NEOCEMBRENE — A NEW DITERPENE HYDROCARBON FROM Picea obovata and Pinus koraensis

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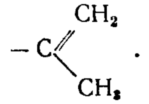
Studying the diterpene hydrocarbons of the oleoresin of Picea obovata Ledb. (Siberian spruce) and Pinus koraensis Sieb Zucc. (Korean pine), we have isolated a compound with the empirical formula $C_{20}H_{32}$, $[\alpha]_D^{20}$ − 20°, n_D^{20} 1.5110, the IR spectrum of which has absorption bands at 890, 1650, and 3080 cm^{-1}, which are characteristic for an exomethylene group, and at 830 and 1666 cm^{-1}, corresponding to a trisubstituted double bond. The UV spectrum has a maximum at 210 nm, which shows the absence of a conjugated diene system from the compound.

The PMR spectrum of the hydrocarbon (Fig. 1) has signals at 1.51 ppm (9H) and 1.60 ppm (3H) relating to four CH_3 groups on double bonds. In the weak-field region at 4.51 ppm there is a broadened singlet with an intensity of 2H relating to the protons of an exomethylene group and a broad signal with a chemical shift of 5.30 ppm and an intensity of 3H due to the protons of trisubstituted double bonds.

The exhaustive hydrogenation of the hydrocarbon over PtO_2 in acetic acid showed the presence of four double bonds in it and led to octahydrocembrene (II). Consequently, the hydrocarbon isolated has the carbon skeleton of monocyclic compounds of the cembrane type.

The PMR spectrum of the hydrocarbon lacks the signals of the methyl protons of an isopropyl group which are characteristic of cembrene (III) [1], and all the methyl groups are on double bonds, while the PMR and IR spectra confirm the presence in the substance of an isoprenyl group



$-C(=CH_2)CH_3$.

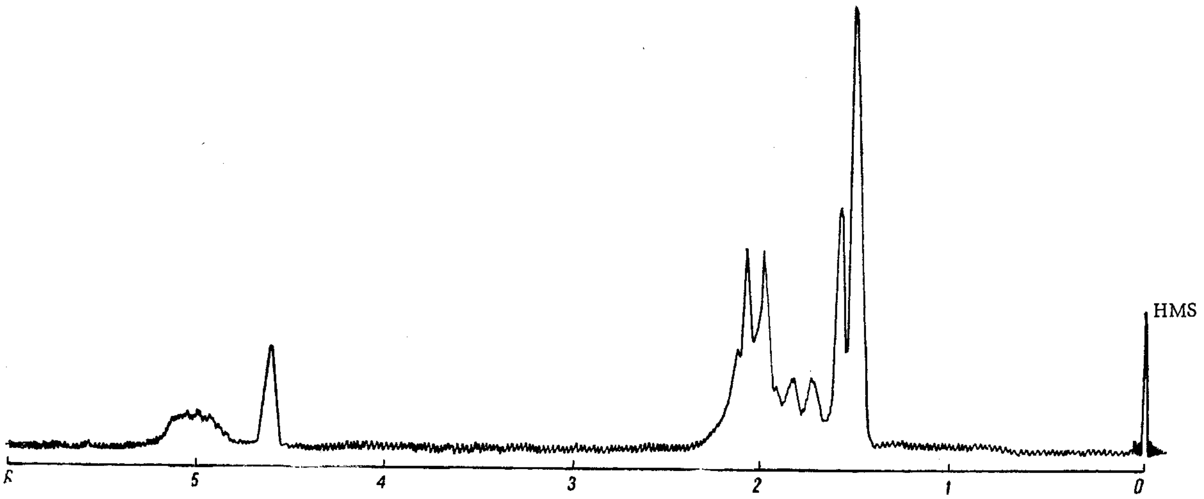


Fig. 1. PMR spectrum of neocembrene (CCl_4).

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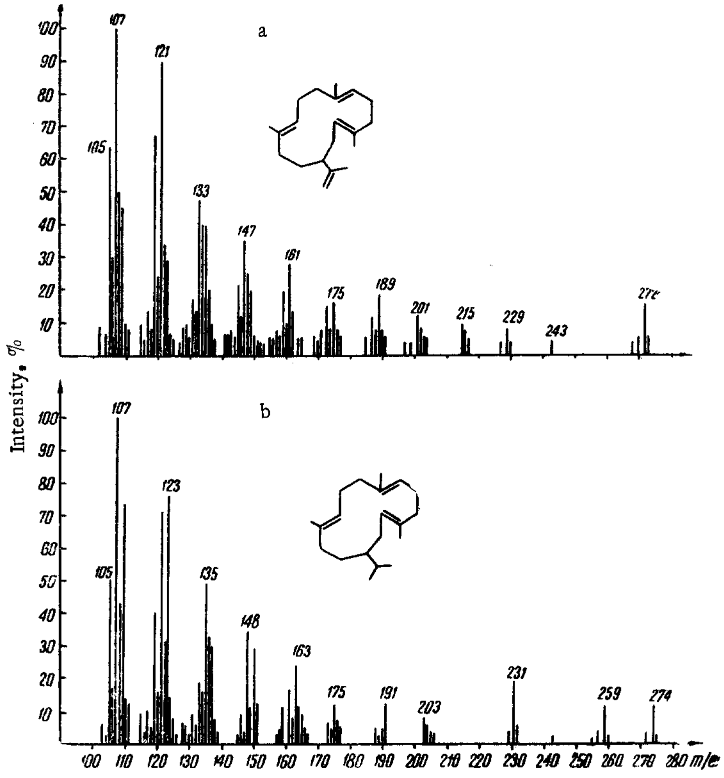
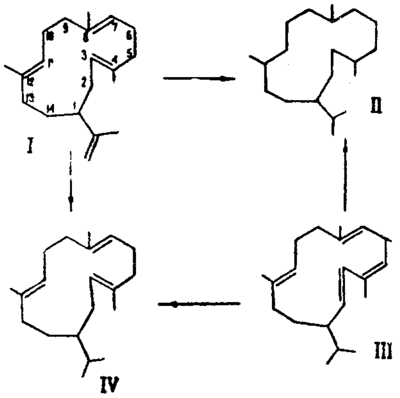


Fig. 2. Mass spectra of neocembrene (a) and its dihydro derivative (b).

The preparation of octahydrocembrene and spectral information permit structure I to be proposed for the hydrocarbon isolated.



In order to confirm the proposed structure, we partially hydrogenated I in the presence of Pd/$CaCO_3$ in ethyl acetate and obtained a dihydro derivative IV. The PMR spectrum of IV clearly shows the presence of two methyls of an isopropyl group at 0.80 and 0.84 ppm (J = 6.6 Hz) and a singlet signal at 1.51 ppm corresponding to three CH_3 groups on double bonds. In the weak-field region at 5.1 ppm there is a signal with an intensity of 3H relating to olefinic protons.

In its spectral properties and physical constants, the dihydro derivative IV is completely identical with the dihydrocembrene obtained by the partial hydrogenation of III in ethyl acetate in the presence of Pd/$CaCO_3$.

A. I. Rezvukhin and V. A. Raldugin in the Novosibirsk Institute of Organic Chemistry have shown that under these conditions the 1,4-addition of hydrogen to the conjugated diene system of cembrene takes place with the formation of IV, the structure of which was shown by PMR spectra.

The mass spectrum of the dihydro derivative of the hydrocarbon I was completely identical with that of an authentic sample of dihydrocembrene. On comparing the mass spectra of I and IV it can be seen that the nature of the decomposition of the two compounds is similar in general: the ion with m/e 107 is the main one (Fig. 2a and b). Apparently, on electron impact the fragmentation of I and IV takes place by the same route.

On the basis of the results of hydrogenation and spectroscopy (IR, UV, PMR, and mass spectrometry), structure I is proposed for the hydrocarbon isolated. We have called it neocembrene (1-isopropenyl-4,8,12-trimethylcyclotetradeca-3,7,11-triene). The amount of it in the diterpene hydrocarbons of the oleoresin fraction of Siberian spruce and Korean pine is low (3-3.5%).

EXPERIMENTAL

Isolation of Neocembrene. A. From Siberian Spruce. The oleoresin (400 g) collected in the Krasnoyarsk region was treated by the usual method [3]. The diterpene fraction (51.7 g) was separated by percolation into hydrocarbons (15.0 g) and oxygen-containing compounds (31.2 g).

The hydrocarbons (3.78 g) were chromatographed on $SiO_2/AgNo_3$ (5%). Elution was carried out with petroleum ether containing increasing amounts of diethyl ether (from 1 to 100% in 2% steps). The diethyl ether yielded 280 mg of a fraction containing the neocembrene; after rechromatography, pure neocembrene was obtained (120 mg) with $[\alpha]_D^{20} - 20°$ (c 0.1; n-heptane), n_D^{20} 1.5110. The individuality of the hydrocarbon was confirmed by thin-layer chromatography on silica gel and on silica gel impregnated with silver nitrate.

Found, %: C 88.12; H 11.86, mol. wt. 272 (mass spectrometry). Calculated for $C_{20}H_{32}$, %: C 88.16; H 11.84, mol. wt. 272.46.

B. From the Oleoresin of the Korean Pine. The oleoresin (500 g) yielded 36 g of hydrocarbons. The mixture of hydrocarbons (3 g) was separated on silica gel impregnated with 10% of $AgNO_3$. Elution with a mixture of petroleum ether and diethyl ether (97 : 3) yielded 100 mg of neocembrene.

Hydrogenation of Neocembrene. Neocembrene (13.0 mg) was hydrogenated in acetic acid over PtO_2. The consumption of hydrogen was 4.73 ml (0°C, 760 mm), which corresponded to four double bonds. The reaction mixture was chromatographed on silica gel (100 μ). Petroleum ether eluted octahydrocembrene (10 mg), $C_{20}H_{40}$ with n_D^{20} 1.4730, mol. wt. 280 (mass spectrometry), identical with an authentic sample according to mass spectra and the results of thin-layer and gas-liquid* chromatography.

Dihydrocembrene. Neocembrene (0.05 g) was hydrogenated in ethyl acetate over $Pd/CaCO_3$ (0.01 g) for 2 h. The consumption of hydrogen was 4.1 ml (0°C, 760 mm), corresponding to one double bond. The mixture of products was chromatographed on silica gel impregnated with 10% of $AgNO_3$. A mixture of petroleum and diethyl ethers (99.5 : 0.5) yielded dihydrocembrene (IV) (0.04 g) with $[\alpha]_D^{20} - 15°$ (c 0.3; n-heptane), n_D^{20} 1.5123, mol. wt. 274 (mass spectrometry), which was identical according to their PMR and mass spectra and physical constants with an authentic sample of dihydrocembrene.

SUMMARY

From the hydrocarbon fractions of the oleoresins of Picea obovata Ledb and Pinus koraensis Sieb. Zucc. a new monocyclic diterpene hydrocarbon – neocembrene – has been isolated, and a structure has been proposed for it.

LITERATURE CITED

1. W. G. Dauben, W. E. Thiessen, and P. K. Resnik, J. Org. Chem., 30, 1693, 1965.
2. A. I. Lisina, A. I. Rezvukhin, and V. A. Pentegova, KhPS [Chemistry of Natural Compounds], 1, 250, 1965.

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*KhROM-2 chromatograph (Czechoslovakia), flame ionization detector; column 3.4 m × 0.6 cm; packing E-301 silicone elastomer (1%) on Chromosorb G (0.177-0.250 mm); carrier gas nitrogen (0.8 atm. gauge); column temperature 160°C; retention time of octahydrocembrene 21.6 min.