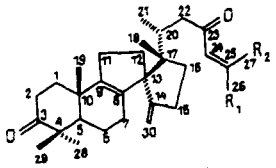
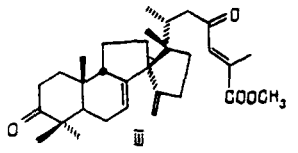
From an acid fraction of an ethereal extract of Siberian fir needles two new stereoisomeric acids, the molecules of which have a modified lanostane carbon skeleton, have been isolated in the form of methyl esters. The structures of the molecules of these substances have been established by the use of ^{13}C and ^{1}H NMR, $^{1}H-^{1}H$ and $^{13}C-^{1}H$ two-dimensional NMR spectra, circular dichroism, and chemical transformations as (24Z)- and (24E)-8(14 → 13)-abeo-17,13-friedo-lanosta-8,14(30),24-triene-3,23-dion-26-oic acids.

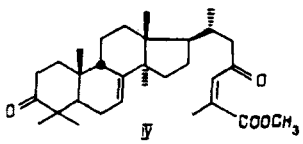
Continuing an investigation of the chemical composition of a methylated acid fraction of an ethereal extract of needles from the Siberian fir Abies sibirica Ledb. [1], we have isolated two new esters, and for their molecules we have established the structures illustrated by formulas (I) and (II). They differ from other esters by the fact that they appear on TLC on Silufol (spraying with H_2SO_4) in the form of bright orange spots. They were isolated by the use of adsorption column chromatography on SiO_2 + 5% of $AgNO_3$ in a mixture of methylene chloride and diethyl ether as eluent. Like other keto esters of a similar type [2, 3], compounds (I) and (II) were readily interconverted on irradiation with the light of a mercury lamp or with daylight. Therefore, in order to establish their structures we analyzed in detail the spectral characteristics of only one of them [the ester (I)] using as model compounds the known methyl mariesiate C (III) [4], lanosta-8,24-dien-3-one [5, 6], and the diketo ester (IV) [2, 7, 8].



I. $R_1 = CH_3$, $R_2 = COOCH_3$
II. $R_1 = COOCH_3$, $R_2 = CH_3$



III



IV

In a primary consideration of the spectral characteristics for compound (I), having the empirical formula $C_{31}H_{44}O_4$ (high-resolution mass spectrometry), it was established that it was the methyl ester of a monobasic diketo acid containing in its molecule an exomethylene group, nonconjugated and conjugated keto groups, five tertiary and one secondary methyl groups, and one tetrasubstituted and one trisubstituted double bonds (NMR spectra, see Tables 1 and 2). These facts, and also the presence in the ^{13}C NMR spectrum of a singlet at 68.04 ppm due to a double allyl nodal carbon atom of the spiran system [4], permitted the assumption that the molecule of the compound under investigation differed structurally from the isomeric (III) only by the position of the endocyclic double bond. The ^{13}C NMR spectrum of ester (I) recorded with incomplete decoupling of protons did not contradict this hypothesis – the number of singlets, doublets, triplets, and quartets of different types in it ac-

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TABLE 1. Chemical Shifts and Multiplicities of the Signals* in the PMR Spectra of the Esters (I) and (V)

H	I ($CDCl_3$)	I (C_6D_6)	V ($CDCl_3$)
2H-1	1,65; 1,87 ddd	1,33; 1,51	1,64; 1,88
2H-2	2,45 ddd 2,56 ddd	2,26; 2,31	2,45 ddd 2,49 ddd
H-5	1,62	1,51	1,59
2H-6	1,56; 1,68	1,42; 1,48	1,54; 1,58
2H-7	1,94; 2,17 dm	1,88; 2,03	1,75m; 1,98
2H-11	2,03; 2,07	1,90; 1,94	2,09; 2,17
2H-12	1,42; 1,98	1,24; 2,00	1,66; 2,03
2H-15	2,32; 2,37	2,25; 2,28	5,19 m
2H-16	1,46; 1,53	1,29; 1,40	1,88; 2,04
3H-18	0,85 s	0,79 s	0,84s
3H-19	1,00 s	0,85 s	0,97 s
H-20	2,37	2,47 ddq	2,29
3H-21	0,84 d	0,89q	0,68d
3H-22	2,20 dd 2,47 dm	2,12dd 2,75dm	2,28; 2,70
H-24	6,06q	5,84 q	7,01 q
3H-27	1,98d	1,71d	2,15d
3H-28	1,08s	1,06s	1,04s
3H-29	1,04s	0,97s	1,02s
H-30	4,62 dt (1H) 4,71 dt (1H)	4,57dt (1H) 4,80dt (1H)	1,43 d (3H)
OCH_3	3,76s	3,50 s	3,78 s

*Observed in one-dimensional spectra.

curately coincided with those expected for structure (I). In the PMR spectrum it was easy to identify signals typical for tetracyclic triterpene 3,23-diketo derivatives [5, 8] and those due to the 2 H-2, 3 H-21, 2 H-22, H-24, and 3 H-27 protons (Table 1). The values of CSs for the latter two indicated [2, 3] the Z-configuration of the trisubstituted bond present in the side chain. The structure and stereochemistry of the side chain of molecule (I) was also confirmed by the coincidence of the signals for the atoms from C-23 to C-26 in the ^{13}C NMR spectra of the ester (I) and of compound (IV) [7] (Table 2).*

In order to confirm the hypothesis concerning the structure of the ester (I), we analyzed its two-dimensional (2D) $^1H-^1H$ and $^{13}C-^1H$ NMR spectra (recorded for solutions in $CDCl_3$ and C_6D_6) with consideration of the ^1H and ^{13}C NMR results. From the $^{13}C-^1H$ 2D NMR spectra we found the values of the CSs for all the protons present at the saturated centers and revealed of methylene protons and two methine protons (H-5 and H-20). Then in a consideration of the 2D $^1H-^1H$ NMR spectra we established the presence of four four-proton systems not connected with one another due to bismethylene fragments [according to formula (I) they were located at C(1)–C(2), C(6)–C(7), C(15)–C(16), and C(11)–C(12)].

The 2 H-1 and 2 H-15 signals were identified from the existence of spin–spin coupling (SSC) of 2 H-1 with 2 H-2 and of 2 H-15 and 2 H-30, respectively. The unambiguous assignment of H-20 (from the SSCCs with 3 H-21 and 2 H-22) enabled the H-5 signal to be identified and the signals for 2 H-6 and 2 H-7 to be assigned. This was not possible in the spectrum recorded for a solution in $CDCl_3$, since the H-5 signal fell between two of the others under consideration which, in this situation can be assigned either to 2 H-6 or to 2 H-7.

In the spectrum recorded for a solution in C_6D_6, the H-5 signal is somewhat displaced in relation to the signals of this pair of protons (see Table 1) and an SSC of it with these protons is observed, which, thus, belong to 2 H-6. In agreement with structure (I), the remaining isolated group of four methylene protons relate to 2 H-11 and 2 H-12.

The following stage of the analysis was connected with a consideration of the long-range SSCs in the PMR spectra. In the $^1H-^1H$ 2D NMR spectrum a long-range SSC appeared between H-1b† and 3 H-19, and also between H-16a and 3 H-18 (for solutions in $CDCl_3$ and C_6D_6). This, on the one hand, enables the corresponding elements of the structure of ester (I) to be con-

*In [7] an incorrect value is given for the CS for the C-26 atom (163.2 ppm) in the ^{13}C NMR spectrum of compound (IV). In actuality it is 169.5 ppm.
†The indices "a" and "b" mark pairs of diastereotopic protons the signals of which are present in the high and low fields relative to one another, respectively, in the PMR spectra.

TABLE 2. Chemical Shifts and Multiplicities in the ^{13}C NMR Spectra of the Esters (I) and (V)*

C	I ($CDCl_3$)	I (C_6D_6)	V ($CDCl_3$)
1	35,50 t	35,58 t	35,78 t
2	34,31 t	34,42 t	34,22 t
3	217,08 s	214,45 s	217,22 s
4	47,06 s	47,02 s	46,95 s
5	50,94 d	51,23 d	51,07 d
6	20,47 t	20,74 t	20,10 t
7	26,33 t	26,66 t	26,27 t
8	136,13 c	136,18 s	137,14 s
9	147,78 s	148,38 s	145,27 s
10	35,81 s	36,00 s	35,99 s
11	26,44 t	26,80 t	28,73 t
12	32,37 t	33,07 t	26,86 t
13	68,04 s	68,45 s	70,54 s
14	155,46 s	156,05 s	144,07 s
15	27,13 t	27,57 t	122,66 d
16	37,74 t	37,99 t	40,79 t
17	49,12 s	49,57 s	50,36 s
18	18,56 q	18,85 q	21,42 q
19	18,46 q	18,39 q	19,18 q
20	34,07 d	34,37 d	36,68 d
21	15,98 q	16,46 q	18,38 q
22	45,01 t	45,28 t	48,63 t
23	199,80 s	198,83 s	202,08 s
24	129,85 d	130,71 d	132,94 d
25	141,18 s	140,97 s	139,80 s
26	169,44 s	169,00 s	167,99 s
27	20,15 q	20,02 q	14,11 q
28	26,53 q	26,77 q	26,80 q
29	20,93 q	21,17 q	20,79 q
30	103,97 t	104,56 t	13,38 q
$\underline{OCH_3}$	52,12 q	51,79 q	52,30 q

*Concentration of the solution 0.5 M.

firmed and, on the other hand, enables unambiguous assignments to be made of the signals of the two tertiary methyl groups (Me-10 and Me-17) in the ^1H and ^{13}C NMR spectra.

In the spectrum recorded for a solution in C_6D_6 an intramolecular NOE was observed (NOESY experiment [9]) between H-5 and the protons of a tertiary methyl group the signal of which in the PMR spectrum was present at 1.06 ppm. This permitted the C(1)–C(3) and C(4)–C(7) fragments to be "linked" since the CS for the carbon atom of this methyl group (26.77 ppm) is characteristic [10] for the C-28 atom in a 3-ketolanost-8-ene fragment. The CS for the carbon atom of the second (C4) methyl group (C-29), 21.17 ppm, and the CSs for C-4 and C-10 correspond to those calculated for the same fragment [10].

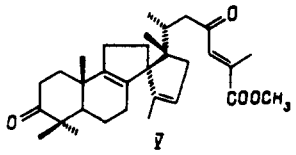
Finally, in the CD spectrum of the ester (I) (for a solution in methanol) a positive CE was observed at 288 nm coinciding in sign and position with that for lanosta-8,24-dien-3-one [5, 6], which showed the same absolute configuration of the asymmetric centers at C-5 and C-10 in the molecules of the compounds compared. This curve also showed a second CE, at 325 nm ($n \rightarrow \pi^*$ transition in the C(23)=O group), the negative sign of which showed [8] the 20-R configuration of the asymmetric center in the side chain of the molecule.

A proof of the presence of the C(7)...C(11) fragment in the molecule of the ester (I) may be the detection of SSC between one of the two H-7 protons and the 2 H-11 protons. The signal of the H-7a proton (spectrum in $CDCl_3$), being superposed on the narrow components of the H-22b signal, was observed in the form of an unsymmetrical doublet with J ~ 16 Hz having broad ($W_{1/2}$ = 10 Hz) components. The absence of fine structure of the signal indicated the existence of a long-range SSC. In actual fact, in the 2D ^1H–^1H spectrum (COSYLR conditions [9]), and SSC of H-7a with protons giving signals at 2.03 and 2.07 ppm was observed. Thus, the latter must be assigned to 2 H-11, and the second pair of signals of the bismethylene fragment (1.42 and 1.98 pm) to 2 H-12. On passing to C_6D_6, the positions of the signals for 2 H-11, 2 H-12, C-11, and C-12 in the spectra did not change appreciably (see Tables 1 and 2), and their assignment in this case was based on this fact.

The exomethylene double bond in the molecule of methyl mariesiate C (III) migrated into the Δ^{14} position when the substance was treated with a solution of HCl/CH_3OH in $CHCl_3$ [4].

The Δ^7 double bond and the spiran system of the molecule (III) were not affected in this process. Under the same conditions, ester (I) gave an analogous isomer (V), but, here again, reversal of the configuration of the Δ^{24} double bond took place as shown by the characteristic CSs for H-24 and 3 H-27 in the PMR spectrum [3] and for C-27 in the ^{13}C spectrum [7] (see Tables 1 and 2).

Isomerization in the side chain of the molecule was irreversible and undoubted has a general nature for such keto esters. It can be explained by the greater thermodynamic stability of the 24E isomer. In this connection, it may be mentioned that Hasegawa et al. [4] carried out the isomerization of the ester (III), the molecule of which already has the 24E configuration.



V

A detailed analysis of the 2D $^1H-^1H$ and $^{13}C-^1H$ NMR spectra has also been made for the ester (V), and this enabled all the signals of its ^1H and ^{13}C NMR spectra to be interpreted (Tables 1 and 2). The 2D $^1H-^1H$ NMR spectrum (COSYLR) showed long-range SSCs between 3 H-19 and H-1b, H-7b and H-11a and H-11b, and H-7a and H-11a, but there was no SSC between 3 H-18 and the protons at C-16, which, however, exhibited to the same degree homoallyl SSC with 3H-30.

The assignment of the multiple signals in all the ^{13}C NMR spectra (Table 2) was made on the basis of an identification of the signals of the corresponding protons. The assignment of the signals for C-4, C-10, and C-13 is discussed above. They were additionally confirmed by the XHCORRD spectrum ($^{13}C-^1H$ correlation with observation of long-range SSCCs between ^{13}C and ^1H) for the ester (V). This showed interaction of C-13 with H-15 and with 3 H-18, of C-10 with 3 H-19, and of C-17 with 3 H-18. The spectrum also permitted an unambiguous assignment of the signals for C-8, C-9, and C-14 and gave additional confirmation of the correctness of structures (I) and (V) (SSC of 3 H-19 with C-9, and of 3 H-13 and C-14 was observed).

The assignment of the signals for C-8 and C-9 in the ^{13}C NMR spectra of the ester (I) was made on the basis of the results for the ester (V). It must be mentioned that the CS for C-17 in the ^{13}C NMR spectrum of ester (I) (49.12 ppm) practically coincided with that for C-17 in the spectrum of the known ester (III) (49.1 ppm [4]), rising by ~1.5 ppm on passing to the isomer (V), as in the case of the corresponding isomer of methyl mariesiate C.

The configurations of the asymmetric centers at C-13 and C-7 shown in formula (I) are in harmony not only with biogenetic considerations [3, 4] but also with the coincidence of the CSs for the C-17 atom in the ^{13}C NMR spectra of the esters (I) and (III).

Thus, the detailed analysis of the NMR spectra and also of the CD results have confirmed the correctness of the proposed structure (I) for the ester under investigation. The methyl ester (II) obtained from an extract of the needles was the 24E isomer of (I), since its PMR spectrum differed only by the predicted position for the signals for H-24, 3 H-27, and 2 H-22 (see the Experimental part), and it can be obtained from ester (I) by irradiation with UV light under conditions described in [3].

EXPERIMENTAL

NMR spectra were recorded on a Bruker AM-400 instrument (400.13 MHz for ^1H and 100.614 MHz for ^{13}C). The CSs for signals in the NMR spectra were measured relative to the residual signals of the solvents – 7.24 ppm ($CDCl_3$) and 7.16 ppm (C_6D_6). In the ^{13}C NMR spectra, the signals of these solvents were taken as 76.90 and 28.00 ppm, respectively, δ scale.

Standard pulse sequences were used for recording the 2D NMR spectra: $^1H-^{13}C$ correlation spectrum – free induction decay (FID) 256 × 4K, spectrum 2K × 4K; $^1H-^1H$ correlation spectrum, including the COSYLR and NOESY experiments – FID 256 × 4K, spectrum 2K × 4K. The mixing time in the NOESY experiment was 0.3 sec.

Optical rotations were measured for solutions in $CHCl_3$ on Zeiss and POLAMAT A polarimeters. CD curves of the ester (I) were recorded for a solution in CH_3OH on a Spectropol 1

spectropolarimeter. IR spectra were obtained on a UR-20 instrument for solutions in CCl_4, and UV spectra on a Specord UV-VIS for solutions in ethanol. Mass spectra were recorded on a Finnigan MAT 8200 instrument.

Chromatography was conducted on air-dry silica gel (SG) of the KSK type (0.05-0.15 mm) and on the same support impregnated with $AgNO_3$ (5% by weight). The ratio of substance to sorbent was ~1:30.

For the investigation we used needles gathered in July, 1989, in the Krasnogorskii region of the Altai range. The primary treatment, and the extraction and isolation of the fractions of "strong" and "weak" acids were carried out as described in [11].

Methyl Ester (I). A portion (10.00 g) of the weak acids was chromatographed on silica gel (SG). A mixture of petroleum ether and diethyl ether (DE) (3:7) eluted a fraction (2.80 g) giving an orange spot on TLC. It was methylated by diazomethane, and crystallization from DE yielded 1.60 g of the ester (IV) [11]. Chromatography of the mother liquor on impregnated SG (the eluent CH_2Cl_2 containing 2% of DE) led to the isolation of 0.20 g of the oily ester (I) with $[\alpha]_D^{24}$ +16.3° (c 2.48). Mass spectrum (m/z) 480.3272, M^+ 23%, calculated for $C_{31}H_{44}O_4$ – 480.3239, 432 (14%, $C_{21}H_{32}O_3$), 309 (100%, $C_{22}H_{29}O$), 289 (87%, $C_{18}H_{25}O_3$). IR spectrum, cm^{-1}: 830, 1640, 3080 (C=CH_2), 1630, 1710 (C=C–C=O), 1735 (C=O). UV spectrum, λ_{max}: 234 nm (shoulder) (log ε 3.80). CD spectrum: $\Delta\varepsilon_{235} = -0.33$, $\Delta\varepsilon_{288} = +0.74$ (c = $7.3 \cdot 10^{-3}$ M).

SSCC values (Hz) in the PMR spectra ($CDCl_3$): 1a-1b = 13.0; 1a-2a = 7.5; 1a-2b = 3.5; 1b-2a = 10.5; 1b-2b = 7.5; 2a-2b = 16.0; 7a-6b ≈ 16; 7a-6a ≈ 2; 20-21 = 6.2; 21-22a ≈ 2; 21-22b = 11; 22a-22b = 15.5; 24-28 = 1.5; 30a-30b = 1.5; 30a-15a = 30b = 30b-15a = 30a-15b = 30b-15b ≈1.2.

For a solution in C_6D_6, the SSCCs for 2 H-1, 2 H-2, and H-24 remained unchanged: 20-21 = 6.0 Hz; 22-22a = 1.5 Hz; 20-22b = 11.0 Hz.

Ester (II). A portion (7.00 g) of the strong acids was chromatographed on SG. Petroleum ether–DE (1:1) eluted a fraction (1.40 g) containing (24E)-9β-lanosta-7,24-diene-3,23-dion-26-oic acid [2, 11]. It was methylated with diazomethane and the product was crystallized from a mixture of DE and petroleum ether. Chromatography of the mother liquor (0.18 g) on impregnated SG (with CH_2Cl_2 containing 0.3-0.5% of DE as eluent) led to the isolation of 0.09 g of the oily ester (II) with $[\alpha]_D^{18}$ –45° (c 1.8).

The IR spectrum contained the same bands as the spectrum of the ester (I). UV spectrum, λ_{max}: 238 nm (log ε 3.55). PMR spectrum ($CDCl_3$, ppm): 0.84 (3H, d, J = 6.2 Hz, 3H-21), 0.86 (3H, s, 3H-18), 1.00, 1.04, and 1.08 (each 3H, singlets, 3H-19, 3H-29 and 3H-28, respectively), 2.17 (3H, d, J = 1.5 Hz, 3H-27), 2.83 (1H, br.d, J ≈ 15 Hz, H-22a), 3.78 (3H, s, $COOCH_3$), 4.48 and 4.73 (each 1H, d.t, J = 1.5 and ≈1.2 Hz; C=CH_2), 7.00 (1H, q, J = 1.5 Hz, H-24).

Photoisomerization of the Ester (I). The reaction and the separation of the products were performed by the procedure described in [3] for dimethyl abiesonate, but with the replacement of pentane by petroleum ether. From 0.06 g of the ester (I) was obtained 0.03 g of the initial compound and 0.02 g of the ester (II) with $[\alpha]_D^{18}$ –45° (c 1.77), identified from its PMR spectrum.

Ester (V). A solution of 0.08 g of the ester (I) in 5 ml of $CHCl_3$ was treated with three drops of a solution of a HCl in CH_3OH and the mixture was left at room temperature in the dark for 24 h. After the usual working up and chromatography on SG, 0.06 g of the oily ester (V) was obtained with $[\alpha]_D^{25}$ +80° (c 3.76). For the NMR spectra, see Tables 1 and 2. SSCCs in the PMR spectrum (Hz): 1a-1b = 13.0; 1a-2a = 8.5; 1a-2b = 4.0; 1b-2a = 9.0; 1b-2b = 8.0; 2a-2b = 16.0; 15-30 = 1.6; 16a-16b = 16.0; 24-25 = 1.5.

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PHYTOECDYSTEROIDS OF PLANTS OF THE GENUS Melandrium

II. MELANDRIOSIDE A — A GALACTOSIDE OF VITICOSTERONE E FROM Melandrium turkestanicum

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UDC 547.926

The isolation and determination of the structure of the new phytoecdysteroid melandroside A are described; it is viticosterone E 22-O-α-D-galactopyranoside.

We have shown that the epigeal organs of the plants Melandrium turkestanicum (Rgl) Vved (family Caryophyllaceae) are a source of various ecdysteroids, including sileneosides A and D [1].

Rechromatography on a column of silica gel of the mother liquors obtained in the isolation of these ecdysteroids led to the isolation of a new phytoecdysteroid (I), with the composition $C_{35}H_{56}O_{13}$, which we have called melandrioside A.

The IR spectrum of compound (I) contained, in addition to the absorption due to hydroxy groups (3400-3450 cm^{-1}) and to an α,β-unsaturated keto grouping (1670 cm^{-1}), absorption bands at 1720 and 1270 cm^{-1} showing the presence of an ester group. The presence of such a group was confirmed by a three-proton singlet in the PMR spectrum at 1.84 ppm.

The results of an analysis by the GLC method of the products of the methanolysis of the ecdysteroid (I) showed that this contained a D-galactose residue and was a monoside.

The enzymatic hydrolysis of melandrioside A by the total enzymes isolated from sweet almond led to the formation of a product (II) which was identified as viticosterone E [2, 3].

Attention is attracted by the small upfield shift of the H-22 signal in compound (I) as compared with that for viticosterone E (II) in the PMR spectra of these substances (Table 1). A similar shift has been observed for sileneoside A (III) in comparison with ecdysterone (V) (see Table 1). If it is also borne in mind that in the mass spectrum of (I) there is the characteristic peak of an ion with m/z 363, it may be assumed that the D-galactose residue in melandrioside A is located at C-22 (see scheme on top of following page).

The spin–spin coupling constant (^3J = 3.2 Hz) and the chemical shift (δ 5.46 ppm) of the signal of the anomeric proton showed the α-configuration of the glycosidic center [4].

To confirm the structure of glycoside (I), we saponified the heptaacetate of sileneoside A (IV), which has been described previously [5], with 0.5 $KHCO_3$ in methanol. As was to be expected, under these conditions the acetyl group at C-25 remained unaffected, and the reaction product coincided in its physicochemical constants and spectral characteristics with melandrioside A (I).

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