MINOR COMPOUNDS OF THE OLEORESIN OF THE KAMCHATKA, JAPANESE, AND SIBERIAN LARCHES

V. I. Bol'shakova, E. N. Shmidt,
V. A. Pentegova, and V. I. Mamatyuk

UDC 547.914.2

The polyfunctional compounds of the oleoresins of three species of larch have been studied. Larixol diacetate, 3β-hydroxyepimanool, and 15-oxopimara-4(14)-enoic 13-hydroxy-7-oxoabicta-8(14)-enoic, 3β-hydroxysandaracopimaric, and 8,15-dihydroxy-abietic acids have been isolated for the first time. The investigation performed has shown that the oleoresins of the larch contain polyfunctional compounds of various structural types. Depending on the species, their composition changes, and this fact can be used in the chemotaxonomy of larches.

We have previously reported the chemical compositions of the oleoresins of the Kamchatka, Japanese, and Siberian larches [1, 2, 3, respectively] a feature of which is a high level of neutral components. In the present paper we consider the minor compounds of the oleoresins of these larches.

Among the neutral components in the oleoresins of the Kamchatka and Japanese larches larixol (Ia) and larixyl acetate (Ib) predominate [1, 2], while, in addition to these, from the oleoresin of the Japanese larch we isolated two new polyfunctional diterpenoids.

The first compound, with mp 112-114°C, wassimilar to larixyl acetate (Ib) in its spectral characteristics, but its IR spectrum contained no absorption band characteristic for a tertiary hydroxy group.

Its PMR spectrum showed two singlets with an intensity of 3 H each having chemical shifts of 1.95 and 2.01 ppm, which are characteristic for the protons of acetate groups. This gave us grounds for assuming that the compound isolated (Ic) was larixol diacetate. Independent synthesis from larixyl acetate gave us the diacetate (Ic) with mp 112-113°C, identical with the natural product.

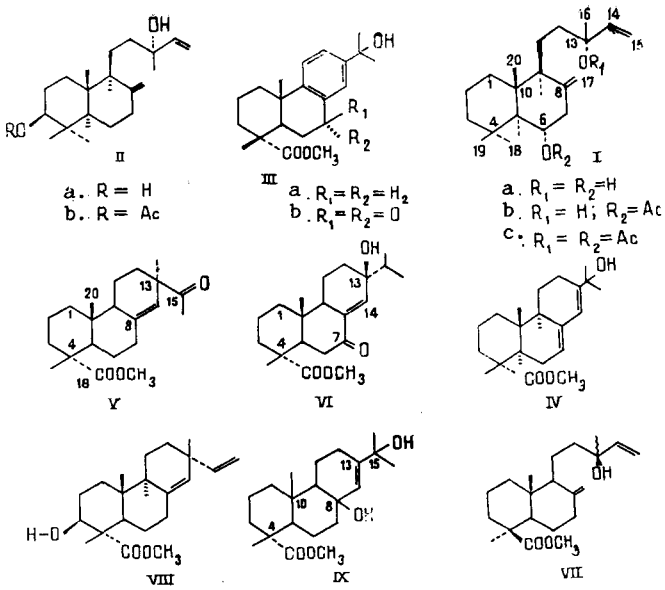
The second compound was almost completely identical with larixol in polarity and spectral characteristics. Acetylation of the compound under mild conditions gave a hydroxyacetate with mp 96-98°C. Analysis of the PMR spectrum using the double-resonance method showed that the secondary hydroxy group in the new compound was in a position different from that in (Ia). A one-proton multiplet with a chemical shift of 3.23 ppm (J_1 = 10 Hz, J_2 = 5 Hz) was assigned to the axial proton of a secondary acetate group. The nature of the signal and the spin-spin coupling constants coincided with those of the diterpenoids having an equatorial hydroxyl function at C_3 [4]. The structure of 3β-hydroxyepimanool (IIa) is suggested for the new compound.

We devoted particular attention to an investigation of the polyfunctional components of the acidic fractions of the oleoresins, which had not been studied previously. The combined acids were treated with diazomethane, and the resulting methyl esters were then analyzed by adsorption chromatography.

Together with the known methyl 15-hydroxydehydroabietate (IIIa) and methyl 15-hydroxy-abietate (IV), which are present in considerable amounts in all the oleoresins of the species mentioned, we isolated several minor compounds not previously found in natural conifer species.

Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the USSR Academy of Sciences. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 571-576, September-October, 1986. Original article submitted February 20, 1986.

 0009-3130/86/2205-0536$12.50



From the nonpolar fractions of the methyl esters of the oleoresins of the Japanese and Kamchatka larches we isolated a crystalline substance with mp 82-83°C the IR spectrum of which contained absorption bands of a double bond (980, 1640 cm^{-1}) and of ester and carbonyl groups (1250, 1720, 1740 cm^{-1}) but no absorption bands characteristic for hydroxy groups.

The PMR spectrum of the compound contained the signals of three tertiary methyls at 0.79, 1.11, and 1.17 ppm, and also of a methyl ketone group (2.08 ppm) and of a methoxy group (3.63 ppm). In the weak-field region of the spectrum there was the singlet of one olefinic proton with a chemical shift of 5.43 ppm. In the mass spectrum of the compound, a peak with m/z 332 corresponded to the molecular ion. According to the results of elementary analysis, the substance had the empirical formula $C_{21}H_{32}O_3$.

In the ^{13}C NMR spectrum, signals with chemical shifts of 212.73 (singlet) and 179.15 (singlet) were assigned to carbonyl and methoxycarbonyl groups, while signals at 138.95 (singlet) and 124.79 (doublet) corresponded to the carbon atoms of a trisubstituted double bond (>C=CH–). On the basis of spectral characteristics and an analysis of the PMR and ^{13}C NMR spectra, the substance isolated was ascribed the structure of methyl 15-oxopimara-8(14)-en-18-oate (V). A compound of this structure has been obtained previously by the oxidation of 15-hydroxypimarate with the Jones reagent [5]. The spectral characteristics of the two substances coincided, but there were differences in the melting points of the natural and synthetic products (82-83°C and 69-70°C, respectively). It must be mentioned that substance (V) is present in considerable amounts in the oleoresin of the Japanese larch and in small amounts in the Kamchatka larch while it is absent from the oleoresin of the Siberian larch.

Substance (IIIb) was isolated in trace amounts from the acidic fraction of the oleoresin of the Japanese larch; its PMR spectrum was almost identical with that of (III), with the exception of the weak-field region, and in the IR spectrum there was an additional absorption band at 1680 cm^{-1}. Analysis of the structural characteristics and a comparison of (IIIa) and methyl 7-oxodehydroabietate permitted the proposal for compound (IIIb) of the structure of methyl 15-hydroxy-7-oxodehydroabietate [6].

A more polar substance isolated from the oleoresin consisted of a polyfunctional compound of the abietin type the IR spectrum of which confirmed the presence of a tri-substituted double bond (980, 1620 cm^{-1}), and of ester (1250, 1720 cm^{-1}), oxo (1680 cm^{-1}), and hydroxy (1150, 3610 cm^{-1}), groups.

In its UV spectrum an absorption maximum was observed at 248 nm, which is characteristic for α,β-unsaturated ketones [7]. The PMR spectrum of the compound was characteristic for polyfunctional derivatives of abietic acid [8]. On the basis of its spectral characteristics, this substance was identified as methyl 13-hydroxy-7-oxoabieta-8(14)-en-18-oate, which is the first time that it has been isolated as a native product although this compound has previously been obtained synthetically [8].

Continuing a study of the polyfunctional acid products of the oleoresin of the Kamchatka larch, we detected two more compounds in addition to methyl 15-oxopimara-8(14)-en-18-oate (V).

From its spectral characteristics (IR, PMR, and mass spectra) and physical constants, one of them was identified a methyl cupressate (VII) [9]. Bicyclic acids of the labdane series – cis-communic and epitorulosic acids [10, 11] – have been found previously in the acidic fractions of larch oleoresins [10, 11].

The second substance, with mp 108-110°C, had absorption bands in the IR spectra of vinyl (920, 1640, 3080 cm^{-1}) and trisubstituted (970 cm^{-1}) double bonds and of ester (1250, 1740 cm^{-1}) and hydroxy (1120, 3630 cm^{-1}) groups. According to its PMR spectrum, the compound was close to diterpenoids of the isopimaric type and contained three methyl groups (0.83, 0.87, and 1.23 ppm), a methoxy group (3.62 ppm), and vinyl (4.86-4.94; 5.85, dd, J_1 = 10 Hz, J_2 = 18 Hz) and trisubstituted (5.29 ppm, singlet, 1 H) double bonds. From the form of the signal of the olefinic proton of the trisubstituted bond it was possible to assume that it was present in the 8.14 position and not the 7.8 position as in methyl isopimarate. The spectrum contained a doublet of doublets at 4.04 ppm (dd, J_1 = 5 Hz, J_2 = 12 Hz, which is characteristic for a proton in the geminal position to a hydroxy group. From its physical constants and spectral characteristics, the hydroxy ester was identified as 3β-hydroxy-sandaracopimarate (mp 111°C) (VIII), which has been isolated from a juniper [12].

Among the polar compounds of the oleoresin of the Siberian larch, in addition to products (III) and (IV) we isolated only one unknown compound, which was similar in its spectral characteristics to methyl 15-hydroxyabietate but differed from it by a higher polarity, which was due to the presence of a second hydroxy group. According to its IR and PMR spectrum, the substance did not contain primary and secondary hydroxy groups. The ^{13}C NMR spectrum showed the presence in the compound of one double bond (123.42 and 143.81 ppm), a methoxy group (179.1 ppm), and of two carbon atoms each having a hydroxy group as one of its substituents (74.61 and 73.98 ppm). The structure of methyl 8,15-dihydroxyabieta-13-en-18-oate (IX) is suggested for this compound.

The investigations showed that larch oleoresins contain a series of polyfunctional compounds of various structural types biogenetically linked with the main components of the oleoresins.

This is the first time that the minor oxidized resin acids of the larch have been studied and it has been shown that, depending on the species, their composition changes from species to species which fact may be utilized in the chemotaxonomy of larches.

EXPERIMENTAL

The oleoresin of the Kamchatka larch was collected in the Kurile Islands in August, 1983, that of the Japanese larch in July, 1983, in the southern part of Sakhalin, and that of the Siberian larch in July, 1984, in the Altai.

IR spectra were taken on a UR-20 instrument in CCl_4 solution and in KBr tablets, ^1H and ^{13}C spectra on Bruker WP 200 SY and Varian A 56/60 A instruments (solvent: $CDCl_3$; δ scale); and UV spectra on a Specord UV-VIS instrument in C_2H_5OH.

Specific rotations were determined for solutions in chloroform. Petroleum ether (PE) with bp 40-60°C and mixtures of it with from 0 to 100% of diethyl ether (DE) were used for absorption chromatography.

Larixol Diacetate (Ic). From the total oxygen-containing neutral diterpenoids of the oleoresin of the Japanese larch (4.3 g) 0.09 g of a substance with mp 112-114°C (petroleum ether) was isolated by chromatography on silica gel [13] in the PE–DE (95:5) system. $[\alpha]_D^{20}$ + 62.8° (c 3.9). $C_{24}H_{38}O_4$. Mol. wt. 390 (mass spectrometry).

IR spectrum (CCl_4): 890, 920, 1050, 1250, 1650, 1740, 3080 cm^{-1}.

PMR spectrum, ppm: 0.71 (s, 3H, C_{10}–CH_3), 0.84 (s, 3H, C_4–CH_3), 0.98 (s, 3H, C_4–CH_3), 1.50 (s, 3H, C_{13}–CH_3), 1.95 (s, 3H, C_6–OAc), 2.01 (s, 3H, C_{13}–OAc), 2.65 (s, 1H, C_5–H), 4.59; 4.90 (2s each 1H, C_8=CH_2), 5.06; 5.14; 5.93 (dd, J_1 = 10 Hz, J_2 = 18 Hz, –CH=CH_2).

^{13}C NMR spectrum, ppm: 172.3 (s), 169.9 (s), 144.1 (s), 141.7 (d), 113.0 (t), 109.3 (t), 82.17 (s), 73.1 (d), 57.4 (d), 56.2 (d), 44.1 (t), 43.3 (t), 39.7 (s), 39.1 (t), 38.9 (t), 36.0 (q), 33.43 (s), 29.6 (a), 23.4 (t), 22.1 (q), 21.8 (t), 18.9 (q), 17.6 (q), 15.9 (q).

Acetylation of Larixyl Acetate [14]. Over 15 min, 0.2 g of freshly distilled acetyl chloride was added to a mixture of 0.5 g of (Ib) and 7 ml of freshly distilled dimethylaniline. The reaction mixture was left overnight at room temperature. After the usual working up, 0.53 g of larixol diacetate (Ic) with mp 112-113°C was obtained. A mixed melting point of the natural and synthetic samples gave no depression.

3β-Hydroxyepimanool (IIa). On the further chromatography of the oxygen-containing diterpenoids with PE–DE (70:30), an oily substance was isolated (0.04 g), which was treated with acetic anhydride in pyridine. After the usual working up, the hydroxy ester (IIb) was obtained with mp 97-98°C.

PMR spectrum of (IIa), ppm: 0.64 (s, 3HO, 0.73 (s, 3H), 0.95 (s, 3H), 1.24 (s, 3H), 3.23 (1H, dd, J_1 = 5 Hz, J_2 = 10 Hz), 4.51 (s, 1H), 4.81 (s, 1H) > C=CH_2; 5.02; 5.17; 5.88 (dd, J_1 = 10 Hz, J_2 = 18 Hz).

IR spectrum of (IIb), cm^{-1}: 890, 920, 1250, 1640, 1740, 3080, 3610 cm^{-1}.

PMR spectrum of (IIb), ppm: 0.67 (s, 3H), 0.82 (s, 6H), 1.24 (s, 3H), 2.02 (s, 3H), 4.48 (dd, 1H), 4.52 (s, 1H), 4.82 (s, 1H), 5.01; 5.18; 5.90. (J_1 = 10 Hz, J_2 = 18 Hz).

Isolation of the Polyfunctional Acidic Components of the Oleoresin of the Japanese Larch. The acidic fraction of the oleoresin (13 g) was dissolved in diethyl ether and the solution was treated with an ethereal solution of diazomethane until a permanent yellow-green coloration appeared. After the mixture has been left for 12 hours, the solvent was driven off and the resulting methyl esters were chromatographed on silica gel (140 μ, ratio 1:20). By means of a mixture of PE and DE, 9.1 g of methyl esters of resin acids was isolated, and diethyl ether eluted 3.3 g of a mixture of polyfunctional compounds. The rechromatography of the combined polar compounds (3.3 g) on silica gel (40-100 μ) followed by elution with PE–DE mixtures containing from 10 to 100% of DE led to the isolation of five fractions: 1) 0.03 g; 2) 0.15 g; 3) 0.22 g; 4) 0.12 g; 5) 2.2 g. Fraction 1 consisted of a mixture of methyl esters of resin acids.

Methyl 15-Oxopimara-8(14)-en-18-oate (V). Fractions 2 and 3 (0.37 g) were combined and chromatographed on silica gel by the method of flash chromatography [13]. This led to the isolation of 0.22 g of a crystalline substance with mp 82-83°C (from hexane), $[\alpha]_D^{21}$ − 16°C (c 5.6), $C_{11}H_{32}O_2$. Mol. wt. 332 (mass spectrometry), according to the literature [5]: mp 69-70°C (methanol), $[\alpha]_D^{25}$ − 32° (c 0.62).

IR spectrum, cm^{-1}: 980, 1110, 1170, 1190, 1250, 1640, 1720, 1740.

PMR spectrum, ppm: 0.79 (s, 3H), 1.11 (s, 3H), 1.17 (s, 3H), 2.08 (s, 3H), 3.63 (s, 3H), 5.43 (s, 1H).

^{13}C NMR spectrum, ppm: 212.73 (s), 179.15 (s), 138.95 (s), 124.79 (d), 51.80 (q), 50.32 (d), 48.90 (d), 47.38 (s), 38.21 (t), 37.70 (s), 30.85 (t), 35.37 (t), 30.69 (t), 29.50 (s), 25.44 (t), 24.61 (t), 23.22 (q), 18.25 (q), 18.03 (t), 16.93 (q), 15.05 (q).

Methyl 15-Hydroxy-7-oxodehydroabietate (IIIb). The chromatography of fraction 4 (0.12 g) led to the isolation of 0.03 g of a substance with n_D^{21} 1.4854, which was identified by its IR, UV, and PMR spectra as (IIIb) [6].

IR spectrum, cm^{-1}: 1250, 1510, 1680, 1720, 3610.

UV spectrum, nm: $\lambda_{max}^{C_2H_5OH}$ 228, 262, 330 (log ε 3.13, 2.83, 2.30).

PMR spectrum, ppm: 1.20 (s, 6H), 1.22 (s, 3H), 1.30 (s, 3H), 3.62 (s, 3H), 7.05; 7.22; 7.49 (m, 3H).

Methyl 15-Hydroxydehydroabietate (IIIa) and Methyl 15-Hydroxyabietate (IV). On the repurification of fraction 5 with PE–DE (80:20), 0.49 g of a combination of substances (IIIa) and (IV) (1:1) was isolated. The compounds were identified from their IR, UV, and PMR spectra, and also by GLC with the addition of markers.

Methyl 13-Hydroxy-7-oxoabiet-8(14)-en-18-oate (VI). From fraction 5 by means of PE–DE (70:30), 0.4 g of a product was isolated the additional purification of which on silica gel with silver nitrate (5%) yielded 0.06 g of compound (VI) with n_D^{21} 1.5082; $[\alpha]_D^{21}$ −3.2° (c 5.72), mol. wt 332 (mass spectrometry). $C_{21}H_{34}O_4$.

IR spectrum, cm^{-1}: 980, 1150, 1250, 1620, 1680, 1720, 3610.

UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 248 nm, log ε 3.53.

PMR spectrum, ppm: 0.79 (d, J = 6 Hz, 3H), 0.82 (s, 3H), 0.91 (d, J = 6 Hz, 3H), 1.19 (s, 3H), 2.26 (m, 1H), 3.61 (s, 3H), 6.70 (s, 1H).

^{13}C NMR, ppm: 199.2 (s), 177.9 (s), 140.1 (d), 138.1 (s), 71.6 (s), 51.98 (q), 51.52 (d), 46.15 (s), 44.21 (q), 38.49 (d), 37.79 (q), 37.69 (t), 36.74 (d), 35.31 (s), 29.58 (t), 18.11 (t), 17.63 (q), 17.10 (q), 16.21 (t), 16.02 (q), 14.27 (q).

Oxidation of Methyl 7α,13β-Dihydroxyabiet-8(14)-en-18-oate. To a cooled solution of 0.15 g of the diol in 3 ml of pyridine was added the CrO_3–pyridine complex from 2 ml of pyridine and 0.15 g of CrO_3. The mixture was left at room temprature for 12 h. After the usual working up procedure, 0.13 g of product was isolated, the subsequent purification of which gave compound (VI), identical with the natural product according to IR and PMR spectra.

Polyfunctional Compounds of the Oleoresin of the Kamchatka Larch. The acids (40 g) were treated with diazomethane as described above. After preliminary chromatography, 38 g of combined resin-acid methyl esters and 5.7 g of polyfunctional compounds were obtained, and these were separated into their main components as fractions A, 1.39 g; B, 0.35 g; C, 0.68 g, and D, 0.72 g.

The highly polar compounds (1.3 g) were not studied because of their instability.

Fraction A contained methyl 15-oxopimar-18(14)-en-18-oate with mp 82-83°C.

Fraction B consisted of a combination of compounds (IIIa) and (IV) in a ratio of 1:2.

Methyl Cupressate (VII). From fraction A was isolated 0.51 g of a product the rechromatography of which on silica gel impregnated with silver nitrate (5%) gave methyl cupressate with mp 65-68°C, $[\alpha]_D^{21}$ + 39.9° (c 2.6), m/z 316 (M − 18). $C_{21}H_{34}O_3$. According to the literature [9]: mp 70-71°C, $[\alpha]_D^{20}$ + 52.3°.

IR spectrum, cm^{-1}: 890, 920, 1150, 1250, 1650, 1720, 3610.

PMR spectrum (ppm): 0.48 (s, 3H), 1.15 (s, 3H), 1.24 (s, 3H), 3.58 (s, 3H), 4.50 (s, 1H), >C=CH$_2$; 5.01; 5.15, 5.90 (J_1 = 10 Hz, J_2 = 18 Hz, J_3 = 2 Hz).

Methyl 3β-Hydroxysandaracopimarate (VIII). Fraction D (0.72 g) was chromatographed by the method of Still et al. [13]. The PE–DE (70:30) system yielded 0.25 g of a substance with mp 108.5-110°C, $[\alpha]_D^{20}$ + 23.1° (c 1.9). Mol. wt. 332 (mass spectrometry). $C_{21}H_{32}O_3$. According to the literature [12]: mp 111°C.

IR spectrum (KBr), cm^{-1}: 920, 970, 1120, 1250, 1640, 1740, 3080, 3630.

PMR spectrum, ppm: 0.83 (s, 3H), 0.87 (s, 3H), 1.23 (s, 3H), 3.62 (s, 3H), 4.01 (dd, J_1 = 5 Hz, J_2 = 10 Hz), 4.86–4.94, >C=CH$_2$, 5.29 (br.s., 1H), 5.14; 5.78; 5.85 (–HC=HC$_2$).

Polyfunctional Acids from the Oleoresin of the Siberian Larch. The acids (10 g) were treated as described above. After the separation of the resin-acid methyl esters (7.5 g), 2.1 g of polar products was obtained. Rechromatography of the combined polyfunctional compounds (2.1 g) in the PE–DE (80:20) system yielded 0.2 g of a mixture of (IIIa) and (IV) in a ratio of 2:3.

Methyl 8,15-Dihydroxyabiet-13-en-18-oate (IX). PE–DE (60:40) eluted 0.09 g of an amorphous product $[\alpha]_D^{20}$ + 20.6° (c 5.3).

IR spectrum, cm^{-1}: 960, 1120, 1160, 1250, 1640, 1720, 2580, 3620.

PMR spectrum, ppm: 0.76 (s, 3H), 0.80 (s, 3H), 1.16 (s, 6H), 3.61 (s, 3H), 5.70 (s, 1H).

^{13}C NMR spectrum, ppm: 179.1 (s), 143.81 (s), 123.42 (d), 74.61 (s), 73.98 (s), 51.77 (t), 51.10 (d), 48.66 (d), 47.27 (s), 38.08 (t), 37.27 (q), 36.82 (t), 34.84 (t), 29.59 (s), 24.30 (t), 24.26 (t), 24.16 (t), 17.95 (q), 17.47 (q), 16.92 (q), 14.83 (q).

SUMMARY

1. The minor polyfunctional compounds of the oleoresins of three species of larch have been studied. The following have been isolated for the first time from conifer oleoresins: larixol diacetate, 3β-hydroxyepimanool, and, from the acid fraction in the form of methyl esters, 15-oxopimara-8(14)-en-18-oic, 13-hydroxy-7-oxoabieta-8(14)-enoic, 3β-hydroxysandaracopimar, and 8,15-dihydroxyabieta-13-en-18-oic acids.

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

P. F. Vlad, A. M. Kyl'chik,
E. N. Schmidt, M. N. Koltsa,
V. N. Odinokov, and V. A. Pentegova

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

Institute of Chemistry of the MSSR Academy of Sciences, Kishinev, and Institute of Organic Chemistry of the Bashkir Branch of the USSR Academy of Sciences, Ufa.

Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 577-584, September-October, 1986. Original article submitted April 22, 1986.

0009-3130/86/2205-0541$12.50