

NEUTRAL FRACTION OF THE OLEORESIN OF PINUS SILVESTRIS

II. Dehydroabietinol Acetate

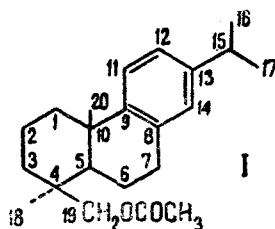
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We have previously [1] reported the isolated from the neutral high-boiling fraction of the oleoresin of Pinus silvestris L. (Scotch pine) of eight diterpene compounds. Continuing a study of the oleoresin, we have chromatographed the neutral fraction on silica gel containing 12% of silver nitrate. Petroleum ether containing 12% of diethyl ether eluted a crystalline substance with mp 60–61° C, $[\alpha]_D^{20} + 62.2^\circ$.

Its IR spectrum had bands at 835 cm^{-1} , 1510 cm^{-1} (aromatic ring), and 1250 and 1740 cm^{-1} (ether linkage). The UV spectrum had two maxima at 267 and 275 $\text{m}\mu$ ($\log \epsilon$ 2.6, 2.7); mol. wt. 318 (mass spectrometry).

From its spectral characteristics and elementary composition, this substance, $\text{C}_{22}\text{H}_{32}\text{O}_2$, must be similar to derivatives of dehydroabietic acid [2,3]. Consequently, it may be assumed that it is the acetate of dehydroabietinol, a diterpene alcohol obtained by the reduction of dehydroabietic acid [4]. Dehydroabietinol acetate has the structure I:



The nuclear magnetic resonance spectrum of the acetate fully confirms its structure. In the NMR spectrum (CCl_4 , 60 MHz) there are signals at 1.08 ppm ($\text{C}_{10}-\text{CH}_3$); 1.13 and 1.18 ppm [C_4-CH_3 ; $\text{C}_{15}-(\text{CH}_3)_2$; $J = 5$ Hz]; 1.81 ppm ($\text{CO}-\text{CH}_3$); and 3.55 ppm (CH_2OAc).

In the weak-field region there are signals at 6.81 ppm (1H) and 6.91 ppm (2H; AB, $J = 7.5$ Hz) which shows the presence of a 1,2,4-trisubstituted aromatic ring in the acetate.

A broadened singlet at 3.55 ppm may be assigned to an equatorial CH_2OAc group at C_4 . The possibility of the determination of the conformation of the side chains by the NMR method for diterpene compounds has been shown previously [5,6].

Thus, the substance that we isolated is dehydroabietinol acetate and this is the first time that it has been obtained as a native product from the oleoresin of the Scotch pine.

The oleoresin of Pinus silvestris L. differs from the oleoresin of other Siberian conifers by the presence of aromatic diterpenes (dehydroabietinal [1], dehydroabietinol acetate), which may probably serve as an additional indication in the taxonomy of the subgenus Diploxylon.

REFERENCES

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