STUDY OF THE NEUTRAL FRACTION OF THE OLEORESIN OF PINUS KORAENSIS

I. Main Diterpenoid Components

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The diterpenoids of one of the species of Pinus (P. sibirica R. Mayr.), which form part of the group Cembrae have been studied previously [1–5]. A comparative study of the diterpenoids of other species of Pinus of the same group appears important from the point of view of chemotaxonomy.

This paper gives information on the main diterpenoids of the neutral fraction of the oleoresin of Pinus koraensis Sieb et Zucc.

We separated the combined neutral diterpenoids, obtained from the oleoresin by the usual method [5], into a hydrocarbon fraction and an oxygen-containing fraction. From the hydrocarbon fraction we isolated the macrocyclic diterpene hydrocarbons, cembrene and isocembrene, with constants corresponding to those given in the literature [4]. The presence of cembrene in the oleoresin of Pinus koraensis was first established by Mirov [6]. After repeated chromatographic separation of the oxygen-containing fraction, six diterpenoids were obtained. Their individuality was confirmed by thin-layer and gas-liquid chromatography. Five of them [isocembrol with $[\alpha]_D^{24}$ +79.5° (c 2.16, $CHCl_3$), n_D^{25} 1.5012; methyl lambertianate with $[\alpha]_D^{25}$ +68.5° (c 2.24, $CHCl_3$), n_D^{24} 1.5140; methyl dehydroabietate with mp 60–61° C (from petroleum ether), $[\alpha]_D^{25}$ +58° (c 0.10, ethanol); agathadiol with mp 108–109° C (from ethanol), $[\alpha]_D^{23}$ +51.5° (c 0.58, $CHCl_3$); and lambertianic acid with mp 125–126° C (from ethanol), $[\alpha]_D^{30}$ +55.5° (c 0.92, $CHCl_3$)] were identified by their IR spectra and by a chromatographic (TLC, GLC) comparison with authentic samples.

The sixth diterpenoid was a primary alcohol ($\nu_{max}^{CCl_4}$ 3650 and 1055 cm^{-1}), $[\alpha]_D^{22}$ +46.9° (c 0.42, $CHCl_3$) having an isopropyl group ($\nu_{max}^{CCl_4}$ 1390 and 1370 cm^{-1}) and a 1, 2, 4-trisubstituted benzene ring ($\nu_{max}^{CCl_4}$ 1620, 1510, 890, and 830 cm^{-1}). Its NMR spectrum (60 MHz, internal standard tetramethylsilane, δ scale) showed the presence of the dehydroabietane carbon skeleton. Thus, a multiplet of three protons of an aromatic ring (6.73–7.24 ppm) was identical in the nature of its splitting with that for methyl dehydroabietate; a distorted doublet (J = 6.6 Hz) with components at 1.17 and 1.28 ppm is the signal of the methyl protons of an isopropyl group, and two singlets (1.22 and 0.90 ppm) relate to two tertiary methyl groups present on C_{10} and C_4, respectively [7]. A hydroxymethylene group is present at C_4. The signals of its methylene protons form an AB system (δ_A 3.23, δ_B 3.47 ppm, J_{AB} = 10.5 Hz) the chemical shift of whose center shows the equatorial configuration of the hydroxymethylene group [8, 9]. Consequently, the isolated alcohol is dehydroabietinol [9, 10]; 3, 5-dinitrobenzoate with mp 123–124° C (from petroleum ether), according to the literature mp 123–124° C [10].

This is the first time that methyl dehydroabietate and dehydroabietinol have been isolated from Pinaceae; it must be mentioned that dehydroabietinol has not previously been found in a natural source. In addition to the diterpenoids described above, the presence of abietinol, abietinal, 3, 5-dimethoxy-trans-stilbene, and 5-hydroxy-3-methoxy-trans-stilbene was established by chromatography (TLC: SiO_2 + 15% gypsum + 5% $AgNO_3$) in comparison with authentic samples.

Thus, the qualitative composition of the complex of the main diterenoids of Pinus koraensis Sieb et Zucc. is basically identical with that for Pinus sibirica R. Mayr.

Further study of the neutral diterpene compounds of Pinus koraensis Sieb et Zucc. is continuing.

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