DITERPENE HYDROCARBONS OF THE OLEORESIN OF Pinus pallasiana

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Continuing an investigation of the composition of the neutral unsaponifiable fraction of the oleoresin of the Crimean pine, we have studied the diterpene components of the hydrocarbon fraction [1] remaining after the mono- and sesquiterpenes have been distilled off in vacuum [2]. The residue, which consisted according to TLC on silica gel impregnated with silver nitrate (SGSN) of a mixture of five compounds, was separated by column chromatography on the same adsorbent. The final purification of the substance isolated was performed by rechromatography on SGSN or by preparative GLC. Below we give, in order of increasing polarity, the diterpene hydrocarbons that were isolated and identified: 1) dehydroabietane, bp 120-122°C (0.06 mm), $[\alpha]^{25}_{D}$ +52.8° (angles of rotation measured in $CHCl_3$ [2]); 2) abietadiene, n^{20}_{D} 1.5300, $[\alpha]^{22}_{D}$ −77°; 3) pimaradiene, which predominated in the mixture (~60-65%), bp 82-84°C (0.07 mm), $[\alpha]^{22}_{D}$ +92°; and 4) isopimaradiene (~20-25%), bp 143-146°C (0.1 mm), $[\alpha]^{22}_{D}$ −31.4°. All the diterpenes listed were identified by direct comparison with authentic samples.

The most polar fraction (620 mg) eluted from the SGSN column consisted, according to GLC [2], of six substances. By a combination of preparative GLC [2] and column chromatography on SGSN we succeeded in isolating from this fraction a liquid hydrocarbon (26.6 mg) with the composition $C_{20}H_{32}$, $[\alpha]^{20}_{D}$ +37.9° mol. wt. 272 (mass spectrometry). IR spectrum (CCl_4): 827, 917, 1003, 1367, 1384, 1420, 1640, 3060, 3100 cm^{-1} (gem-dimethyl and vinyl groups), similar to the IR spectra of pimaradiene and isopimaradiene. The NMR spectrum (taken in CCl_4 on a Varian HA 100 instrument with TMS as internal standard, δ, ppm) had the following signals: singlets (3 H) at 0.62, 1.00, 1.01, and 1.06 (CH_3 group on quaternary carbon atoms), a poorly resolved triplet at 5.42 $\left(\gt C{=}C\lt_{H}\right)$ and signals of an ABC system – an octet with its center at 4.82 (2 H, J_{AB} = 10.5 Hz, J_{AC} = 17.5 Hz, J_{BC} = 1.5 Hz) and a quartet with its center at 5.72 (1 H, J_{AB} = 10.5 Hz, J_{AC} = 17.5 Hz). The signal from one of the methyls was present in a fairly strong field (0.62 ppm), which is characteristic only for a rimuene structure with a β-methyl at C_9 and a Δ^5 double bond. The position and form of the signal of the vinyl proton on a trisubstituted double bond, which are analogous to those in the PMR spectrum of rimuene [4], also agree with this structure. However, the region of the vinyl group of the PMR spectrum of the hydrocarbon that we had isolated differs from the corresponding region of the PMR spectrum of rimuene given by Wenkert and Beak [4] and is almost identical with the analogous region of the spectrum sandaracopimaradiene. Its physical constants also differed from those of rimuene. As has been established [5], the position of the double bond in the ring and the configuration at C_{13} affect the nature of the signals of a vinyl group in the PMR spectra of tricyclic diterpene dienes. In view of this, we have ascribed to the hydrocarbon investigated the structure of 13-epirimuene. So far as we know, this is the first case of the isolation of 13-epirimuene from a natural source.

The bulk of the residue after the distillation off of the mono- and sesquiterpenes from the hydrocarbon fraction of the oleoresin of the Crimean pine consists of a polymeric product.

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