DITERPENE HYDROCARBONS OF THE RESIN OF PINUS SIBIRICA R. MAYR.

V. A. Pentegova and N. K. Kashtanova

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The following diterpene hydrocarbons have been isolated from the high-boiling neutral fraction of the resin of the Siberian sine by column and thin-layer chromatography on silica gel impregnated with silver nitrate [1, 2]: cembrene, abietadiene, and three hydrocarbons not described in the literature, which we have called A, B, and C.

Cembrene – $C_{20}H_{32}$, mp 59-60°; $[\alpha]_D^{20}$ + 234° [8] (c 3.0; chloroform); λ_{max}^{EtOH} 244 mμ (log ε 4.15); IR and UV spectra identical with a sample of cembrene [3, 4, 5].

Abietadiene – $C_{20}H_{32}$, n_D^{20} 1.5320; $[\alpha]_D^{20}$ – 75° (c 2.9; chloroform); λ_{max}^{EtOH} 241-242 mμ (log ε 4.02). The adduct with maleic anhydride was obtained, mp 148-149°. The hydrocarbon was shown to be identical in respect of its IR and UV spectra with an authentic sample of abietadiene.

Hydrocarbon A – mp 59-60°; $[\alpha]_D^{20}$ + 30° (c 3.0; chloroform). The consumption of hydrogen on hydrogenation in the presence of Adams' catalyst corresponded to four double bonds. UV spectrum in n-heptane – λ_{max}: 244 mμ (log ε 4.01). The IR spectrum of the hydrocarbon had maxima at 750, 840, 870, 970, 1370, 1380, 1670, 1680 cm^{-1}.

Found: C 87.88; H 12.12%; molecular weight (mass spectrometry). Calculated for $C_{20}H_{32}$: C 88.16; H 11.84%; molecular weight 272.

Hydrocarbon B – n_D^{20} 1.5340; $[\alpha]_D^{20}$ – 200°. Hydrogenation showed the presence of two double bonds. UV spectrum in n-heptane – λ_{max}: 253 mμ (log ε 4.08); the IR spectrum of the hydrocarbon had maxima at 770, 790, 850, 970, 1180, 1370, 1380, 1670, 1680 cm^{-1}.

Found: C 87.4; H 12.6%; molecular weight 276 (mass spectrometry). Calculated for $C_{20}H_{36}$: C 86.9; H 13.1%; molecular weight 276.

Hydrocarbon C – n_D^{20} 1.5360; $[\alpha]_D^{20}$ + 165°. Hydrogenation of the hydrocarbon showed the presence of two double bonds, and the UV spectra had no maxima in the 200-400 mμ region. The IR spectrum of hydrocarbon C had maxima at 760, 790, 820, 910, 1180, 1370, 1380, 1660, 1680 cm^{-1}.

Found: C 87.23; H 12.77%; molecular weight 276 (mass spectrometry). Calculated for $C_{20}H_{36}$: C 86.9; H 13.1%; molecular weight 276.

Hydrogenation of hydrocarbons A, B, and C in the presence of Adams' catalyst gave a saturated hydrocarbon which was identical in its physicochemical constants and IR spectrum with octahydrocembrene.

The product of the dehydrogenation of hydrocarbons A, B, and C, was one and the same aromatic hydrocarbon – 2, 9-dimethyl-7-isopropylphenanthrene, which is also formed in the dehydrogenation of cembrene [5].

From the consumption of hydrogen on hydrogenation and the identification of the dehydrogenation product, it may be concluded that the diterpene hydrocarbons A, B, and C have a 14-membered ring, like cembrene.

On studying the properties of hydrocarbon A, we found that it is unstable. Over 15-20 days, its specific rotation gradually rises to +232°, i.e., to the specific rotation of cembrene. In contrast to cembrene, hydrocarbon A is sparingly soluble in ethanol and we were therefore able to separate it from cembrene. Hydrocarbon A is apparently a close isomer of cembrene, but differs from it in location of the double bonds.

The study of the diterpene hydrocarbons is proceeding.

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Novosibirsk Institute of Organic Chemistry, Siberian Division AS USSR

INVESTIGATION OF THE ALKALOIDS OF *VINCA MAJOR*, *V. PUBESCENS*, AND *V. ROSEA*. THE STRUCTURE OF MAJDINE [1]

N. Abdurakhimova, P. Kh. Yuldashev, and S. Yu. Yunusov

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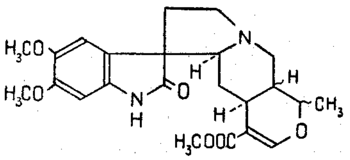
We have isolated three alkoloids from *Vinca major*: reserpinine, akuammine, and majdine [1].

On heating with acetic anhydride, majdine, $C_{23}H_{28}O_6N_2$, isomerizes into isomajdine with mp 204-206°, $[\alpha]_D^{18}$ –90° (methanol). By comparing the IR and NMR spectra and other properties, it was found that majdine is possibly a stereoisomer of the hydroxyindole alkaloid carapanaubine, which has been isolated from *Aspidosperma carapanaubica* [2].

The mass spectra of majdine and carapanaubine were found to be identical. Consequently, majdine is a hydroxyindole base of the following structure:



The isomerization of majdine to isomajdine shows the presence in majdine of the α-orientation of the hydrogen atom at C_4 and of the β-orientation in isomajdine. Isomerization at C_4 is characteristic of the hydroxyindole alkaloids [3].

This indicates that majdine differs from carapanaubine by the configuration of the C_{15}, C_{19}, and C_{20} carbon atoms.

If we take into consideration the fact that in the δ-yohimbine and hydroxyindole bases the hydrogen at C_{15} has the α-orientation [4], the configuration of the C_{19} and C_{20} atoms in majdine remain undetermined.

A. P. Orekhov et al. [5] have isolated three bases from *V. pubescens*: vinine, pubescine, and a base with mp 194-195°.

The ethereal extraction of 1 kg of the above-ground parts of the plant *Vinca pubescens*, collected in the environs of the town of garga in the fruit-bearing season (12 October, 1959), yielded 6.35 g of total alkaloids (0.64%). They were separated with respect to their basicities into ten fractions. The third fraction yielded 200 mg of pubescine with mp 228-230°. After its purification by chromatography on alumina, it was found that it melted at 236-237°.

The IR spectra of pubescine are identical with those of reserpinine which we isolated from Vinca erecta [6]. The 6th-7th fractions gave 50 mg of vinine with mp 210-213°. After its recrystallization from acetone, it had mp 216-217°; molecular weight 428 (by mass spectroscopy).

A comparison of their mass spectra and other properties showed that vinine is identical with carapanaubine.

After the isolation of the alkaloids, the ethereal extract gave 0.59% of ursolic acid.

Ninety grams of the roots of *V. rosea* grown in the Botanical Garden of the UzSSR Academy of Sciences yielded 0.5% of total alkaloids, 10% of which consisted of a base with mp 256-257°, $[\alpha]_D$ – 49° (methanol), $C_{21}H_{24}ON_2$, forming a hydrochloride with mp 281-283°. A study of the UV and IR spectra and other properties of the base showed that it was ajmalicine [7].

Thus, reserpinine, akuammine, carapanaubine, ajmalicine, and the new base majdine have been isolated from *Vinca major*, *V. pubescens* and *V. rosea*.