4-EPIISOCEMBROL – A NEW DITERPENOID FROM THE OLEORESIN OF *Pinus koraiensis* AND *P. sibirica*

V. A. Raldugin and V. A. Pentegova

UDC 547.596

By the chromatographic separation of the neutral diterpenoids of the oleoresin of *Pinus koraiensis* Sieb. et Zucc. and *P. sibirica* R. Mayr we have obtained a new compound, $C_{20}H_{34}O$, n_D^{22} 1.5010, $[\alpha]_D^{22}$ +110.5° (c 3.35; chloroform). Mol. wt. 290 (mass spectrometry).

The spectral characteristics of the compound isolated are close to those of isocembrol [1, 2]. In the IR spectrum (CCl_4) there are absorption bands at 3620 and 1108 cm^{-1} (tertiary OH group), 1675 and 985 cm^{-1} (trans-disubstituted double bond), and 1393 and 1378 cm^{-1} (isopropyl group). In its NMR spectrum (60 MHz in CCl_4 with TMS as internal standard, δ scale) there are the signals of the methyls of an isopropyl group (two doublets at 0.75 and 0.78 ppm, J = 6.0 Hz), of a methyl group adjacent to a hydroxyl (1.21 ppm), of two methyl groups on double bonds (1.51 and 1.58 ppm), and of two protons of a trans-disubstituted double bond forming an AB system with J_{AB} = 15 Hz, δ_A = 5.26, and δ_B = 5.49 ppm. The components of the A part of the AB system are split into doublets with J = 7.0 Hz because of vicinal interaction analogous to that which is shown in isocembrol between H_1 and H_2. At 4.85-5.15 ppm there is a broad multiplet of two protons present on trisubstituted double bonds.

The dehydration of this alcohol with phosphorus oxychloride in pyridine gave a mixture of two hydrocarbons, which were identified as cembrene and isocembrene. Since the cembrene from this mixture is dextrorotatory, $[\alpha]_D^{18}$ +234° (c 1.71; chloroform), like natural cembrene with the 1S configuration [3], the diterpenoid isolated is the epimer of isocembrol at C_4, i.e., 4-epiisocembrol.

The two epimers cannot be separated on Al_2O_3 and SiO_2, but differ strongly in their degree of retention on SiO_2 + 5% of $AgNO_3$. The ratios of cembrene and isocembrene formed in the dehydration of isocembrol and 4-epiisocembrol with phosphorus oxychloride in pyridine are different: for isocembrol 85 : 15, and for 4-epiisocembrol 66 : 34 (NMR spectra). Isocembrol and 4-epiisocembrol are present in the oleoresin of *Pinus koraiensis* Sieb. et Zucc. in a ratio of 4 : 1 [determined from the NMR spectrum of the fraction enriched with these compounds obtained by the chromatography of the total neutral diterpenoids of the oleoresin on Al_2O_3 (activity grade II-III)].

The absolute configuration of the epimeric isocembrols at C_4 is still unknown.

LITERATURE CITED

1. N. K. Kashtanova, A. I. Lisina, and V. A. Pentegova, Khim. Prirodn. Soedin., 4, 52 (1968).
2. B. Kimland and T. Norin, Acta Chem. Scand., 22, 943 (1968).
3. W. G. Dauben, W. E. Thiessen, and P. R. Resnick, J. Org. Chem., 30, 1693 (1965).

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 669-670, September-October, 1971. Original article submitted May 18, 1971.