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TRITERPENOIDS FROM SPECIES OF *Abies* HILL.

II. ABIESOLIDIC ACID — A NEW 3,4-SECOLANOSTANOID FROM THE OLEORESIN

OF *Abies sibirica*

V. A. Raldugin, Yu. V. Gatilov,   UDC 547.914.2+543.51+539.26
T. V. Rybalova, and Ya. V. Rashkes

The oleoresin of the Siberian fir has yielded a new 3,4-secolanostanoid for which the structure of (20R,23S,25R)-3,4-seco-9β-lanosta-4(28),7-dien-26,23-olid-3-oic acid has been established by x-ray structural analysis. The pathways of the mass-spectrometric fragmentation of this acid and its esters have been investigated.

The oleoresin of the Siberian fir differs from the oleoresin of pines, spruces, and larches by a large amount (up to 30%) of resin acids insoluble in petroleum ether [1]. In a preliminary communication [2] we showed that these compounds consisted of triterpene acids, two of which were isolated in the form of methyl esters and were characterized by their constants and some spectral characteristics. One of them, abiesonic acid, was described in the first communication [3]. The structure and stereochemistry of the second new acid — abiesolidic — are considered in the present paper.

Abiesolidic acid was isolated in the form of its methyl ester by the chromatography of the methylated fraction of polar "weak" acids of the oleoresin of the Siberian fir [2]. Its ester (methyl abiesolidate, empirical formula $C_{31}H_{48}O_4$) was the only well-crystallizing compound among the components of this mixture. The UV spectrum of methyl abiesolidate had no absorption bands in the 210-400 nm region, while the IR spectrum (in KBr) showed the bands of a γ-lactone ring (1770 cm^{-1}) and of methoxycarbonyl (1745 and 1190 cm^{-1}) and exomethylene (915, 1650, and 3080 cm^{-1}) groups. The last-mentioned group is present as part of an isopropenyl group, as was established on the basis of PMR using double resonance. The multiplet signals of its protons (at 4.79 and 4.85 ppm, 1 H each) were converted into doublets forming an AB system with J_{AB} = 2 Hz when the signal of a tertiary methyl group located at 1.77 ppm was suppressed. The other methyl groups of the methyl abiesolidate molecule gave singlets in the PMR spectrum at 0.73, 0.81, 1.00, and 3.64 ppm (COOCH$_3$) and doublets at 0.93 (3 H, J = 6.3 Hz) and 1.26 ppm (3 H, J = 7.3 Hz).

In addition to the exomethylene bond, the molecule of the compound under investigation contained one trisubstituted double bond, as was shown by the signal at 5.29 ppm in the PMR spectrum (1 H, quartet with poorly resolved natural components, J = 3 Hz). Of the six signals observed of sp^2-hybridized carbon atoms in the ^{13}C NMR spectrum, four (triplet at 111.83, doublet at 117.81, and singlets at 146.22 and 149.53 ppm) relate to C=CH— and C=CH$_2$ fragments, and the other two (singlets at 174.87 and 189.93 ppm) to the carbon atoms of the methoxycarbonyl and the lactone fragments, respectively. The latter is expressed by formula A (where R is the residue of the remainder of the methyl abiesolidate molecule).
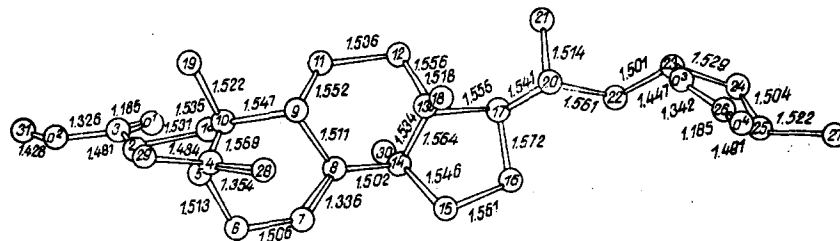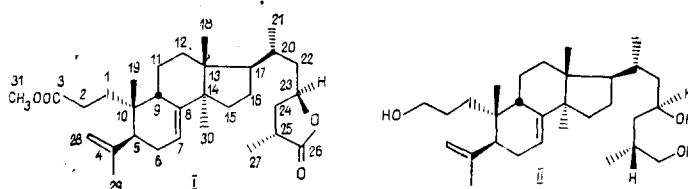
Molecular structure of methyl abiesolidate (I). The probable
errors in the lengths of the bonds are 0.007–0.009 Å
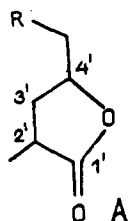
It is based on the following features of the PMR spectrum. The signal of the H_4' proton appearing at 4.62 ppm has the form of a complex multiplet containing not less than 10 components. Since it is not linked by spin–spin coupling with any of the secondary methyl groups present in the molecule (double-resonance experiments were performed), its neighbors can only be two methylene groups. The H_2' proton gives a sextet (J = 7.3 Hz) at 2.68 ppm which is converted into a triplet (J = 7.3 Hz) on double resonance with the suppression of the signal of the C_2'-methyl group (doublet at 1.26 ppm, J = 7.3 Hz).

The results obtained concerning the fragments of the methyl abiesolidate molecule permitted the assumption that it is based on a 3,4-secolanostane or analogous (with a different stereochemistry) carbon skeleton. The structure of methyl abiesolidate was established unambiguously by x-ray structural analysis and is expressed by formula I. The structure of the molecule is also shown in Fig. 1, and the coordinates of the nonhydrogen atoms are given in Table 1. The bond lengths and valence angles in it are the usual ones, with the exception of the C_5–C_{10} and C_{16}–C_{17} bonds, which are lengthened to 1.569(9) and 1.572(7) Å. The conformation of the 6-membered ring with the double bond is close to the envelope type in which the C_{10} atom departs from the plane of the other atoms. The second 6-membered ring has a distorted twist form. Its unusual conformation is apparently due to the stereochemistry of the ring linkage, since on Dreiding models it is impossible to transform this ring into the usual chair conformation. The torsional angles characterizing the conformations of the rings are given in Table 2.

Formula I shows the relative configuration of the molecule but it also expresses the absolute configuration, since, in the first place, it corresponds to the absolute configuration of natural triterpenoids (presence of a 10β-methyl group in an unrearranged carbon skeleton). In the second place, the triol (II) obtained by reducing methyl abiesolidate with lithium tetrahydroaluminate, like methyl abiesolidate itself, has a negative circular dichroism curve in the 220–205 nm region analogous in form to that for 24,25-dihydroabieslactone (III) [4]. The later is evidence in favor of the same mutual orientation of the C_7 double bond and the H_9 atom in their molecules [4, 5].

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

Atom	x	y	z	Atom	x	y	z
C₁	2366(9)	0623(7)	—3061(3)	C₂	2042(11)	0386(8)	—3895(4)
C₃	2313(8)	—0945(9)	—4136(4)	C₄	1293(8)	4269(8)	—3056(4)
C₅	1020(7)	2842(7)	—3100(3)	C₆	—0621(8)	2439(8)	—2699(3)
C₇	—0348(7)	2059(8)	—1896(3)	C₈	1225(6)	1889(7)	—1573(3)
C₉	2884(6)	2153(7)	—1997(3)	C₁₀	2647(7)	2024(7)	—2852(3)
C₁₁	4474(6)	1414(8)	—1666(3)	C₁₂	4719(7)	1511(8)	—0815(3)
C₁₃	3050(6)	1930(7)	—0391(3)	C₁₄	1409(7)	1354(7)	—0799(3)
C₁₅	—0066(7)	1668(8)	—024G(3)	C₁₆	0809(7)	1475(9)	0532(3)
C₁₇	2843(7)	1396(7)	0413(3)	C₁₈	2930(8)	3370(7)	—0368(3)
C₁₉	4279(8)	2535(9)	—3229(3)	C₂₀	3894(7)	2027(7)	1054(3)
C₂₁	5849(8)	1920(8)	0935(3)	C₂₂	3445(9)	1355(8)	1804(3)
C₂₃	4301(9)	1916(7)	2487(3)	C₂₄	3590(9)	1385(9)	3218(3)
C₂₅	2399(9)	2415(9)	3496(4)	C₂₆	2993(10)	3596(9)	3115(4)
C₂₇	2279(10)	2586(11)	4337(4)	C₂₈	1129(9)	4954(9)	—2421(4)
C₂₉	1678(11)	4927(9)	—3768(4)	C₃₀	1516(9)	—0097(8)	—0873(3)
C₃₁	2399(10)	—2290(10)	—5189(4)	O₁	2562(9)	—1833(7)	—3742(3)
O₂	2177(7)	—1056(7)	—4871(3)	O₃	3966(7)	3268(0)	2528(2)
O₄	2678(8)	4669(7)	3263(3)				

TABLE 2. Intracyclic Torsion Angles of the Methyl Abiesolidate (I) Molecule

Angle	Degrees	Angle	Degrees
C₇C₆C₅C₁₀	37,2	C₁₄C₈C₉C₁₁	19,1
C₆C₅C₁₀C₉	—57,4	C₈C₉C₁₁C₁₂	—48,5
C₅C₁₀C₉C₈	51,3	C₉C₁₁C₁₂C₁₃	19,6
C₁₀C₉C₈C₇	—25,8	C₁₁C₁₂C₁₃C₁₄	35,0
C₉C₈C₇C₆	3,8	C₁₂C₁₃C₁₄C₈	—64,0
C₈C₇C₆C₅	—10,0	C₁₃C₁₄C₈C₉	36,1
C₁₆C₁₅C₁₄C₁₃	—37,8	C₂₆O₃C₂₃C₂₄	—7,6
C₁₅C₁₄C₁₃C₁₇	48,0	O₃C₂₃C₂₄C₂₅	17,8
C₁₄C₁₃C₁₇C₁₆	—38,7	C₂₃C₂₄C₂₅C₂₆	—21,2
C₁₃C₁₇C₁₆C₁₅	15,6	C₂₄C₂₅C₂₆O₃	17,6
C₁₇C₁₆C₁₅C₁₄	13,9	C₂₅C₂₆O₃C₂₃	—6,2
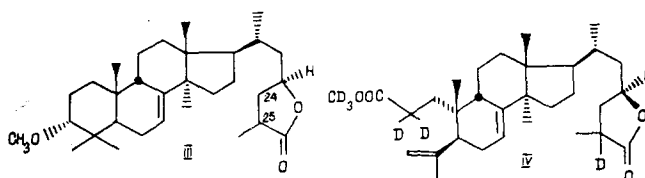
Thus, abiesolidic acid is (20R,23S,25R)-3,4-seco-9β-lanosta-4(28),7-dien-26,23-olid-3-oic acid.

3,4-Secotriterpenoids with isopropenyl groups at C_5 have been known since 1960 [6]. Mass spectrometry is very useful for determining the structures of similar triterpenoids. Aplin [7] has specially investigated features of the mass-spectrometric fragmentation of these compounds while, however, considering only pathways connected with the splitting out of the side chains and the cleavage of ring B. Characteristic for compounds of this type is the splitting out of the CH_2CH_2COOR (where R = H, CH_3) fragment and also the formation of the $(M - 43)^+$, $(M - 81)^+$, and $(M - 82)^+$ ions.

We have made a detailed study of the pathways of the mass-spectrometric fragmentation of methyl abiesolidate, also using abiesolidic acid and its ethyl ester (mixtures of epimers at C_{25}) obtained specially for this purpose, and the hexodeutero derivative of methyl abiesolidate (IV). Details of the mass spectra of abiesolidic acid and its methyl and ethyl esters (denoted as AA, ME, and EE, respectively) are given in Table 3.

The strongest peak in the spectrum of each of the esters was that of an ion with m/z 397 $(C_{27}H_{41}O_2)$ corresponding to the splitting out of the CH_2CH_2COOR fragment. Two other char-

TABLE 3. Intensities of the Peaks of the Ions in the Mass Spectra of Abiesolidic Acid (AA) and Its Methyl and Ethyl Esters (ME and EE)

Ion	AA		ME		EE	
	m/z	%	m/z	%	m/z	%
M^+	470	100	484	95	498	96
$(M-CH_3)^+$	455	15	469	23	483	19
$(M-OR)^+$	453	1.8	453	4.3	453	7.6
$(M-HOR)^+$	452	3.1	452	2.7	452	2.0
$(M-CH_3-HOR)^+$	437	11	437	10	437	10
$(M-C_3H_7)^+$	427	3.0	441	4.0	455	4.3
$(M-C_4H_8)^+$	414	2.0	428	2.1	442	1.7
$(M-C_5H_{11})^+$ $(M-C_4H_8-CH_3)^+$	399	4.5	413	11	427	10
$(437-H_2O)^+$	419	5.5	419	4.1	419	3.0
$(437-CO)^+$	409	5.6	409	4.7	409	6.0
$(M-C_6H_{10})^+$	388	6.8	402	9.2	416	5.7
$(M-CH_2CH_2COOR)^+$	397	72	397	100	397	100
$(M-C_6H_{10}-CH_2)^+$	373	3.5	387	3.7	401	3.3

m/z	AA	ME	EE	m/z	AA	ME	EE
		%				%	
383	6.5	10	11	301	13	23	22
370	6.3	6.5	5.0	287	13	16	14
369	7.5	10	12	283	7.2	10	8.8
357	—	—	3.5	275	7.0	11	14
355	10	14	13	274	9.5	13	17
343	—	3.4	—	273	8.0	7.2	6.2
341	6.8	8.2	8.0	261	7.2	14	—
337	6.9	7.7	6.5	255	11	12	14
329	4.8	—	—	249	10	16	16
327	6.3	5.5	4.6	247	16	13	17
316	8.5	12	15	235	35	48	51
315	5.0	7.1	8.3				

acteristic ions, $(M-43)^+$ and $(M-82)^+$ [7], were also observed in each of the spectra of the three compounds under consideration. The $(M-43)^+$ ion arises as the result of the cleavage of the C_4-C_5 bond after the migration of two hydrogen atoms into the fragments splitting off, while the $(M-82)^+$ ion arises by cleavage at C_5-C_{10} and C_7-C_8. By accurate mass measurements we confirmed that these ions were formed as the result of the splitting out of C_3H_7 and $C_6H_{10}^*$. The capacity of the molecule for undergoing cleavage at the position of the C_7-C_8 bond is undoubtedly due to the greater tendency of this bond to migrate under electron impact, as is the case for the C_4-C_{28} bond in the formation of the $(M-43)^+$ ions [7]. The ions $(M-C_4H_8)^+$ and $(M-C_5H_{11})^+$, not mentioned in Aplin's paper, must be ascribed to the same group of fragments. Both these ions arise from M^+ on the cleavage of the C_5-C_{10} bond with subsequent splitting at C_5-C_6 or at C_6-C_7. The second of them may also be formed through the primary elimination of a methyl radical. The spectra of the three compounds also contain a whole series of reproducible peaks of medium and low intensity the appearance of which has permitted a more complete characterization of the mass-spectral behavior of these substances of a not completely usual type. We judged the fragments formed (scheme, top following page) on the basis of a determination of the elementary compositions and analyses of metastable defocussing (MD) spectra and of the mass spectrum of deuterated methyl abiesolidate (IV). These facts are all the more useful since the origin of a series of fragments is unexpected from the point of view of the laws of decomposition of triterpenoids close in structure to the compounds under consideration. Thus, in the spectrum of eupha-7,24-diene (V) [8]

V
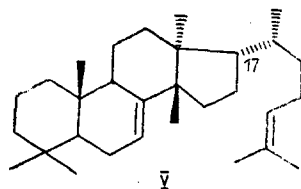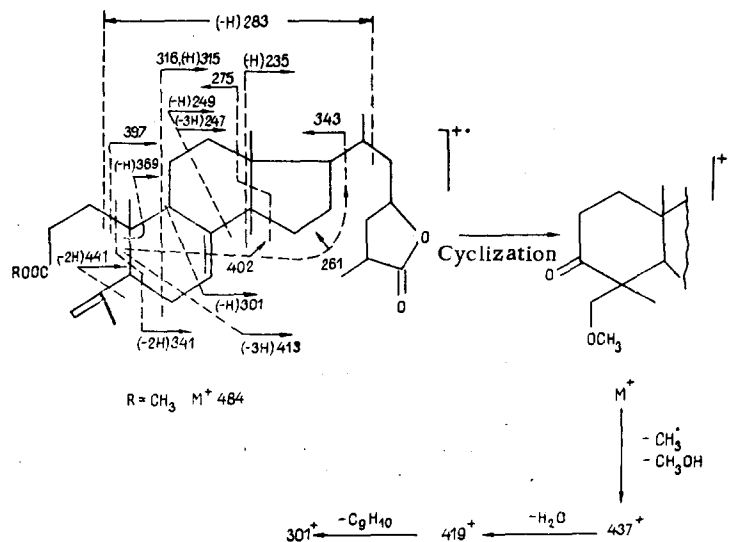
Scheme of the mass-spectrometric fragmentation of methyl
abiesolidate (I).

the peak of an ion with m/z 297 was detected, which the authors considered as the product of
the splitting out of the side chain at C_{17} with the migration of two H atoms to the neutral
fragment. A fragment with the corresponding mass number (341) was observed in the spectrum of
methyl abiesolidate. Its composition ($C_{23}H_{33}O_2$) does not contradict the method of formation
described above. At the same time, on passing to the spectra of the acid and of the ethyl
ester there was no appreciable increase in the intensity of the peaks of the ions with m/z 327
and 355 and the height of the peak of the ion with m/z 341 did not decrease appreciably. The
MD spectrum of the ion with m/z 341 shows as precursors, in addition to M^+, ions with m/z 428
$(M - C_4H_8)^+$ and 397. Thus, the ion with m/z 341 can be formed as a consequence of the succes-
sive elimination of $\cdot CH_2CH_2COOR$ and C_4H_8 in either order, which leads to the same elementary
composition. In the spectrum of the deuterium analog (IV), the ion with m/z 341 is shifted by
1 mass unit; this confirms the given variant of its formation. We may note that a less common
fragment with m/z 343 ($C_{23}H_{35}O_2$), which is shifted by 5 mass units in the same spectrum, is
formed on the splitting out of the side chain at C_{17} without the migration of a hydrogen atom.

There are also other differences in the behavior of the diene (V) and of the three com-
pounds under investigation. Cleavage at the $C_{12}-C_{13}$ and C_8-C_{14} bonds led in the former to an
ion with m/z 203 with the charge on rings A and B. In the spectra of abiosolidic acid and its
esters, cleavage of the same bond led to an ion with m/z 235 of considerable intensity but with
the charge on ring D. The observation of the processes of appearance of the ion with m/z 301
completely refute the possibility of its formation by cleavage at the $C_{13}-C_{17}$ and $C_{14}-C_{15}$
bonds, as takes place in eupha-7,24-diene. The mass number of 301 is characteristic for the
spectra of all three of the compounds under investigation, while in the spectrum of the deuter-
ium analog (IV) this ion is shifted to m/z 302. Analysis of the MD spectra of the ion with m/z
301 showed the following parental ions: M^+, and m/z 419, 397, and 316. In the first three cas-
es, the ion with m/z 301 is formed after the cleavage of the C_9-C_{10} and C_6-C_7 bonds in M^+ or
the ion with m/z 397, or in the way shown in the scheme (from the ion with m/z 419). The
$316^+ \rightarrow 301^+$ transition must be considered especially, since the origin of the m/z 316 parental
ion is also ambiguous. Judging from the elementary composition ($C_{21}H_{32}O_2$) and the shift in
the spectrum of the deuterium analog (IV) by 1 mass unit, it is formed as the result of a re-
trodiene breakdown of ring B. The MD spectrum of this ion showed the maternal ions M^+ and
m/z 402. It follows from this that the latter can break down with the elimination of a molecule
of methyl methyacrylate at the expense of the C_1-C_3 bond and differs in structure from the
product of the retrodiene reaction with the same mass number. Both variants of the ion with
m/z 316, by losing CH_3 (either from C_{14} or from C_{10}) are converted into an ion with m/z 301.
The ion with m/z 315 is formed in a similar manner to the ion with m/z 316 but with the loss
of one hydrogen atom.

The processes involved in the formation of some other fragments requiring no comments,
are reflected in the scheme. A considerable proportion of the ions given in Table 3 are doub-
lets. We have not considered it possible to discuss the multiplicity of the pathways for
their formation within the framework of the present paper.

Mass spectra were taken on a MKh 1310 instrument with a SVP5 system for the direct introduction of the sample. The temperature of the ionization chamber and of the evaporator bulb was 80-90°C, the ionizing voltage 50 V, and the collector current 80 μA. Elementary compositions were measured at R = 10,000 with an accuracy of $5 \cdot 10^{-6}$, the reference substance being perfluorokerosine. Metastable defocussing: E, H = const, scanning of U from 2.5 to 4.5 kV at the rate of 0.1 kV/sec.

Circular dichroism curves were obtained for solutions in methanol on a Spectropol 1 instrument. The other instruments used and also the conditions for chromatography have been described previously [3]. NMR (^{1}H and ^{13}C) spectra were recorded for solutions in CDCl$_3$ (δ scale, internal standard TMS).

Methyl Abiesolidate (I). A solution of 87.2 g of the oleoresin in 2 liters of diethyl ester was shaken vigorously with 1 liter of a saturated aqueous solution of sodium bicarbonate. The aqueous layer was separated off and the ethereal layer was shaken similarly with 1 liter of 1% aqueous sodium hydroxide solution. The alkaline aqueous layer was separated off and was washed with diethyl ether (0.2 liter), acidified to pH 2 with hydrochloric acid, and extracted with diethyl ether (2 × 0.2 liter). The combined ethereal extracts were washed with saturated aqueous sodium chloride solution (2 × 0.2 liter), dried with sodium sulfate, and evaporated to dryness. This gave 34.9 g (40% of the oleoresin) of the combined "weak" [2] acids. To these were added an ethereal solution of diazomethane until the appearance of a permanent yellow coloration. A portion (2.32 g) of the resulting methyl esters was separated by chromatography into two fractions — methyl esters of resin acids (1.10 g, eluent — petroleum ether containing 5% of diethyl ether) and methyl esters of polar acids (1.22 g, eluent — diethyl ether). In order to produce more of the latter, this operation was repeated and a portion of the esters of the polar acids (13.48 g) was rechromatographed on silica gel using petroleum ether with increasing amounts, from 5 to 40%, of diethyl ether as eluent. A mixture of petroleum ether with 25% of diethyl ether eluted crude methyl abiesolidate (1.5 g) the crystallization of which from petroleum ether—diethyl ether (1:2) gave 0.94 g of methyl abiesolidate with mp 154-155°C, $[\alpha]_D^{21}$ + 10.3° (c 3.86 CHCl$_3$), m/z 484, 3557 (C$_{31}$H$_{48}$O$_4$). Yield — 7% of the total amount of methyl esters of polar resin acids. In its IR spectra, the carbonyl band of a γ-lactone ring was present at 1765, 1770, and 1785 cm^{-1} when the spectra were recorded in CHCl$_3$, KBr, and CCl$_4$, respectively.

^{13}C NMR spectrum: singlets at 179.93, 174.87, 149.53, 146.22, 51.41, 43.65 and 36.17 ppm, triplets at 111.83, 42.44, 36.31, 33.86, 29.49, 29.02, 28.81, 28.11, 33.86, and 18.44 ppm, and quartet at 51.41, 27.29, 25.69, 23.89, 21.55, 18.03, and 15.75 ppm. Circular dichroism: $[\theta] \cdot 10^4$: —0.5° (220 nm), —4.0° (204 nm).

Crystals for x-ray structural analysis were obtained by crystallization from acetonitrile.

The x-ray structural experiment (λ Mo-K$_\alpha$, 2θ/ω scan, 2θ < 50°, 2030 reflections with I > 2σ) was performed on a Syntex P2$_1$ diffractometer. The crystals were monoclinic: a = 7.625 (4), b = 10.520(6), c = 17.923(9) Å, β = 90.79(4)°, z = 2, space group P2$_1$.

The structure was interpreted by the direct method using the SHELX program (in one of the E-syntheses it was possible to localize only part of the molecule). The refinement of the structure was carried out by the method of least squares in the anisotropic approximation (the parameters of the hydrogen atoms were not refined) to R = 0.071.

The Triol (II). With stirring, 0.1 g of lithium teta-hydroaluminate was added to a solution of 0.16 g of methyl abiesolidate in 30 ml of diethyl ether and the mixture was kept at room temperature for 30 min. After the usual working up, 0.15 g of the triol (II) was obtained with mp 177-178°C (from methanol), mass spectrum: m/z 460 (100%, M$^+$, C$_{30}$H$_{52}$O$_3$). PMR spectrum: 3.44-3.65 ppm (4 H, multiplet, protons at C$_3$ and C$_{26}$) and 3.87 ppm (1 H, multiplet, W$_{1/2}$ = 23 Hz, H$_{23}$). Circular dichroism: $[\theta] \cdot 10^4$: —0.5° (220 nm), —4° (205 nm). The triacetate had mp 63-64°C (from hexane); PMR spectrum: 1.94, 1.95, and 1.97 ppm (3 H each, singlets, methyls of acetyl groups).

Abiesolidic acid (Mixture of the 25R- and 25S-Epimers). A solution of 0.05 g of methyl abiesolidate in 10 ml of hot methanol was treated with 5 ml of a 20% solution of potassium hydroxide in methanol—water (5:1) and the mixture was kept at 50-60°C for an hour. Then it was acidified with 10% hydrochloric acid to pH 2, diluted with a saturated aqueous solution of sodium chloride, and extracted with diethyl ether. The product (0.04 g) was crystallized

from methanol, mp 209–212°C. PMR spectrum: 0.73, 0.83, 1.00, 1.77 ppm (3 H each, singlets, tertiary methyl groups), 0.92 ppm (3 H, doublet, J = 6.3 Hz, Me_{20}), 1.27 and 1.25 ppm (in combination, 3 H, doublets, J = 7.3 Hz for each, Me_{23} of the (I) and 25-epi(I) molecules, respectively), and 4.62 and 4.45 ppm (multiplets identical in form, with a ratio of their integral intensities of 2:1, totaling 1 H; H_{23} of the (I) and 25-epi(I) molecules, respectively). The signals of the olefinic protons coincided in form and position with those for methyl abiesolidate.

Ethyl Abiesolidate (Mixture of the 25R- and 25S-Epimers). A solution of 0.03 g of abiesolidic acid, obtained as described above, in 1 ml of acetone was treated with 0.04 g of ethyl bromide and 0.1 g of potassium carbonate, and the mixture obtained was boiled under reflux for an hour. After the usual working up procedure, 0.03 g of ethyl abiesolidate was obtained with mp 125–126°C (from a mixture of pentane and diethyl ether). PMR spectrum: 1.23 ppm (3 H, triplet, J = 7 Hz) and 4.10 ppm (2 H, quartet, J = 7 Hz) — the protons of an ethyl group. The other signals were the same as in the spectrum of abiesolidic acid.

The deuteration of methyl abiesolidate was carried out by heating the ester (I) in solution in a mixture of $(C_2H_5)_2$ ND and methanol-d_4 in a sealed tube at 120° for 4 h and then leaving it at room temperature for 3 days. After this, the tube was opened, the volatile products were driven off in vacuum, and the residue (the ester (IV) contaminated with other polydeuterated derivatives with a lower degree of deuteration) was used for the mass-spectrometric investigation.

SUMMARY

1. The structure of the methyl ester of abiesolidic acid has been established by x-ray structural analysis.

2. The pathways of the mass-spectrometric fragmentation of abiesolidic acid and its esters have been studied by the methods of high-resolution mass spectrometry and metastable defocussing.

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