ABIETIC AND DEHYDROABIETIC ACID DERIVATIVES FROM NEEDLE-FREE SHOOTS OF SHOOTS OF *Pinus sylvestris*

V. I. Roshchin, L. A. Kolodynskaya,
V. A. Raldugin, and V. A. Pentegova

UDC 547.595.9

Methyl ethers of hydroxy and keto derivatives of abietic and dehydroabietic acids – 12α-hydroxy- and 12-ketoabietic and 12-hydroxy-, 15-hydroxy-, and 17-ketodehydroabietic acids – have been isolated from an extract of needle-free shoots of the Scotch pine and have been identified in the form of methyl esters.

The terpenoid components of the oleoresin [1-3], of the extractive substances of the trunk part of the tree [4-6], of the bark [7, 8], and of the needles [9, 10] of the Scotch pine (*Pinus sylvestris* L.) have been studied in detail. Of the diterpenoids in the oleoresin, compounds of the pimaric and isopimaric structural groups predominate [1-3], while in the needles the main components among the diterpenoids are isoabienol [11] and labdane acids – pinifolic acid and its derivatives [9, 10, 12].

The chemical compositions of needle-free shoots of the Scotch pine, which is an element of the technical verdure, has not previously been studied. Below we give informtion on the composition of the polar acids of the abietic and dehydroabietic group isolated from an acid fraction of the petroleum-ether soluble substances of an isopropanol extract. The yield of isopropanol extract amounted to 29.3% and that of the petroleum-ether-substances to 10.3%, of the weight of the absolutely dry shoots, the latter consisting to the extent of 53.0% of free acids. The free acids were isolated from the petroleum-ether-soluble fraction of the isopropanol extract in the usual way [13]. The isolated acids were separated by column chromatography into a series of fractions differing in polarity. The results of the separation are given in Table 1.

The first fraction eluted from the column consisted of higher fatty acids and resin acids, and the second of monomethyl pinifolate contaminated with higher fatty and resin acids. In the total free acids the resins acids made up 42.5%, the higher fatty acids 12.2%, and the monomethyl pinifolate (taking fraction 3 into account) 3.84%. Fraction 3 contained, in addition to the monomethyl pinifolate, acids with the following functional groups: an aromatic ring (IR spectrum: 1500-1600 cm^{-1}), carbonyl (1680 cm^{-1}) and acetate (1725 and 1240 cm^{-1}) groups, and hydroxy groups (3610 cm^{-1}). Fractions 4 and 5 consisted to hydroxy acids (1240, 1720, and 3620 cm^{-1}), and the fractions eluted from the column by ethanol consisted mainly of pigments and waxy substances.

The fractions obtained were methylated and separated into individual components by rechromatography on silica gel. Fractions 3 yielded dimethyl pinifolate (0.11 g), methyl 18-acetoxyanticoplate (0.81 g), and the monomethyl ester of pinosilvin (0.26 g). The same fraction also yielded the dimethyl ether of pinosilvin (0.03 g), probably produced from the monomethyl ether by its methylation by diazomethane. In addition to the components mentioned, two esters containing conjugated carbon groups in their molecules (1680 cm^{-1}) were isolated from this fraction.

The PMR signal of the first ester (0.16 g, 0.25% on the free acids) showed the signals of two olefinic protons (6.01 and 6.53 ppm), of an isopropyl group (two doublets with centers at 0.90 and 0.98 ppm, J = 7.0 Hz, each, 3 H each), and of two methyl groups (singlets at 0.80 and 1.20 ppm, 3 H each). The general form of the PMR spectrum made it possible to assume that the compound isolated with the methyl ester of a diterpene acid of the abietic type. A comparison of the UV and PMR spectra of this ester and the corresponding spectrum of methyl abietate permitted its structural features to be revealed. The positions of the absorption

S. M. Kirov Leningrad Academy of Wood Technology. Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 345-351, May-June, 1985. Original article submitted July 23, 1984.

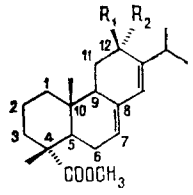
 0009-3130/85/2103-0322$09.50

bands in the UV spectrum of the compound under investigation (λ_{max} 295 nm, ε 10,100) showed that the keto groups was conjugated with a dienic structure [14].

In order to satisfy the IR and UV spectra obtained, the carbonyl group must be located at C_6 or C_{12} in the structure of methyl abietate, and it was possible to determine its position from the shift of the signals in the PMR spectrum of the protons at the carbon atoms of the trisubstituted double bonds of the compound isolated and of methyl abietate. A carbonyl group conjugated with the polyenic structure will exhibit a larger descreening effect on a closer proton at a carbon atom of a double bond than on a more remote one. This will lead to a greater downfield displacement of the signal of a proton attached to the carbon atom of the trisubstituted bond that is near to the carbonyl groups than of more remote proton of the polyenic system, as compared with the corresponding signals of methyl abietate. The signal of the proton at C_7 was shifted by 0.65 ppm and the signal of the proton at C_{14} by 0.78 ppm in comparison with the corresponding signals of the protons of the methyl abietate. Consequently, the carbonyl group must be located by C_{12} of the methyl abietate structure, i.e., the ester under investigation has the structure of methyl 12-oxoabietate (I).

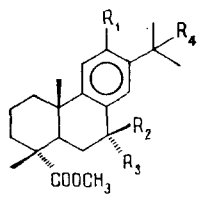
Our hypothesis was confirmed by a comparison of the compound isolated with an authentic sample of methyl 12-oxoabietate using TLC, GLC, and PMR methods.

The second ester, with mp 65-67°C contained a trisubstituted aromatic nucleus (IR spectrum: 1495, 1580, 1615 cm^{-1}; PMR spectrum: signals at 7.23 and 7.84 ppm, 3 H each), and a fragment representing an aryl alkyl ketone (1690 cm^{-1}). The presence in the structure of the compound of a ketone group conjugated with an aromatic nucleus was also indicated by features of its UV spectrum (λ_{max}, nm 212 ε 21,300; 255, ε 9800; 303, ε 1700). The general form of the PMR spectrum of the compound isolated permitted it to be assigned to the diterpenoids — to a methyl oxodehydroabietate. In accordance with spectral charcteristics for dehydroabietate derivatives, the keto group could be only at C_7. A comparison of the IR, UV, and PMR spectra of the ester isolated and of methyl 7-oxodehydro abietate (II) [15] showed their identity.



I. $R_1 + R_2 = O$

IV. $R_1 = H$; $R_2 = OH$



II. $R_1 = R_4 = H$; $R_2 + R_3 = O$

III. $R_1 = OH$; $R_2 = R_3 = R_4 = H$

V. $R_1 = R_2 = R_3 = H$; $R_4 = OH$

From the more polar fractions we isolated three methyl esters of hydroxy acids. The IR spectrum of a compound with mp 162-163°C, $[\alpha]_D^{23}$ + 75° showed absorption bands of an aromatic ring (1505 and 1620 cm^{-1}), of a phenolic hydroxyl (3610 cm^{-1}), of an ester group (1725, 1250 cm^{-1}), and of an isopropyl group (1370, 1387 cm^{-1}). The PMR spectrum of the compound had the signals of two methyls (1.12 and 1.21 ppm, singlets, 3 H each), the signals of the methyls of an isopropyl group (1.18 ppm, doublet, J = 7 Hz), of a $-COOCH_3$ group (3.6 ppm, singlet, 3 H), and the signals of the protons of a tetrasubstituted aromatic ring (6.59 and 6.83 ppm, singlets, 1 H each).

The IR and PMR spectra indicated that the compound isolated was a dieterpene hydroxy ester of the dehydroabietate series with a phenolic hydroxyl. On the basis of the PMR spectral characteristics for the signals of the protons of the aromatic ring it could be assumed that the phenolic hydroxyl was present at C_{12}. The correctness of the proposed structure was confirmed by a comparison of the IR, UV, and PMR spectra and other characteristics of the compound isolated with those published previously for methyl 12-hydroxydehydroabietate (III), obtained by the oxidation of methyl abietate with manganese dioxide [16].

The second hydroxy acid methyl ester, with $[\alpha]_D^{22}$ −86.4° was isolated in the form of the acetate after the acetylation of fraction 5. The UV spectrum of this compound had λ_{max} (nm) 244, ε 18,900; 238 (shoulder); ε 16,00; and 250.5 (shoulder), ε 13,000, and was close to the UV spectrum of methyl abietate [15]. The abietate type of structure for the compound isolated was also confirmed by its PMR spectrum. In the weak-field part of the PMR spectrum there were the signals of protons at the carbon atoms of trisubstituted double bonds, the

TABLE 1. Results of the Separation of the Free-Acid Fraction by Column Chromatography

Fraction No.	Eluent	Content in the free acids		Notes
		g	%	
1	Petroleum ether–diethyl ether 7:3	36.55	53.0	Sum of the resin acids and higher fatty acids
2	" 7:3	4.81	7.0	Sum of the resin acids and higher fatty acids and of monomethyl pinifolate
3	" 6:4	4.90	7.1	Monomethyl pinifolate and oxoditerpene acids
4	" 1:1	2.43	3.5	Hydroxyditerpene acids
5	" 21:75	3.35	4.9	
6	" 2:8	3.64	5.2	Dibasic acids and hydroxy and dihydroxy acids
7	Diethyl ether	4.68	6.8	
8	Ethanol	8.60	12.5	Pigments and waxes
	Total	68.96	100	
	Taken for separation	69.94		
	Losses	0.55	0.79	

signals of which, at 5.53 and 5.98 ppm, were shifted more in the downfield direction than the analogous signals in the spectrum of compound (I) and were in a weaker field than the corresponding signals in the PMR spectrum of methyl abietate (5.35 and 5.75 ppm). The intensity of the multiplet with its center at 5.53 ppm was twice that of the signals with their center at 5.98 ppm. The second proton giving a signal in the PMR spectrum coinciding in its chemical shift with the signal of the proton at C_7 can be assigned to a proton geminal to an acetate group. The acetate group (PMR spectrum: 2.00 ppm, 3 H, singlet; IR spectrum: 1243 and 1725 cm^{-1}) in this case should be present in the allyl position with respect to the double bond at C_{12}. Saponification of the compound isolated gave the methyl ester of an hydroxy acid the PMR spectrtum of which was similar to that of methyl 12-hydroxyabietate (IV) obtained by the oxidation of the levopimaric acid with hypochlorite in an alkaline medium [17].

Fraction 6 yielded dimethyl pinifolate, which was obtained from pinifolic acid after the methylation of the fraction with diazomethane, and a crystalline hydroxy ester with mp 80-82°C. IR spectrum: free hydroxyl (3610 cm^{-1}), ester (1730 cm^{-1}). The PMR spectrum of the compound had the signals of the protons of a trisubstituted aromatic nucleus at 6.97 ppm, 1 H, and 7.17 ppm, doublet, J = 1.5 Hz, 2 H. In contrast ot the PMR spectrum of methyl 12-hydroxydehydroabietate the spectrum of the compound isolated lacked the signals of the protons of an isopropyl group and showed a singlet with an intensity of 6 H and a chemical shift of 1.38 ppm. The value of the chemical shift showed the presence in the compound of a gem-dimethyl group at a carbon atom with an electrophilic substituent. On the basis of its spectral characteristics, the compound isolated was identified as methyl 15-hydroxydehydroabietate.

The ketones of the extractive substances of different arts of coniferous trees are represented mainly by two groups – neutral triterpenes and norditerpene compounds [18-20]. This is the first time that 12-oxoabietate acid, identified in the form of its methyl ester, has been found in natural sources. It has been obtained previously by the oxidation of methyl abietate with potassium permanganate in pyridine [21] and with chromium trioxide in acetic acid [21], by photooxidation [22], and by the odidation of methyl levopimarate [17]. 7-Oxodehydroabietate acid has been isolated from the bark of Calocedrus decurrens [23] and 7-oxodehydroabietinol from the bark of the jack pine [24].

This is the first time that hydroxy acids of the abietate and dehydroabietate series with the hydroxy group in the C_{12} position have been isolated from plants, but they have been obtained as products of the oxidation of levopimaric and abietate acids with various oxidizing agents [16, 17]. 12-Hydroxydehydroabietane has been found in the resin of Cupressus sempervirens [25]. Methyl 15-hydroxydehydroabietate has been isolated from the neutral fraction of the oleoresin of the Japenese stone pine [26]. 15-Hydroxydehydroabietatic acid is present in the oleoresin of the Korean pine [27] and in the bark of the Norway spruce [28] and of Agathis species [29].

A comparison of the composition of the polar diterpene acids from the extractive substances of the needles [9, 10, 12] and shoots of the Scotch pine shows a difference in their composition. The dieterpene acids from the needles consisted mainly of acids of the labdane type belonging to the 4-epiagathic and 4-epiimbricatolic series. The acids from the shoots contains – in addition to the acids of the labdane type, which were present in the shoots in considerably smaller amount than in the needles – keto and hydroxy acids of the abietic and dehydroabietic series.

EXPERIMENTAL

PMR spectra (δ scale, HMDS, CCl_4) were recorded on a Varian A 56/60 instrument and IR and UV spectra on UR-20 and Specord UV-VIS instruments using solutions in CCl_4 and ethanol, respectively. Optical radiation was measured on a Zeiss polarimeter.

For chromatography we used air-dry silica gel of type L (0.100-0.160 mm) with, as eluent, petroleum ether containing increasing amounts (from 2 to 100%) of ethyl ether.

Isolation of the Total Acids. The wood of the pine Pinus sylvestris felled in March 1982, in the Lisinskaya forestry farm, Leningrad province, was freed from branches, which were then sorted according to thickness, and for the investigation the branches with a diameter of not more than 10 mm were collected. The needles were removed from the shoots by hand and the needle-free shoots were ground to a powder. Extraction with isopropanol was carried out in Soxhlet apparatuses for 10 h. The isopropanol was distilled off and the residue was extracted successively with petroleum ether, diethyl ether, and butanol. The yield of the petroleum ether fraction was 10.3% on the weight of the absolutely dry shoots. The free acids were isolated from an ethereal solution of the petroleum ether-soluble fraction of the isopropanol extract with a 2% aqueous solution of NaOH. The aqueous solution of salts of the free acids was acidified with 12% sulfuric acid to pH 1, and the liberated organic acids were extracted with ether. Yield: 70.0 g.

Separation of the Total Acids into Individual Components. The acids obtained were chromatographed on a column of silica gel. The results of the separation are given in Table 1. Fractions 1-3 were methylated with a mixture of methanol and sulfuric acid [30], and the resulting fatty acids methyl esters from fractions 1 and 2 were separated from the resin acids on a column of silica gel. The fatty acid methyl esters were eluted with petroleum ether containing 5% of diethyl ether, and the resin acids with petroleum ether containing 25% of diethyl ether. From fraction 2, petroleum ether containing 10% of diethyl ether eluted dimethyl pinifolate. The methylatable (methanol–sulfuric acid) part of fraction 3 also yielded dimethyl pinifolate together with methyl 18-acetoxyanticopalate.

Dimethyl Pinifolate: 3.84% of the total free acid, $[\alpha]_D^{25}$ +26.2° (chloroform was compared with an authentic sample of dimethyl pinifolate by GLC and TLC. According to the literature: $[\alpha]_D$ +27° (chloroform) [9].

Methyl 18-Acetoxyanticopalate: 0.81 g $[\alpha]_D^{23}$ +36.5° (c 10; chloroform), isolated from the acid fraction of the shoots with ether was identified according to its PMR spectrum with a sample of methyl 18-acetoxyanticopalate from the needles [12].

Isolation of Methyl Esters of Keto Acids. The part of fraction 3 not methylated by the methanol–sulfuric acid mixture was methylated with diazomethane, and chromatography yielded the dimethyl ether of pinosilvin (0.03 g, identified by GLC and TLC with an authentic sample), two esters of oxo acids (IR spectrum: 1260 and 1730, 1680 cm^{-1}), and the monomethyl ether of pinosilvin (0.26 g, mp 120-121°C, identified by GLC and TLC with an authentic sample of the monomethyl ether of pinisilvin). Rechromatography of the esters of the oxo acids on a column of silica gel yielded the ester (I) and the crystalline ester (II).

Methyl 12-Oxoabietate (I): 0.16 g, colorless oil, UV spectrum, λ_{max}, nm: 295, ε 10,100; IR spectrum, cm^{-1}: 870, 980, 1650, (>C=CH–), 1680 (>C=C–C=O), 1250 and 1730 (–COOC–); PMR spectrum, ppm: 0.80 and 1.20 (singlets, 3 H each, CH_3 at C_{10} and C_4); doublets with centers at 0.90 and 0.98 (3 H each, J = 7 Hz, methyls of an isopropyl group); 3.58, singlet, 3 H, $-COOCH_3$); 6.01 (multiplet, 1 H, H_7); 6.53 (singlet, 1 H, H_{14}).

Methyl 7-Oxodehydroabietate (II): 0.89 g, mp 65-67°C, $[\alpha]_D^{22}$ +7.8 (c 5.2; ethanol). UV spectrum: λ_{max}, nm, 212, 255, 303 (ε 21,300, 9800, 1700). IR spectrum, cm^{-1}: 1260, 1730 ($-COOCH_3$); 1495, 1580, 1615 (aromatic ring); 1680 (–C=O conjugated with an aromatic ring). PMR spectrum: 1.13 and 1.23 (6 H, doublet, J = 7 Hz, isopropyl group); 1.18 (3 H, singlet,

(C_{10}–CH_3); 1.23 (3 H, C_4–CH_3), 3.57 (3 H, singlet, –$COOCH_3$), 7.23 (2 H, singlet, H_{11} and H_{12}); 7.84 (1 H, singlet, H_{14}). According to the literature [15]; mp 66-67°C, $[\alpha]_D$ +6.7°.

Isolation of Methyl Esters of the Hydroxy Acids. Methyl 12-Hydroxydehydroabietate (III). Fraction 4 was methylated with diazomethane. By chromatography on silica gel of the methyl esters of fraction 4 (petroleum ether with the addition of 15% diethyl ether) a fraction was first eluted which contained crystals, and these were recrystallized from acetonitrile giving 0.32 g of a product with mp 162-163°C, $[\alpha]_D^{23}$ +75° (c 0.93; ethanol). UV spectrum λ_{max} 283 nm, ε 3400; IR spectrum, cm^{-1}: 910, 1505, 1620 (aromatic ring); 1250, 1725 (–$COOCH_3$); 3610 (phenolic hydroxyl); 1370-1387 cm^{-1} (isopropyl group). PMR spectrum, ppm: 1.12 (3 H, singlet, C_{10}–CH_3); 1.21 (3 H, singlet, C_4–CH_3); doublet with its center at 1.18, J = 7 Hz, 6 H (methyls of an isopropyl group); 3.60 (3 H, singlet, –$COOCH_3$); 6.83 (1 H, singlet, H_{11}); 6.59 (1 H, singlet, H_{14}). According to the literature [16], mp 160-161°C, $[\alpha]_D$ +74°.

Isolation of Methyl 12-Hydroxyabietate. The IR spectrum of fraction 5 after its methylation with diazomethane had adsorption bands in the 3615 cm^{-1} region with an inflection at 3630 cm^{-1} of secondary and primary hydroxyls, and also the absorption bands at 1730 and 1250 cm^{-1} of an ester. The methyl esters were separated into a number of fractions by chromatography on a column of silica gel. The first fraction contained the methyl esters of saturated aliphatic hydroxy acids (PMR) of unknown structure (three components difficult to resolve by the GLC method on the liquid phase SE-30). According to its PMR spectrum the second fraction consisted of the methyl esters of hydroxy acids of the labdane and abietate type: 5.45 and 5.55 ppm, multiplet and singlet, respectively, from H_7 and H_{14} for the compounds of the abietic type; 4.46 and 4.76 – signals of the protons of an exomethylene group of compounds of the labdane type. These compounds were difficult to separate by chromatography on plates coated with silica gel impregnated with 5% of $AgNO_3$. Acetylation of the fraction with acetic anhydride in pyridine gave acetates which had close but different R_f values on TLC. These compounds were separated by column chromatography on silica gel. The compound eluted first was identified as methyl 12-acetoxyabietate, and the second as methyl 18-acetoxyanticopalate.

Methyl 12-Acetoxyabietate. UV spectrum, nm: λ_{max} 244, ε 18,000 with a shoulder at 238, ε 16,000, and 250, ε 13,000. IR spectrum, cm^{-1}: 1243 and 1725 (acetate), 895, 1645 (trisubstituted double bond; 1200, 1725 (–$COOCH_3$). PMR spectrum, ppm: 0.75 (3 H, singlet, C_{10}–CH_3); 0.98 and 1.00 (6 H, doublets with J = 7 Hz, methyls of an isopropyl group); 1.21 (3 H, singlet, C_4–CH_3); 2.00 (3 H, singlet, acetate), 3.60 (6 H, singlet, –$COOCH_3$, 5.53 (2 H, multiplet, H_7 and H_{12}); 5.98 (1 H, singlet, H_{14}).

Saponification in 0.5 N KOH (ethanol) gave 0.25 g of methyl 12α-hydroxyabietate in the form of an oil, $[\alpha]_D^{23}$ –116° (c 3.2; chloroform). The UV and PMR spectra of the compound isolated were similar to those of methyl 12α-hydroxyabietate [17]. According to the literature: $[\alpha]_D$ –117° [17]; $[\alpha]_D$ –120° [31].

Isolation of Methyl 15-Hydroxydehydroabietate. The chromatography of fraction 6 after its methylation with diazomethane yielded a fraction containing crystals. After recrystallization from petroleum ether with the addition of diethyl ether, 0.25 g of crystals with mp 80-81°C was obtained. UV spectrum, nm: 275, ε 560; 267, ε 580; 260, ε 430. PMR spectrum, ppm: 1.11 (C_4–CH_3); 1.17 (C_{10}–CH_3); 1.38 (6 H, singlet, gem-dimethyl group); 3.54 (3 H, singlet, –$COOCH_3$); 6.97 (1 H, H_{14}); 7.17 (2 H, doublet, J = 1.5 Hz, H_7). According to the literature [29]: mp 82° for $C_{21}H_{30}O_3 \cdot H_2O$; after sublimation of the crystals, mp 90-91°C.

SUMMARY

Diterpene keto and hydroxy acids of the abietic and dehydroabietic type have been isolated in the form of methyl esters from the extractive substances of needle-free shoots of the pine Pinus sylvestris L. This is the first time that 12-oxoabietic, 12-hydroxyabietic, and 12-hydroxyhydroabietic acids have been isolated from a natural source.

LITERATURE CITED

1. É. N. Shmidt and V. A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., No. 9, 144 (1968).
2. V. K. Morozkov, É. N. Shmidt, and V. A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., No. 2, 128 (1972).
3. I. I. Bardyshev and E. P. Dontsova, in: Synthetic Products from Rosin and Turpentine [in Russian], Gor'khii (1970), p. 36.

4. A. I. Lisina, N. V. Svirskaya, and V. A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 5, No. 12, 142 (1974).
5. L. Westfelt, Acta Chem. Scand., 20, 2829 (1966).
6. D. Manell, G. Pensar, Paper och Trä, 57, No. 3, 1 (1975).
7. T. Norin and B. Winnel, Acta Chem. Scand., 26, 2297 (1972).
8. V. I. Lutskii, A. S. Gromova, and N. A. Tyukavkina, Khim. Prir. Soedin., 367 (1970).
9. C. Enzell and O. Theander, Acta Chem. Scand., 16, 607 (1962).
10. I. I. Bardyshev, A. S. Degtyarenko, T. I. Pekhk, and S. A. Makhnach, Khim. Prir. Soedin., 568 (1981).
11. R. Ekmanm, R. Sjöholm, and K. Hannus, Acta Chem. Scand., 31, 921 (1977).
12. V. I. Roshin, L. A. Kolodynshaya, V. A. Raldugin, and V. A. Pentegova, Khim. Prir. Soedin. 114 (1984).
13. V. I. Roshchin, V. A. Baranova, O. A. Belozerskikh, and V. A. Solov'ev, Khim. Drev., No. 4, 56 (1983).
14. L. Bellamy, Infrared Spectra of Complex Molecules, 2nd ed., Methuen, London/Wiley, New York (1958).
15. A. Koptyug, Atlas of Spectra of Natural Compounds and Their Analogs, [in Russian], Novosibirsk, No. 1 (1978).
16. R. C. Cambie and R. A. Franich, Austral. J. Chem., 24, 117 (1971).
17. W. Herz, H. Wahlborg, W. Lloyd, W. Schuller, and G. Hedrick, J. Org. Chem., 30, 3190 (1965).
18. J. W. Rowe and C. L. Bower, Tetrahedron Lett., 2745 (1965).
19. J. W. Rowe, Phytochemistry, 4, 1 (1965).
20. T. Norin and B. Winnel, Cata Chem. Scand., 25, 611 (1971).
21. M. I. Goryaev, E. B. Popova, F. S. Sharipova, and L. K. Tikhonova, Izv. Akad. Nauk Kaz-SSR, Ser. Khim. Nauk, No. 6, 59 (1974).
22. R. N. Moore, R. W. Lawrence, J. Am. Chem. Soc., 81, 458 (1959).
23. L. J. Gough and J. S. Mills, Phytochemistry, 13, 1612 (1980).
24. J. W. Rowe, B. A. Nagasampagi, A. W. Burgstahler, and J. W. Fitzsimmons, Phytochemistry, 10, 1647 (1971).
25. L. Mangoni and R. Caputo, Gazz. Chim. Ital., 97, 908 (1967).
26. V. A. Raldugin and V. A. Pentegova, Khim. Prir. Soedin., 595 (1971).
27. V. A. Raldugin and V. A. Pentegova, Khim. Prir. Soedin., 158 (1983).
28. T. Norin and B. Winnel, Acta Chem. Scand., 26, 2289 (1972).
29. R. M. Carman and R. A. Marty, Austral. J. Chem., 1457 (1970).
30. V. P. Sumarokov, M. L. Vap'yan, and A. I. Askinazi, Tall Oil [in Russian], Moscow (1965), p. 146.
31. Yu. A. Silko, V. A. Raldugin, V. I. Mamatyuk, and V. A. Pentegova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 1, 106 (1984).