LITERATURE CITED

1. A. P. Nechaev and Zh. Ya. Sandler, Grain Lipids [in Russian], Kolos, Moscow (1975), p. 160.
2. J. M. Arnold, A. Piovarci, F. L. Bauman, and C. G. Poneleit, Crop. Sci., 14, 598 (1974).
3. F. L. Bauman, Proceedings of the 25th Corn and Sorghum Research Conference, Vol. 2 (1971), p. 139.
4. C. G. Poneleit, Crop. Sci., 12, 839 (1972).
5. M. A. Kates, Techniques of Lipidology, American Elsevier, New York (1972) [Russian translation, Mir, Moscow (1975), p. 322].
6. S. D. Gusakova, S. G. Yunusova, T. V. Chernenko, I. P. Nazarova and A. I. Gushenkova, Khim. Prir. Soedin., 677 (1986).
7. R. K. Salyaev, S. P. Makarenko, and V. Ya. Kuzevanov, Izv. Sib. Otd, Akad. Nauk SSR, Ser. Biol. Nauki, 76 (1986).
8. L. J. Bellamy, Infrared Spectra of Complex Molecules, 2nd Edn., Wiley, New York (1958) [Russian translation, IL, Moscow (1963), p. 590].
9. J. Fischmeister, Prog. Chem. Fats Other Lipids, 14, 91 (1979).
10. G. E. Komarova. T. N. Palladina, T. N. Gynkul, G. F. Nasyrova, and A. F. Palii, Rast. Res., 31, 1170 (1984).
11. M. B. Bazzoz, Naturwissenschaften, 68, 94 (1984).
12. H. L. Galliher, D. E. Alexander, and E. J. Weber. Crop. Sci., 25, 574 (1985).
13. G. F. Nasyrova and T. A. Pallodoma, Rast. Res., 31. 351 (1984).
14. G. Khegen, K. Sinyak, R. Rigage, and G. Fri, Izv. Akad, Nauk. Ser. Biol. Nauk, 31, 441 (1971).

TRITERPENOIDS OF Abies SPECIES.

V. STRUCTURE AND SPECTRAL PROPERTIES OF THE MAIN 9βH-LANOSTANE ACIDS OF SIBERIAN FIR NEEDLES

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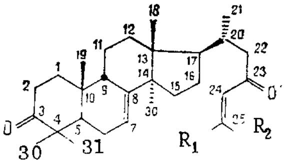
UDC 547.595.9:547.914.4

A four-stage conversion into a ketolactone has confirmed the structure proposed previously for two 3-ketolanostane acids isolated from an extract of Siberian fir needles. Features of the mass, PMR, and CD spectra of the methyl esters of these acids and of triterpenoids related to them are explained and discussed.

In [1], two new stereoisomeric acids isolated from the needles of the Siberian fir (Abies sibirica Ledeb), in which they are the main representatives of the 9βH-lanostanoids [2], were described. On the basis of spectral characteristics and biogenetic considerations, the probable structures expressed by formulas (I) and (II) were proposed for their methyl esters. A proof of the correctness of the proposed structures would be a basis for the futher chemical modification of the compounds under investigation and their conversion into other, still little studied, representatives of this peculiar group of triterpenoids found in Abies species [3, 4] and in marine organisms [5].



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

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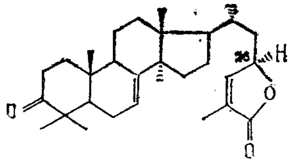
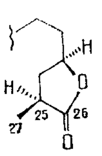
The methyl esters (I) and (II) are readily interconverted under ultraviolet light irradiation [2], and therefore the problem of establishing their structures amounts in fact to the proof of the structure of one of them. It was solved by a chemical correlation of the ester (II) with the known lactone (III) isolated by Kutney [4] from the bark of Abies amabilis (Dougl.) Forbes.


III

This correlation was made by the following sequences of reactions with the ester (II), without purification of the intermediate products: reduction of the two keto groups (sodium tetrahydroborate in ethanol), saponification of the methoxycarbonyl group (sodium hydroxide in ethanol), separation of the neutral by-products (extraction with diethyl ether from the alkaline aqueous reaction mixture), lactonization (acidification with a solution of hydrochloric acid), and, finally, conversion of the 3-hydroxy group into a keto group (pyridinium chlorochromate in methylene chloride). According to TLC, the total products obtained contained two main components. After chromatography on silica gel, a mixture of them was obtained and also one of them, the more polar, in the pure from. These substances, according to the scheme of transformation of the ester (II), should be the lacton (III) and its C-23 epimer. In actual fact, the pure substance proved to be the desired lactone (III) and the second, which could not be isolated, its C-23 epimer. This was established by a comparison of the PMR spectra of the mixture obtained and of the lactone (III) with the spectra of cycloartane α-butenolides close in structure — cyclograndisolide and 23-epicyclograndisolide, having similar side chains in their molecules [6]. The signal of the H-24 proton in the spectrum of the lactone synthesized (III) was present in a higher field (6.98 ppm, apparent triplet, J = 1.7 hz: for cyclograndisolide the same signal is at 6.98 ppm [6]) than for the second substance, its 23-epimer (7.06 ppm; for 23-epicyclograndisolide — 7.02 ppm [6]). The CH_3-26 signal for lactone (III) appeared in the form of a triplet with J = 1.7 Hz at 1.90 ppm, while the H-23 proton gave a multiplet at 4.96 ppm having the form of a doublet with greatly broadened components (J ~ 10 Hz). The retention of the C-7 double bond in the molecule of the lactone synthesized (III) was confirmed by the low-field position of the H-7 signal (5.62 ppm), which is characteristic for 9βH-lanost-7-enoids [4, 5].

The ORD curve for lactone (III) practically coincided with that given for the same compound in Kutney's paper [4]. The 24,25-dihydro derivative of lactone (III), obtained by catalytic hydrogenation, gave an ORD curve which likewise coincided with that given in the same paper [4]. It must be mentioned that on the ORD curves in the cited paper 10^{-4} is erroneously shown on the axis of ordinates, and this should be read as 10^{-3}. This was established by a comparison of the optical rotations for 5α-lanost-9(11)-en-3-one, the ORD curve for which is also given in a figure [4] with accurate quantitative ORD results for the same ketone given in Uyeo's paper [3].

Thus, the correctness of the structure and stereochemistry of the ester (II) proposed previously and, accordingly, those of its isomer (I) have been confirmed. It is interesting to note that the hydrogenation of the butenolide ring of the molecule of lactone (III) took place stereospecifically, and the structure of its dihydro derivative ((20R, 23R, 25S)-3-oxo-15α, 9β-lanost-7-en-26,23-olide) is expressed by formula (IV). The latter conclusion followed from a comparison of the PMR spectra of this dihydro derivative and A-secolanostane lactones of close structure — abiesolidic and 25-epiabiesolidic acids (the structures of the side chains of their molecules being expressed by formulas (V) and (IV), respectively) [7]. The signal of the H-25 proton in the PMR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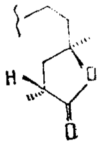
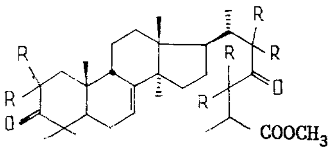

V

spectrum of 24,25-dihydro-(III) practically coincided in form and position with that for the unnatural 25-epiabiesolidic acid, which indicates their identical stereochemistries at C-25. This fact is extremely interesting and shows that the formation of the lactone ring in the biosynthesis of abiesolidic acid — a component of the oleoresin of the species of fir investigated [7] — takes place differently from the hydrogenation of lactone (III) in vitro, the stereochemistry of which is determined by the asymmetric center at C-23.

The determination of the structure and stereochemistry of the esters (I) and (II) permits us to analyze in more detail their mass and PMR spectra, which were given partially in communication [1] and also to dwell specially on the optical properties of these compounds.

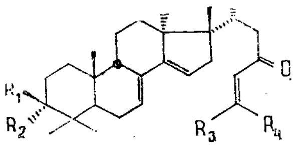
A feature of the mass spectra of the esters (I) and (II), which practically coincide with one another [1], is the presence in them, of only one strong peak, of ions having m/z 325 (100% in both spectra). The same ion is the main one in the mass spectrum of the free acid corresponding to the ester (I) [1] and in the spectrum of the 24,25-dihydro derivative (VI) obtained from the ester (II) by catalytic hydrogenation.



VI. R = H
VII. R = D

The ion with m/z 325 has the same elementary composition for the ester (I) and for the corresponding acid — $C_{23}H_{33}O$ — and corresponds to the cleavage of the side chain at C(20)—C(22) and the loss of H (m/z 340, 8% in the spectra of compounds (I) and (II)) and the subsequent elimination of the CH_3 group from the cyclic part of the molecule. In the mass spectrum of the hexadeutero derivative (VII), obtained by the deuteration of the diketoester (VI), the main ion (100%) is heavier by two mass units (m/z 327), which is in harmony with this interpretation. The ion corresponding to the splitting out of the side chain of the molecule in the mass spectra of esters (I) and (II) (m/z 313) has a low intensity (11%). Of the other ions the peaks of which are observed in the spectrum under discussion we may mention M^+ (482; 15%), $(M-15)^+$ (467; 20%), $(C(O)CH = C(CH_3)COOCH_3)^+$ (127; 22%), and $(CH_3CHCH_2C(O)CH = C(CH_3)COOCH_3)^+$ (169; 21%). The other ions give peaks of even lower intensity. It may be assumed that the ion with m/z 325 will have diagnostic value in the chromato-mass spectrometric analysis of 3,23-diketo derivatives of lanostenes.

On considering the PMR spectra, three fragments can be seen in the molecules of the esters (I) and (II) which are responsible for the appearance of characteristic signals in the spectra: C(7)—C(8), the side chain, and the C(2)-methylene group. The signal of the H-7 proton, as already observed by Kutney [4] for abieslactone, has a characteristic downfield shift, and in the spectra of compound (I) and (II) — and also in those of (III), 24,25-dihydro- (III), (VI), and (VII) — this proton gives at 5.62 ppm a doublet of triplets, the same in all cases, with J = 7.0, 3.0, and 3.0 Hz. Judging from the large value of $J_{7,9}$ (3 Hz), the C(9)—H bond is directed perpendicularly to the plane of the Δ^7-double bond [8].



	VIII	IX	X	XI
R_1 R_2	=O	=O	H OAc	H OAc
R_3	CH_3	$COOCH_3$	CH_3	$COOCH_3$
R_4	$COOCH_3$	CH_3	$COOCH_3$	CH_3

The signals of the 24-H and CH_3—C(25) protons in the PMR spectra of esters (I) and (II) have been discussed previously [1]. In addition to them, the spectra exhibit the signals of two protons present at C-22 (see Table 1). These signals are fairly characteristic in form, and one of them appears in the PMR spectra of the mariesianoids (VIII)—(XI), which have a

TABLE 1. Chemical Shifts (ppm) and Spin-Spin-Coupling Constaants (Hz, shown in parentheses) for the Signals in the PMR Spectra of Compounds (I)—(III), (IX—XI), and (VII)

Compound	H-22a*	H-22b	H-2a	H-2b	H-7
I	2,27 dd (16,0; 10,0)	2,61 dd (16,0; 2,0)	**	**	***
II	2,19 dd (16,0; 10,0)	2,55 dd (16,0; 2,0)	**	**	***
III	—	—	**	**	***
VIII	—	2,54 d (14,0)	—	2,72 ddd (14,0; 14,0; 5,0)	5,59 t (~3,3)
IX	—	2,50 d (15,0)	—	2,72 ddd (14,0; 14,0; 5,0)	5,58 t (~3,3)
X	—	5,57 d (14,0)	—	—	5,55 dm (~4,0)
XI	—	2,53 d (15,0)	—	—	5,55 dm (~4,0)

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*The symbol a denotes the signal the proton of which is located in a higher field than the signal of the second proton (b), geminal to the first.

**For (I)-(III), the two protons at C-2 give a single signal at 2.47 ppm (2 H, dd, J = 8.0 and 6.5 Hz).

***For (I)-(III) the signal is present at 5.62 ppm (dt, J = 7.0, 3.0, and 3.0 Hz).

similar side chain, described in [2]. Their assignment to (I) and (II) is confirmed by the absence of such signals in the spectra of the lactone (III) and of 24,25-dihydro- (III), and for the mariesianoids by the absence of the signals under discussion in the PMR spectrum in a synthesized [2] sample of methyl mariesiate A, in the molecule of which there is a hydroxy group at C-23.

The third fragment of the molecules of (I) and of (II) — ring A — is represented in the PMR spectra in the form of the signal of the two protons of the C(2)-methylene group, similar in form and position not only for (I) and (II) but also for lactone (III), its 24,25-dihydroderivative, and the dihydro ester (VI). It has the form of a doublet of doublets with a chemical shift of 2.47 ppm, J = 8.0 and 6.5 Hz. Its unambiguous assignment to 2-H (2) is determined by the absence of this signal in the PMR spectrum of the hexadeutero derivative (VII).

The agreement of the chemical shifts for the protons under consideration does not as yet have analogies in the spectra of other known 4,4-dimethyl-3-oxasteroids and indicates the peculiar nature of the conformation of ring A in the 3-oxo-9βH-lanost-7-enes. It must be mentioned that the question of the conformation of ring A in the molecules of 4,4-dimethyl-3-oxosteroids has now attracted the attention of research workers for about 30 years [9, 10]. It has been solved unambiguously only for a crystalline compound [11], but, for solutions, different physicochemical and spectral methods lead to different conclusions [12]. The same can be said about quantum-chemical and molecular-mechanical calculations [12]. The optical methods (CD, ORD) actively being used for answering conformational questions are very sensitive to a change in ring A. It has been found that on passing from the 3-oxosteroids to the 4,4-dimethyl-3-oxosteroids an inversion of the sign of the Cotton effect for the n→π* transition in the C=O group from positive to negative is observed. This "4,4-dimethyl effect" takes place, for example, on passing from cholestan-3-one to 4,4-dimethylcholestan-3-one and to 9αH-lanost-7-en-3-one [13].

For the ketones (I) and (II) under consideration, the CD curves were discussed briefly in [1], and in the present work we have considered them in more detail for the 250-500 nm region where ultraviolet absorption is minimal and a fairly accurate quantitative estimation of the observed maxima is possible. On these curves (see Fig. 1), there are two Cotton effects for (I) and for (II), the shorter-wave one of which relates to the n→π* transition in the C(3)=O group and the longer-wave one to the analogous transition in the keto group of the side chain. This interpretation is based on the positions of these effects and the absence of a long-wave Cotton effect on the CD curve for lacton (III). The observed signs of the effects are not connected with asymmetric solvation, since they do not change on

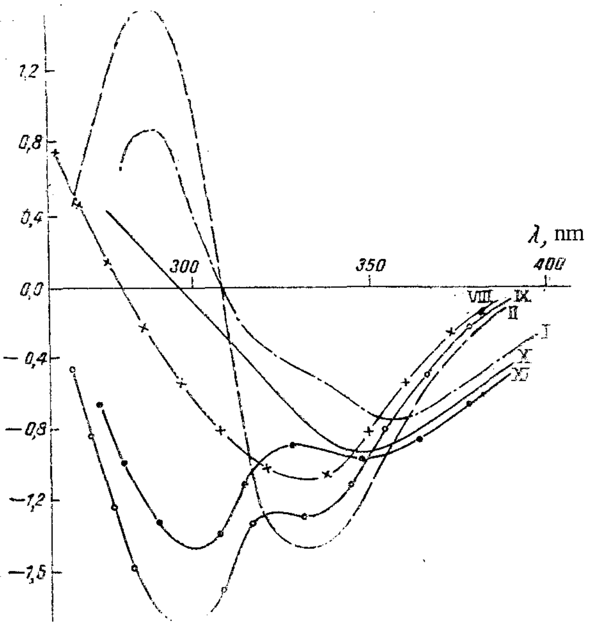

Fig. 1. CD curves for compounds (I), (II), (VIII), (IX), (X), and (XI). The CD curves are given for solutions in methanol using the following concentrations (M): 5.4×10^{-3} (I); 4.17×10^{-3} (II); 8.7×10^{-3} (VIII); 7.3×10^{-3} (IX); 4.4×10^{-3} (X); 9.55×10^{-3} (XI). The values of the extrema for the dichroic absorption of (I) are: $\Delta\varepsilon_{288} + 0.88$; $\Delta\varepsilon_{357} - 0.74$; for (II) $\Delta\varepsilon_{288} + 1.59$; $\Delta\varepsilon_{334} - 1.48$; for (III) ($c = 1.8 \times 10^{-3}$ M, methanol). $\Delta\varepsilon_{290} + 2.45$ ($n\to\pi^*$ transition in C(3)=O); $\Delta\varepsilon_{250} + 0.48$ (shoulder). On the CD curve for ester (II) in chloroform solution ($c = 2.5 \times 10^{-3}$ M) there is a maximum at 290 nm ($\Delta\varepsilon + 1.87$) and a minimum at 341 nm ($\Delta\varepsilon - 0.84$).

passing from methanol and dioxane to chloroform and are due only to the structure (conformation) of the cyclic moiety of each of molecules (I)-(III).

The positive sign of the Cotton effect for (I)-(III) indicates that the "4,4-dimethyl effect" does not appear for these compounds. If we compare the ketones under consideration with 9αH-lanost-7-en-3-one [14], this could be explained by a change in the conformation of ring A through an inversion of the configuration of the 9-H hydrogen atom from α to β. However, it was unexpectedly found that the mariesianic 3-ketones (VIII) and (IX), each having a 9βH atom in its molecule, give negative Cotton effects (see Fig. 1). The assignment of this effect to the $n\to\pi^*$ transition in the C(3)=O group is completely unambigous in view of its absence from the CD curves of the 3-acetoxy derivatives (X) and (XI) where only a long-wave Cotton effect having the same origin as the analogous effects for (I) and (II) is observed. The Cotton effect corresponding to the $\pi\to\pi^*$ transition in the dienic system is located outside the region under consideration. For mariesi acid A it is located at 227 nm and has a positive sign, which corresponds to the left-handed helicity of the heteroannular dienic system [15, 16].

Thus, what is decisive for the appearance of the anomalous optical properties of ketones (I)—(III) is the nature of the substitutions of rings C and D, which is different for these compounds and the mariesianoids. The conformations of rings B in the molecules of the two types of triterpenes under consideration are also different, as is shown by the form of signal for 7-H in their PMR spectra (see Table 1). The available facts permit the assumption that the conformation of ring A in the molecule of each of the compounds (I)—(III) is close to the flattened chair conformation (the atoms from C-1 to C-4 are approximately in one plane [17]). In this case, according to the octant diagram for ketones [18], the contributions of the two C(4)-methyl groups will compensate one another and the the two H-2 atoms will be present under the same anisotropic influence of the C=O group (which explains the coincidence of their chemical shifts in the PMR spectra), while the observed positive Cotton effect for the C(3)=O group will be due to the atoms of ring B that are present in the rear upper left octant.

The same negative sign of the longest-wave Cotton effect observed for compounds (I), (II), and (VIII)—(XI) and relating to the n→π* transition in the C(23)=O group shows a definite influence of the asymmetric center at C-20 which has the same (R) configuration in each of these molecules.

EXPERIMENTAL

PMR spectra were recorded on a Bruker WP-200 SY instrument (200.13 Hz) for solutions in deuterochloroform (δ scale: internal standard chloroform, the signal of which was taken as 7.24 ppm; arbitrary descriptions of the signals: s — singlet; d — doublet; t — triplet; q — quartet; m — multiplet; the accuracy of the measurement of the spin-spin-coupling constants was ± 0.2 Hz). High-resolution mass spectra were obtained on a Finnigan MS-9200 instrument (direct introduction, 120°C). IR spectra were recorded on a UR-20 spectrophotometer for solutions in chloroform, and CD and ORD curves on a Spectropol I spectropolarimeter.

For chromatography we used type L silica gel (Czechoslovakia) with a grain size of 0.100—0.160 mm at a ratio of substance and sorbent of ~1:20, the eluent being petroleum ether (PE) with increasing (from 20 to 60%) amounts of diethyl ether (DE).

Synthesis of Lactone (III). With stirring, 0.50 g of sodium tetrahydroborate was added to a solution of 0.66 g of the ester (II) in a mixture of 20 ml of dioxane and 20 ml of ethanol, and the resulting mixture was left at room temperature for 2 h. After this, 3 ml of 15% ethanolic sodium hydroxide was added and the reaction mixture was heated in the water bath to 90°C and was then left to cool to room temperature over 0.5 h. The mixture was diluted with water (50 ml) and was extracted with DE (2 × 50 ml). The aqueous layer was separated off and it was acidified with hydrochloric acid to pH 2 and was extracted with DE (3 × 100 ml). The ethereal extract was washed with saturated aqueous sodium chloride and dried with sodium sulfate, and the solvent was evaporated from it.

The residue (0.52 g) was dissolved in 50 ml of methylene chloride, and 0.30 g of anhydrous sodium acetate and 0.75 g of pyridinium chlorochromate were added to the solution. After stirring at room temperature for 1 h and the usual working up treatment, 0.47 g of a product was isolated the chromatography of which on silica gel gave, successively, 0.11 g of a mixture of lactone (III) and its C(23)-epimer (~1: 1; PMR spectrum: 6.98 and 7.06 ppm, apparent triplets with J = 1.7 Hz, H-23 for (III) and for 23-epi-(III), respectively); and 0.04 g of lactone (III) with mp 224-228°C (from methanol), $[\alpha]_D^{20}$ + 66.7° (c 0.048; methanol). IR spectrum, cm^{-1} 1710 (C(3)=O) and 1765 (α-butenolide). The ORD curve (in dioxane) corresponded to that given in the literature [4]. PMR spectrum ppm: 0.78, 0.97, 0.99, 1.07, 1.08 (3 H each, singlets, angular methyl groups); 0.98 (3 H, d, J = 6.0 Hz, 21-CH_3); 1.90 (3 H, t, J = 1.7 Hz, 27-CH_3); 2.17 (1 H, m, unidentified proton of the cyclic moiety of the molecule); 4.96 (1 H, dm, J ~ 10 Hz, H-23); and 6.98 (1 H, apparent triplet, J = 1.7 Hz, H-24). The signals of the H-7 and the two H-2 protons are given in Table 1.

Hydrogenation of Lactone (III). A solution of 0.028 g of the lactone in 15 ml of a mixture of ethyl acetate and dioxane (4:1) was treated with 20 mg of $Pd/CaCO_3$ and was stirred in an atmosphere of hydrogen for 2 h. The reaction mixture was filtered through silica gel, the solvent was driven off, and the product was chromatographed. This gave 0.017 g of the 24,25-dihydro derivative of lactone (III) with mp 182—185°C (from a mixture of PE and DE), $[\alpha]_D^{22}$ + 54.2° (c 0.29; dioxane). IR spectrum (CCl_4), cm^{-1}; 1720 (C(3)=O), 1790 (saturated γ-lactone ring). The ORD curve (in dioxane) corresponded to that given in the literature [4]. PMR spectrum, ppm; 4.43 (1 H, m, H-23); 2.66 (1H, m, H-25); 1.25 (3 H, d, J = 7.0 Hz, 27-CH_3). The remaining signals in the 0—3 ppm interval were the same as in the spectrum of lactone (III). The signals of the H-7 and the two H-2 protons are given in Table 1.

Hydrogenation of the Ester (II). By the procedure described above, 0.23 g of the ester (II) yielded 0.09 g of the ester (6), with mp 131—134°C (from a mixture of PE and DE (4:1)). IR spectrum, cm^{-1}; 1715, 1735 (C=O). Mass spectrum (m/z, %): M^+ 484 (17): $(M - 15)^+$ 469 (38): 325 (100). PMR spectrum, ppm: 0.86 (3H, d, J = 6.0 Hz, 21-CH_3), 1.16 (3H, d, J = 7.0 Hz, 27-CH_3), 2.16 (1H, dd, J = 15.4, 10.0 Hz, H-22a), 2.17 (1H, m), 2.40—2.48 (2H, m), 2.75—3.00 (2H, m), 3.65. (3H, s, $COOCH_3$). The signals of the other methyl groups were as in the spectrum of the ester (II) [1]. The signals of the H-7 and two H-2 protons are given in Table 1.

The deuteration of the ester (VI) was performed by the method described by Shapiro et al. [19] for 5α-androstan-3-one; the reaction mixture was acidified with hydrochloric acid to pH 2 and was extracted with DE. An ethereal solution of the product was treated with an excess of a solution of diazomethane in DE and, after this the DE and excess of diazomethane were eliminated rapidly in a rotary evaporator. The product was crystallized from DE. From 0.050 g of the ester (VI) was obtained 0.035 g of substance (VII); IR spectrum, cm^{-1}: 1715, 1745 (C=O). Mass spectrum (m/z, %); 490 (15) M^+; 475 (34) $(M - 15)^+$; 327 (100). PMR spectrum: in the 2.15–3.50 ppm region only two signals out of all those present in the spectrum of the ester (VI) were observed — at 2.17 ppm (1 H, m, unidentified proton of the cyclic moiety of the molecule), and 2.91 ppm (1 H, q, J = 7.0 Hz, 25-H). The assignment of the latter was confirmed by double resonance with the suppreseion of the 27-CH_3 signal (1.16 ppm, 3 H, d, J = 7.0 Hz).

SUMMARY

1. The structures of two new types of terpene acids from the needles of the Siberian fir having 9βH-lanost-7-ene carbon skeletons have been established.

2. 9βH-Lanost-7-en-3-ones do not exhibit the "4,4-dimethyl effect" and give a positive Cotton effect for the n→π* transition in the C(3)-carbonyl group.

LITERATURE CITED

1. V. I. Roshin, V. A. Raldugin, R. A. Baranova, and V. A. Pentegova, Khim. Prir. Soedin., 648 (1986).
2. V. A. Raldugin, S. A. Shevtsov, N. I. Yaroshenko, Yu. V. Gatilov, I. Yu. Bagryanskaya. and L. I. Demenkova, Khim, Prir. Soedin., 824 (1987).
3. S. Uyeo, I. Okada, S. Matsunaga, and J. W. Rowe, Tetrahedron, 24, 2859 (1968).
4. J. P. Kutney, N. D. Westcott, F. N. Allen, N. W. Issacs, O. Kennard, and W. D. S. Motherwell, Tetrahedron Lett., 3463 (1971).
5. I. Kitagawa. M. Kobayashi, T. Inamoto, T. Yasuzawa, Y. Kyogoku, and M. Kito, Chem. Pharm. Bull., 29, 1189 (1981).
6. J. P. Kutney, D. S. Grierson, G. D. Knowles, N. D. Westcott, and I. H. Rogers, Tetrahedron, 29, 13 (1973).
7. V. A. Raldugin, Yu. V. Gatilov, T. V. Rybalova, and Ya. V. Rashkes, Khim. Prir. Soedin., 688 (1986).
8. D. J. Collins, J. J. Hobbs, and S. Sternhell, Austr. J. Chem., 16, 1030 (1963).
9. C. Djerassi, J. Osoeclo, and W. Closson, J. Am. Chem. Soc., 81, 4587 (1959).
10. D. Loganathan, G. K. Trivedi, and K. V. R. Chari, J. Org. Chem., 51, 3366 (1986).
11. G. Ferguson, E. W. Macaulay, J. M. Midgley. J. M. Robertson, and W. B. Whalley, J. Chem. Soc., D, 954 (1970).
12. D. A. Dougherty, K. Mislow, J. W. Huffmann, and J. Jacobus, J. Org. Chem., 40, 1585 (1979).
13. C. Djerassi, O. Halpern, V. Halpern, and B. Rinker, J. Am. Chem. Soc., 80, 4001 (1958).
14. J. S. E. Holker and W. B. Whalley, Proc. Chem. Soc., London, 464 (1961).
15. S. Hasegawa, T. Miura, T. Hirose, and Y. Itaka, Chem. Lett., 1589 (1985).
16. A. W. Burgstahler and R. S. Barkhurst, J. Am. Chem. Soc., 92, 7601 (1970).
17. N. L. Allinger and M. A. Da Rooge, J. Am. Chem, Soc., 84, 4561 (1962).
18. W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, J. Am. Chem. Soc., 83, 4013 (1961).
19. R. H. Shapiro, D. H. Williams, H. Budzikiewicz, and C. Djerassi, J. Am. Chem. Soc., 86, 2837 (1964).