2. The presence in the oleoresin of the Japanese larch of 15-oxopimar-8(14)-enoic acid, in that of the Kamchatka larch of 3β-hydroxysandacopimaric and cupressic acids, and in that of the Siberian larch of 8,15-dihydroxyabiet-13-enoic acid may serve as chemotaxonomic characteristics of these species.

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INVESTIGATION OF THE PRODUCTS OF THE OZONOLYSIS OF LARIXOL

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UDC 547.596/599

On the ozonization of larixol in methanol followed by treatment with ammonium chloride, the main reaction products were 15,16,20-trisnorlabd-6-ene-8,13-dione and 6-hydroxy-8,13;8,14-diepoxy-15,20-bisnorlabd-14-one. When ozonization was performed in methanol in the presence of dimethyl sulfide or in methylene chloride in the presence of pyridine, 6,14-dihydroxy-8,13;8,14-diepoxy-15,20-bisnorlabdane and 6-hydroxy-14,50,20-trisnorlabd-8,13-dione predominated in the reaction products.

Larixol (I) is one of the few labdane diterpenoids accessible in large amounts, being, together with its monoacetate (II), the main component of the oleoresins of various species of larch [1-4]. Some products of its oxidative transformations have found use in the perfumery industry [5, 6]. The oxidative cleavage of larixol (I) has been carried out under the action of potassium permanganate [7] and chromic acid mixture [8]. In the latter case, only a small amount (∿20%) of a neutral fraction was formed which consisted almost entirely of the keto anhydride (III) in which not only the side chain of larixol (I) but also its ring B had been cleaved. When potassium permanganate was used as the oxidant the yield of the neutral fraction of the oxidation product was greater (∿68%) but it consisted

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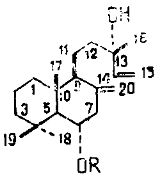
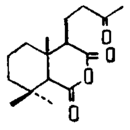
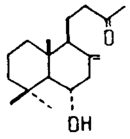
of a fairly complex mixture of substances and the amounts of the main components — the hydroxy ketone (IV) and the intramolecular ketal (V) — in it were low.



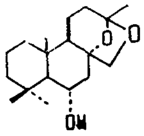
I. R = H
II. R = Ac



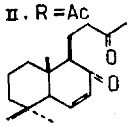
III



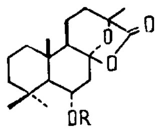
IV



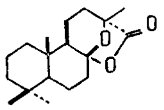
V



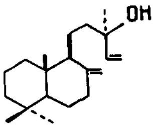
VI



VII. R = H
X. R = Ac



VIII



IX

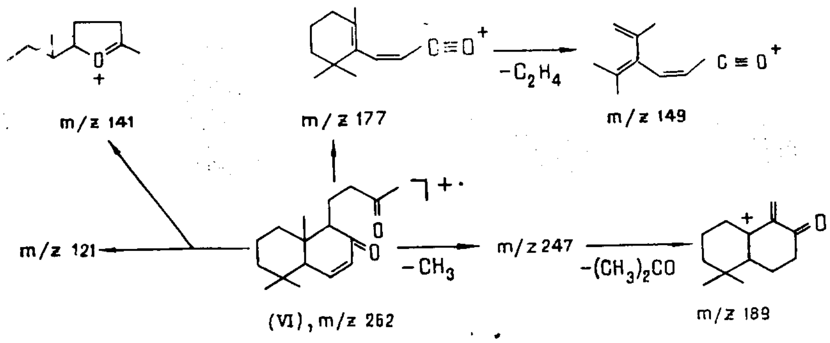
In view of the facts presented, we were interested to investigate the ozonization of larixol. It has been reported [4] that the ozonization of larixol in acetic acid forms a stable peroxide of undetermined structure with the composition $C_{19}H_{32}O_7$, the decomposition of which was, however, not undertaken.

Since it is well known that the course of an ozonization reaction is substantially affected by the solvent used and the method of treatment of the ozonide, we performed the ozonolysis of larixol (I) under various experimental conditions.

When ozonization was performed in absolute methanol at −70°C and the reaction product was treated with ammonium chloride, a mixture of not less than seven products, according to TLC on silica gel, was obtained, and these were separated by column chromatography on the same adsorbent into five fractions of increasing polarity. The first and smallest of them consisted of a complex mixture of substances and was not investigated further. The second fraction was acetylated, and its main component was isolated by chromatography on silica gel. It proved to be a liquid compound with the composition $C_{17}H_{26}O_2$. According to its IR spectrum, its molecule contained a methyl ketone group and an α,β-unsaturated ketone group. The presence of the latter was confirmed by a maximum at 238 nm in the UV spectrum. The conjugated double bond was α,β-disubstituted (calculated absorption maximum according to Woodward's rule [9], 237 nm).

In the PMR spectrum of the substance under investigation there were the signals of three methyl groups at quaternary carbon atoms, of a methyl ketone group, and of two vinyl protons. According to the ^{13}C NMR spectrum, two out of the 17 carbon atoms of this compound belonged to carbonyl groups, and two others were linked by an ethylenic bond. The assignment of the signals in the ^{13}C NMR spectrum (Table 1) was made on the basis of off-resonance results by comparing the spectra of the substances being studied with one another and with the spectra of labdane diterpenoids given in the literature [10, 11], and also by taking into account the nature of the functional groups and their influence on the positions of the signals of the α-, β-, and γ-carbon atoms [12].

The combination of the facts mentioned leads to structure (VI) for the subsance under investigation, and this was confirmed by the mass spectrum, which contained the peak of the molecular ion with m/z 262 and the peaks of fragmentary ions with m/z 247, 189, 177, 149, 141, and 121. A possible route for the formation of some of them is shown in scheme 1. The ions with m/z 141 and 121 apparently arise through the cleavage of the C_2–C_3, C_5–C_{10}, and C_8–C_9 bonds with the transfer of hydrogen atoms to the fragments obtained from the top part of the diketone molecule (VI), although another route of their formation is not excluded, either.



Scheme 1

The rechromatography of fraction 3 on silica gel led to the isolation of a crystalline product with the comosition $C_{18}H_{28}O_4$. Its IR spectrum contained maxima characteristic for an oxide ring and for hydroxy and γ-lactone groups, and its PMR spectrum the signals of four methyl groups at quaternary carbon atoms and of the carbinol proton of the secondary hydroxy group present in the initial larixol. The position of the signal of the methyl group at C_{10} (1.03 ppm) indicated that there was an oxide oxygen atom in the cis position to it at C_8, descreening it. The strong descreening of the methyl group at C_{13} (1.37 ppm) is due to the fact that this carbon atom is simultaneously linked to an oxide oxygen and to the carbonyl group of a γ-lactone ring.

The facts mentioned above, and also the ^{13}C NMR spectrum (see Table 1) lead to structure (VII) with an intramolecular ketal grouping at C_8 for the substance under investigation. Also in its favor is the fact that the spectral characteristics of the ketal-lactone (VII) are close to those for the product (VIII) of the ionization of the diterpenoid manool (IX); in particular, the methyl groups of the lactone (VIII) at C_{10} and C_{13} resonate at 1.06 and 1.32 ppm, respectively [13]. Since compounds (VII) and (VIII) are formed without cleavage of the bonds at C_{13}, while the configurations of manool (IX) and larixol (I) at C_{13} are different [14], the lactones (VII) and (VIII) must also differ by their configurations at this chiral center.

Chromatographic fraction 4 also consisted mainly of the hydroxy lactone (VII), since when it was acetylated with acetic anhydride in pyridine the acetate (X) of the hydroxy lactone (VII) was obtained in good yield. Its spectral properties (see the Experimental part) were close to those of the hydroxy lactone (VII) and confirmed both structures.

When larixol (I) was ozonized in methanol followed by the decomposition of the product with dimethyl sulfide, or in methylene chloride in the presence of pyridine, a mixture of substances identical in qualitative composition according to TLC and containing not less than five components was formed. The product obtained by the first of these methods was separated by chromatography on a column of silica gel into four fractions of increasing polarity. The first of them, a small one, consisting of a mixture of three substances, has not yet been studied. The two following liquid fractions with approximately identical compositions were combined and acetylated, and the product was purified by crystallization. Its IR spectrum contained the maxima of acetate and ketal groups. It followed from its PMR spectrum that the molecule of the substance contained two secondary acetate groups and four methyl groups at quaternary carbon atoms. The signal of one proton, apparently attached to the carbon atom bearing the second acetoxy group and one of the oxygens of the ketal grouping, appeared in a fairly weak field (6.04 ppm). The number and nature of substitution of the carbon atoms of the compound under investigation followed from the ^{13}C NMR spectrum (see Table 1). The PMR and IR spectra of this compound were similar to the corresponding spectra of product (XI) from the ozonization of manool (IX) [15] allowing for the fact that in the first of them there was not a hydroxy but an acetoxy group at C_{14} while the second acetoxy group was present at C_6. The facts presented lead to structure (XII) for the substance under investigation (in the light of the S-configuration of larixol at C_{13}), which was confirmed by its mass spectrum. In this there were the peak of the molecular ion at m/z 394, with a low intensity, and, in the region of high mass numbers, the peaks of ions with m/z 350, 318, 303, 258, 243, 205, and 192; a possible route to their formation is shown in Scheme 2.

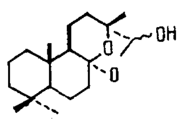
TABLE 1. ^{13}C NMR Chemical Shifts and Off-Resonance Characteristics of the Larixol Ozonization Products

Carbon atom	Compound			
	VI	VII	XII	XIII
1	40,51 t	38,96 t	38.47 t	39,10 t
2	18,09 t	17,83* t	17,95 t	18,33 t
3	42,99 t	43,54 t	43,37 t	42,47* t
4	32,44 s	33,33 s	33.15 s	39,93 s
5	56,26 d	59,61 d	58.71 d	59,47 d
6	148,89 d	67.46 d	69 26 d	70,58 d
7	129,70 d	45,50 t	41,66 t	52,82 t
8	201,35 s	109,30 t	102,10 s	208,95* s
9	61,72 d	50,38 d	53,11 d	62,22 d
10	44,02 s	37.24 s	37,82 s	39,74 s
11	16,38 t	17,44* t	19,11 t	16,20 t
12	37,14 t	30,67 t	29,91 t	43.43* t
13	208,67 s	79.60 s	70,62 s	208,59* s
14	—	175,12 s	97,24 d	—
15	—	—	—	—
16	29,60 q	19,80 q	20.58 q	29,79 q
17	13,25 q	15,22 q	14.74 q	15,82 q
18	32,13 q	36,35 q	36,11 q	36,33 q
19	21,95 q	22,27 q	21.95 q	22,10 q
20	—	—	168,70** s 169,37 s 21,58 q 23,52 q	

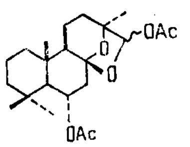
s — singlet; d — doublet; t — triplet; q — quartet.

*Signals that may change places.

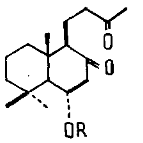
**Signals of acetate groups.



XI



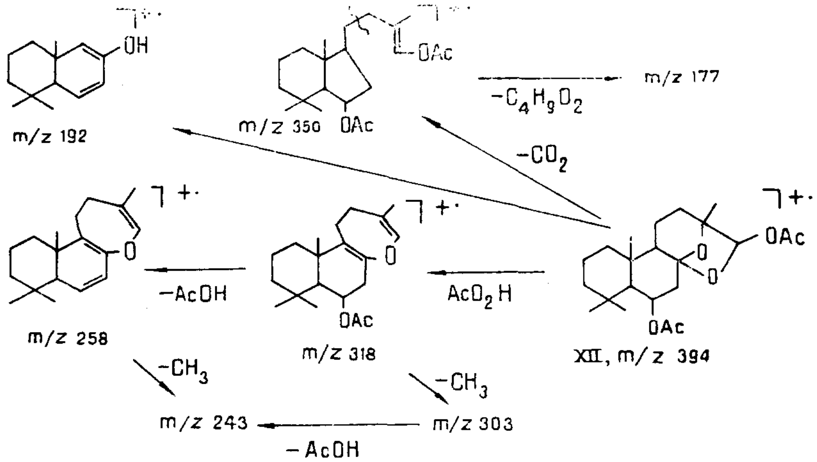
XII



XIII. R = H

XIV. R = Ac

The rechromatography of part of the last chromatographic fraction led to the isolation of the hydroxy lactone (VII) and of a crystalline subsance with the composition $C_{17}H_{28}O_3$, the molecule of which, judging from its IR spectrum, contained two carbonyl and one hydroxy group. Their presence also followed from the ^{13}C NMR spectrum (see Table 1) and the PMR spectrum. In the latter there were the signals of a methyl ketone group, of three tertiary methyl groups, and of a proton geminal to a hydroxy group. It follows from the facts mentioned that this compound was the hydroxy diketone (XIII).



Scheme 2

Another part of the last chromatographic fraction was acetylated and the products were chromatographed. In this case, as well, only two compounds were isolated: the acetoxy lactone (X) and the acetoxy diketone (XIV). The structure of the latter was shown spectrally and was confirmed by its formation on the acetylation of the hydroxy diketone (XIII). We may note that the peak of the molecular ion was absent from the mass spectrum of the diketo ester (XIV), and the peak with the greatest mass belonged to the fragmentary ion with m/z 262 (M − AcOH). Consequently, as was to be expected, the mass spectrum of compound (IV) was similar − especially in the region of high mass numbers − to the spectrum of the unsaturated diketone (VI).

Thus, the results obtained show that the main products of the ozonization of larixol (I) are formed as the result of the cleavage of its double bonds and of the ordinary C_{13}–C_{14} bond and by the interaction of the keto group at C_8 with the hydroxy group at C_{13} and with the functional group appearing at C_{14}. When the ozonization product is decomposed with ammonium chloride, the splitting out of the hydroxy group at C_6 also takes place.

EXPERIMENTAL

The melting points of the substances were determined on a Kofler heated stage. IR spectra were taken on a UR-20 spectrophotometer. PMR and ^{13}C NMR spectra were recorded in deuterochloroform on a Bruker WP-200 SY instrument. Mass spectra were obtained on a MS-902 spectrometer with a glass system for the direct introduction of the sample into the ion source at an ionizing energy of 70 eV and a temperature of 120°C. Type KSK (70 μ) silica gel, petroleum ether with bp 40-60°C and gradient mixtures of it from 0 to 100% of diethyl ether were used for adsorption chromatography.

Ozonization of Larixol (I). a) A current of ozonized oxygen was passed through a solution of 4.6 g of larixol (I) in 100 ml of absolute methanol at −70°C until a permanent blue coloration had appeared. The excess of ozone was driven off by passing dry nitrogen through the solution, and then the reaction mixture was left to assume room temperature and 4.6 g of dry ammonium chloride was added to it. After four days, the methanol was evaporated off in vacuum, the residue was extracted with benzene. The extract was washed with water and was dried over sodium sulfate, and the solvent was distilled off in vacuum. The residue (4.6 g) was dissolved in diethyl ether and the solution was percolated through a column of alumina (activity grade 2.5) with diethyl ether as the eluent. After the solvent had been distilled off, 3.5 g of combined neutral ozonization products was obtained.

b) A current of ozonized oxygen was passed through a solution of 1 g of larixol (I) in 7 ml of methanol at −55 to −60°C until the solution had acquired a blue coloration (2 h). Then the excess of ozone was driven off by the passage of nitrogen through the solution, 1 ml of dimethyl sulfide was added to the reaction mixture and it was stirred for one hour each at −10°C, 0°C, and room temperature. The solvent was driven off in vacuum and the residue was dissolved in ether; the solution was washed with water, with sodium bicarbonate solution, and again with water, and it was dried over anhydrous sodium sulfate and evaporated in vacuum. This gave 1.12 g of neutral fraction.

c) A current of ozonized oxygen was passed through a solution of 1 g of larixol (I) in 20 ml of dry methylene chloride and 1 ml of dry pyridine at −65 to −70°C for 1.5 h, when the ozone broke through. The reaction mixture was left to assume room temperature and was washed with a 10% solution of sulfuric acid, with water, with sodium bicarbonate solution, and again with water and was dried and the solvent was distilled off in vacuum. This gave 1.12 g of neutral fraction.

Chromatographic Separation of the Ozonization Product Obtained by Method a). The ozonization product obtained by method a) (3.5 g), consisting, according to TLC, of a mixture of not less than seven components, was chromatographed on a column containing 70 g of SiO_2. The column was eluted with hexane–diethyl ether (7:3), which gave five fractions of increasing polarity: 1) 0.15 g; 2) 0.85 g; 3) 0.45 g; 4) 0.35 g; and 5) 1 g. The last fraction consisted of a complex mixture of substances and was not investigated further.

15,16,20-Trisnorlabd-6-ene-8,13-dione (VI). Fraction 2 (0.85 g) was dissolved in 3 ml of dry pyridine, the solution was treated with 3 ml of acetic anhydride, and the mixture was kept at room temperature for 15 h and was then worked up in the usual way. The residue (0.7 g) was chromatographed on a column containing 20 g of SiO_2. Elution with petroleum ether–diethyl ether (7:3) led to the isolation of 0.5 g of the oily 15,16,20-trisnorlabd-6-ene-

8,13-dione (VI), n_D^{20} 1.5210. Mol. wt. 262.1940 (high-resolution mass spectrometry); calculated for $C_{17}H_{26}O_2$, mol. wt. 262.1933. IR spectrum (CCl_4, cm^{-1}): 1180, 1720 ($-\overset{\overset{O}{\|}}{C}-CH_3$), 1650 (conjugated >C=C<); 1680 (conjugated ketone). UV spectrum (ethanol): λ_{max} 238 nm (log ε 3.45). PMR spectrum (δ, ppm): 0.73 (s, 3H), 0.82 (s, 3H), 0.94 (s, 3H) [$C_4-(CH_3)_2$ and $C_{10}-CH_3$], 2.04 (s, 3H, $-\overset{\overset{O}{\|}}{C}-CH_3$), 5.94 (dd, 1H, J_1 = 4 Hz, J_2 = 10 Hz; C_7-H), 6.84 (dd, 1H, J_1 = 4 Hz; J_2 = 10 Hz; C_6-H). For the ^{13}C NMR spectrum, see Table 1. Mass spectrum m/z (%): 262 (M^+ 29), 247 (42), 229 (8), 209 (8), 205 (7), 204 (8), 190 (16), 189 (100%), 177 (24), 149 (18), 141 (58), 140 (58), 128 (10), 125 (26), 121 (39), 109 (46), 99 (97), 69 (52), 55 (84).

6-Hydroxy-8,13;8, 14-diepoxy-5,20-bismorlabd-14-one (VII). Fraction 3 (0.45 g) was rechromatographed on a column containing 10 g of SiO_2. Elution with hexane–ether (1:1) yielded 0.35 g of 6-hydroxy-8,13;8,14-diepoxy-15,20-bisnorlabd-14-one (VII) with mp 144-144.5°C (from petroleum ether–diethyl ether). Found, %: C 69.48; H 9.04; mol. wt. 308 (mass spectrometry). $C_{18}H_{28}O_4$. Calculated, %: C 70.10; H 9.15. IR spectrum (CCl_4, cm^{-1}): 950, 1050, 1150 (C–O–C); 1780 (γ-lactone); 3550 (band) (OH). PMR spectrum (δ, ppm): 0.90 (s, 3H), 1.16 (s, 3H) [$C_4-(CH_3)_2$], 1.03 (s, 3H, $C_{10}-CH_3$), 1.38 (s, 3H, $C_{13}-CH_3$), 2.35 (m, 2H, C_7-CH_2), 4.10 (m, 1H, C_6-H). For the ^{13}C NMR spectrum, see Table 1.

6-Acetozy-8,13;8,14-diepoxy-15,20-bisnorlabd-14-one (X). Fraction 4 (0.35 g) was acetylated with acetic anhydride in pyridine as described above. This gave 0.3 g of 6-acetoxy-8,13;8,14-diepoxy-15,20-bisnorlabd-14-one (X), mp 197-200°C (from petroleum ether–diethyl ether (1:1) and from methanol). Found, %: C 67.73; H 8.55. $(M - 60)^+$ 290. $C_{20}H_{30}O_5$. Calculated %: C 68.54; H 8.63. Mol. wt. 350.44. IR spectrum (KBr, cm^{-1}) 1040, 1060, 1075 (C–O–C); 1250, 1740 (OAc); 1775 (γ-lactone). PMR spectrum (δ, ppm), singlets of 3 H each at 0.88; 1.03 [$C_4-(CH_3)_2$], 0,96 ($C_{10}-CH_3$), 1,37 ($C_{13}-CH_3$), 2,03 ($-\overset{\overset{O}{\|}}{C}-CH_3$), 2,48 2H, C_7-CH_2), 5.25 (m, 1H, C_6-H).

Chromatographic Separation of the Ozonization Products Obtained by Methods b) and c). According to TLC, the ozonization products obtained by methods b) and c) had identical qualitative compositions and each consisted of five components. The product obtained by method b) (3g) was chromatographed on a column containing 90 g of SiO_2. The column was washed with mixtures of petroleum ether and diethyl ether with a gradient increase in the amount of the later from 20 to 100%. This gave four fractions with increasing polarity: 1) 0.5 g; 2) 0.7 g; 3) 0.7 g; and 4) 0.5 g).

6,14-Diacetoxy-8,13;8,14-diepoxy-15,20-disnorlabdane (XII). Chromatographic fractions 2 and 3 obtained above were combined and were acetylated with a mixture of 10 ml of acetic anhydride and 10 ml of dry pyridine as described above. After the usual working up procedure, 1.5 g of crystalline 6,14-diacetoxy-8,13;8,14-diepoxy-15,20-bisnorlabdane (XII) was obtained with mp 152-154°C (from methanol). Found, %: C 66.74; H 8.73. $C_{22}H_{34}O_6$. Calculated, %: C 66.98; H 8.69. IR spectrum (KBr, cm^{-1}): 990, 1040, 1060, 1110, 1120, 1150 (ketal group), 1230, 1260, 1740, and 1760 (two OAc groups). PMR spectrum (δ, ppm): 0.88 (s, 3H), 0.98 (s, 3H) [$C_4-(CH_3)_2$], 1.09 (s, 6H, $C_{10}-$ and $C_{13}-CH_3$); 1.99 (s, 3H), 2.11 (s, 3H) (two $-O-\overset{\overset{O}{\|}}{C}-CH_3$ of groups), 5.17 (m, 1H, C_6-H), 6.04 (s, 1H, $C_{14}-H$). For the ^{13}C NMR spectrum, see Table 1. Mass spectrum m/z (%): 394 (M^+, 9), 350 (97), 318 (100), 303 (34), 276 (17), 258 (74), 243 (24), 205 (83), 192 (61), 189 (27), 177 (37).

6-Hydroxy-14,15,20-trisnorlabdane-8,13-dione (XIII). Part of the chromatographic fraction 4 obtained above (0.3 g) was rechromatographed on a column containing 10 g of SiO_2. Petroleum ether–diethyl ether (3:2) eluted 0.1 g of the hydroxylactone (VII) with mp 144-145°C, and a 1:1 mixture of the same solvents eluted 0.15 g of 6-hydroxy-14,15,20-trisnorlabdane-8,13-dione (XIII) with mp 104-105°C (from methanol–ether). Mol. wt. 280 (mass spectrometry). $C_{17}H_{28}O_3$. Calculated, mol. wt. 280.41. IR spectrum (CCl_4, cm^{-1}): 1110, 3610 (OH); 1180, 1720 (>C=O group). PMR spectrum (δ, ppm): 0.67 (s, 3H, $C_{10}-CH_3$), 1.00 (s, 3H), 1.18 (s, 3H) [$C_4-(CH_3)_2$], 2.07 (s, 3H, $-\overset{\overset{O}{\|}}{C}-CH_3$), 2.72 (dd, 1H, J_1 = 4.5 Hz; J_2 = 11 Hz; C_7-H_9), 4.07 (m, 1H, C_6-H). For the ^{13}C NMR spectrum, see Table 1.

6-Acetoxy-14,15,20-trisnorlabdane-8,13-dione (XIV). The remainder of chromatographic fraction 4 (0.2 g) was acetylated with a mixture of acetic anhydride and pyridine and, after working up, the product was chromatographed on a column containing 5 g of SiO_2. Petroleum ether–diethyl ether (86 g) [sic] eluted 0.05 g of the acetoxy lactone (X) with mp 197-200°C (from methanol–ether), and petroleum ether–diethyl ether (7:3) eluted 0.15 g of 6-acetoxy-14,15,20-trisnorlabdane-8,13-dione (XIV) with mp 132-134°C (from methanol). Found, %: C 72.03; H 9.28. $C_{19}H_{30}O_4$. Calculated, %: 70.77; H 9.38. IR spectrum (CCl_4, cm^{-1}): 1180, 1720 ($-\overset{\overset{O}{\|}}{C}-CH_3$ and >C=O in a six-membered ring); 1250, 1740 (OAc). PMR spectrum (δ, ppm): 0.74 (s, 3H, $C_{10}-CH_3$), 0.89 (s, 3H), 1.03 (s, 3H) [$C_4-(CH_3)_2$], 2.02 (s, 3H, OAc), 2.07 (s, 3H, $-\overset{\overset{O}{\|}}{C}-CH_3$), 2.25 (m, 1H, C_7-H_a), 2.83 (dd, 1H, J_1 = 7.5 Hz, J_2 = 10 Hz, C_7-H_a), 5.28 (dd, 1H, J_1 = 5 Hz, J_2 = 11 Hz, C_6-H). Mass spectrum, m/z 177 (17), 161 (8), 135 (22), 121 (20). The acetoxy diketone (IV) was obtained by acetylating the hydroxy diketone (XIII) under the same conditions.

SUMMARY

On the ozonization of larixol in methanol followed by treatment with ammonium chloride the main reaction products are 15,16,20-trisnorlabd-16-ene-8,13-dione and 6-hydroxy-8,13;8,14-diepoxy-15,20-bisnorlabd-14-one. When ozonization is performed in methanol in the presence of dimethyl sulfide or in methylene chloride in the presence of pyridine, 6,14-dihydroxy-8,13;8,14-diepoxy-15,20-disnorlabdane and 6-hydroxy-14,15,20-trisnorlabd-8,13-dione predominate in the reaction product.

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