(−)-GERANYLLINALOOL FROM THE OLEORESIN OF Picea obovata

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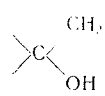
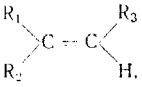
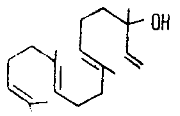
We have previously reported the isolation from the high-boiling neutral faction of the oleoresin of Picea obovata Ledb. (Siberian spruce) of cembrene, isocembrol, neoabienol, dehydroabietinol, neocembrene, and epimanoyl oxide [1]. Continuing our investigation of this fraction of the oleoresin, we have isolated a compound with the empirical formula $C_{20}H_{34}O$ (n_D^{24} 1.4878), $[\alpha]_D$ −14.1° (c 0.34; chloroform), mol. wt. 290 (mass spectrometry), the hydrogenation of which in acetic acid in the presence of PtO_2 showed the presence of four double bonds in it. The UV spectrum of the compound lacks a maximum in the 220-240 nm region.

The IR spectrum contains absorption bands characteristic for a hydroxy group (3615, 1120 cm^{-1}), a vinyl group (930, 1000, 1655, 3090 cm^{-1}), and a trisubstituted double bond (850, 1680 cm^{-1}).

The NMR spectrum (CCl_4, 60 MHz) has the signals of four methyl groups at 1.56 ppm (9H) and 1.65 ppm (3H), these being present on double bonds. A singlet with a chemical shift of 1.20 ppm is assigned to a methyl in a  $>C<^{CH_3}_{OH}$ fragment. In the low-field region a signal at 5.00 ppm with an intensity of 3H is due to the olefinic protons of a  $^{R_1}_{R_2}>C=C<^{R_3}_{H}$ bond, and multiplets with chemical shifts of 5.80, 5.18, and 4.86 ppm are characteristic for the protons of a vinyl double bond.

The facts above enable the compound isolated to be identified as geranyllinalool (I) [2].



I

Geranyllinalool, like geranylgeraniol, is considered a possible biogenetic precursor of the cyclic diterpenoids [3]. Its presence in a natural material rich in diterpenes may be considered as an indirect confirmation of Ruzicka's hypothesis of the formation of bi- and tricyclic diterpenes from an acyclic compound [4].

In addition to geranyllinalool, we isolated a norditerpene alcohol of the dehydroabietane type with mp 91-92°C, $[\alpha]_D$ +53.3° (c 0.34; methanol) with spectral characteristics and a melting point close to those for 18-nordehydroabietan-4-α-ol [5, 6] and to the hydrocarbon 18-nordehydroabiet-4(19)-ene, with n_D^{24} 1.5300, $[\alpha]_D$ +154° (c 0.40; chloroform). Literature data: $[\alpha]_D$ +152° (c 0.20; methanol) [6].

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