# DEHYDROABIETANE FROM THE OLEORESIN OF Pinus pallasiana

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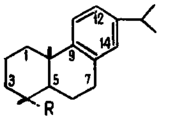
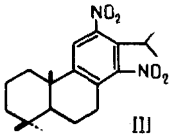
We have previously [1] established the composition of the oxygen-containing neutral unsaponifiable fraction of the oleoresin of the Crimean pine. In the present paper we describe the isolation from the same oleoresin of the diterpene hydrocarbon dehydroabietane (I) and its identification. Synthetic dehydroabietane was known previously [2] and has been obtained repeatedly [3-6], but this is the first time it has been found in a natural source. From the hydrocarbon fraction isolated previously [1], traces of monoterpenes and sesquiterpenes were eliminated by redistillation in vacuum. The residue was chromatographed on a column of silica gel impregnated with silver nitrate. The first fraction, by polarity, taken from the column consisted, according to GLC, of two components. The predominating component was purified by preparative GLC. Its analysis and mass spectrum showed it to be a diterpene hydrocarbon. Its IR spectrum had maxima characteristic for an aromatic ring substituted in positions 1, 2, and 3 (830, 1500, 1610, and 3030 $cm^{-1}$). The presence of such a ring was also confirmed by its UV spectrum (shoulder at 262 nm and maxima at 268 and 276 nm) and by its NMR spectra (there is a one-proton singlet in the region of aromatic protons at 6.70 ppm which is superposed on a two-proton AB quartet with a center at 6.86 ppm). In addition, the NMR spectrum has three three-proton singlets at 0.96, 1.09, and 1.16 ppm showing the presence of three methyl groups attached to tertiary carbon atoms, a six-proton doublet at 1.13 ppm due to an isopropyl group, and a multiplet of three benzyl protons at 2.76 ppm.

The spectral characteristics given above are similar to those for dehydroabietic acid and its derivatives [6-8]. Consequently, the hydrocarbon that we isolated is dehydroabietane (I). In actual fact, a comparison of its mass spectrum with that given for dehydroabietane by Enzell and Ryhage [9] showed that they were identical.



I $R = CH_3$, IV $R = CO_2CH_3$,
II $R = CHO$. V $R = CH_2OH$



III

Finally, the natural hydrocarbon was shown to be identical with a synthetic dehydroabietane obtained by the reduction of the semicarbazone of dehydroabietinal (II) by the Wolff–Kishner method. The two hydrocarbons had the same spectral characteristics and chromatographic behavior. Their titration with a mixture of nitric and sulfuric acids [3] gave the same product – 12,14-dinitrodehydroabietane (III).

## EXPERIMENTAL

The IR spectra were taken in carbon tetrachloride on a UR-10 spectrophotometer, the UV spectra on an SF-4 instrument in ethanol, the NMR spectra in carbon tetrachloride on a Varian 100 instrument (with hexamethyldisiloxane as internal standard), and the mass spectra on an MKh-1303 instrument.

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Isolation of Dehydroabietane (I). From the hydrocarbon fraction of the oleoresin (91 g) [1], a fraction boiling up to 80°C (bath temperature) at 7 mm was first distilled off, and then a fraction boiling up to 140°C at 0.7 mm. The residue (34 g) was chromatographed on a column containing 320 g of silica gel impregnated with silver nitrate [10]. Light petroleum ether (bp 40-60°C) containing 1% of benzene eluted 0.97 g of a mixture of two components (TLC on the same adsorbent [11] using 5% of benzene in petroleum ether as the mobile phase, $R_f$ 0.31 and 0.49). It was rechromatographed on a column containing 30 g of the same adsorbent. Petroleum ether eluted 630 mg of a product giving a single spot on TLC in silica gel impregnated with silver nitrate. However, according to GLC [glass column $l$ = 2 m, d = 3 mm, 10% of SE-30 on silanized Chromosorb W (60-80 mesh), $t_{evap}$ = 270°C, $t_{col}$ = 214°C, rate of flow of argon 17 ml/min, flame ionization detector] it consisted of two hydrocarbons in a ratio of 3 : 7 ($K_{sep}$ = 1.14).

Preparative separation (490 mg) was carried out on a UKh-1 instrument [steel column, $l$ = 2.2 m, d = 6 mm, 6% of SE-30 on silanized Chromosorb W (60-80 mesh) at 180°C, rate of flow of helium 80 ml/min, katharometer detector]. The amount of mixture separated in each run was 35-40 mg. The yield of dehydroabietane $C_{20}H_{30}$(I) was 260 mg, bp 120-122°C (0.06 mm), $[\alpha]_D^{25}$ +53.8° (c 10, $CHCl_3$), mol. wt. 270 (mass spectrometry). IR spectrum, $cm^{-1}$: 830, 894, 976, 1500, 1610, and 3030; $\lambda_{max}$ 262 (shoulder), 268, and 276 nm (log ε 2.82, 2.90, and 2.89). NMR spectrum (δ, ppm): singlets (3 H) at 0.96, 1.09, and 1.16 ($C_4$– and $C_{10}$–$CH_3$ groups), doublet (6 H) at 1.13 (J = 7 Hz) (isopropyl group), singlet (1 H) at 6.70 ($C_{14}$–H), AB quartet (2H) at 6.86 (J = 8 Hz), ($C_{11}$– and $C_{12}$–H), multiplet (3 H) at 2.76 ($C_{15}$– and $C_{17}$–H). It was impossible to bring about the crystallization of the dehydroabietane isolated. According to the literature, mp 41-44°C [2], bp 135°C (0.05 mm), $[\alpha]_D$ 50° [3].

Synthesis of Dehydroabietane (I). Methyl dehydroabietate (IV) (1 g, mp 58-59°C) was boiled with 900 mg of lithium aluminum hydride in 100 ml of absolute ether for 5 h. After the usual working up, 900 mg of pure (according to TLC) dehydroabietinol (V) was obtained, and this was dissolved in 9 ml of dry pyridine and the solution was added to the complex prepared from 900 mg of chromic anhydride and 9 ml of dry pyridine. The solution was left at 22°C for 17 h and was worked up in the usual manner. This gave 740 mg of dehydroabietinal (II) which, without further purification, was converted into the semicarbazone with mp 222-223°C (from methanol). Yield 540 mg. According to the literature, mp 225-226°C [3].

In an atmosphere of nitrogen, 6.8 g of caustic potash was added to a solution of 540 mg of the semicarbazone in 20 ml of diethyleneglycol heated to 100°C, and the temperature of the solution was gradually raised to 205°C and was kept there for 3 h. Then it was cooled and extracted with petroleum ether. The extract was washed with water to neutrality and dried with sodium sulfate, and the solvent was distilled off. The residue (330 mg) was chromatographed on a column containing 10 g of alumina (activity grade II). Petroleum ether eluted 269 mg of dehydroabietane (I), bp 123-125°C (0.06 mm), $[\alpha]_D^{23}$ +51.5° (c 5; $CHCl_3$). According to chromatographic and spectroscopic characteristics it was identical with the natural hydrocarbon.

12,14-Dinitrodehydroabietane (III). The natural and the synthetic dehydroabietanes (30 mg in each case) were nitrated as described by Jeger et al. [3]. After three recrystallizations from ethanol, the products and a mixture of them melted at 185-186.5°C. According to the literature, mp 189-190°C [3].

## SUMMARY

The known diterpene hydrocarbon dehydroabietane has been isolated from a natural source – the oleoresin of the Crimean pine – for the first time.

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