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A TRICYCLIC TERPENE HYDROCARBON — CYCLOPINENE

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The reduction of the tosylate of filipendulol (2,7,7-trimethylbicyclo[3.1.1]hept-2-en-6-ol) with lithium tetrahydroaluminate in ether has given a hydrocarbon (I), $C_{10}H_{16}$ (bp 66.5°C/50 mm, n_D^{20} 1.4565, d_{20}^{20} 0.8599, $[\alpha]_D^{19}$ –104.5°. NMR: 0.69 ppm (CH_3); 0.95 ppm (CH_3); 1.17 ppm (CH_3); no signals of olefinic protons. IR: 3054 cm^{-1} (three-membered ring with gem-protons); 1363 and 1387 cm^{-1} (gem-CH_3); absorption bands of multiple bonds absent. Heating (70°C) (I) with a sulfonated cation-exchange resin in hexane gave α-pinene. The hydrogenation of (I) over PtO_2 in acetic acid gave pinane. The most probable structure of (I) is 2,7,7-trimethyltricyclo[3.1.1.0^{2,4}]heptane. The substance has been called cyclopinene.

We have reported the isolation from the essential oil of *Achillea filipendulina* Lam. (fernleaf yarrow) of an unknown terpene alcohol, which was called filipendulol [1]. On the basis of a study of the composition, spectral characteristics and chemical transformations, it was assigned the structure of 2,7,7-trimethylbicyclo[3.1.1]hept-2-en-6-ol [2].

When filipendulol tosylate was reduced with lithium tetrahydroaluminate in ether [3], in addition to d-α-pinene a hydrocarbon was obtained with bp 66.5°C/50 mm, n_D^{20} 1.4565, d_{20}^{20} 0.8599, $[\alpha]_D^{19}$ –104.5°. The molecular weight determined mass-spectroscopically was 136.

The NMR spectrum of the hydrocarbon obtained contained three singlets at 0.69 ppm, (3 H), 0.95 ppm (3 H), and 1.17 ppm (3 H), relating to methyl groups, and a methylene hump in the 1.30–2.10 ppm region (7 H). There were signals in the region of resonance of olefinic protons.

The IR spectrum of this compound (Fig. 1) shows no bands in the region of the stretching vibrations of multiple carbon–carbon bonds. The strong band at 3054 cm^{-1} shows the presence in the molecule of a three-membered ring having geminal protons [4, 5]. The spectrum also showed the characteristic splitting of the band at 1380 cm^{-1} due to symmetrical deformation vibrations of methyl groups. It shows that the molecule contains geminal methyl groups [5]. The existence of the latter was confirmed by mass spectrometric characteristics. Thus, in the mass spectrum of the hydrocarbon obtained (Fig. 2) the strongest peak is that of an ion with m/z 93 which is obviously formed as the result of the cleavage of the ring and the subsequent ejection of an isopropyl group.

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*Deceased.

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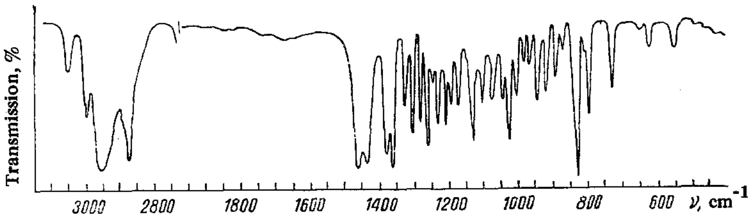


Fig. 1. Infrared spectrum of cyclopinene (UR-20 spectrophotometer; layer thickness 0.032 mm).

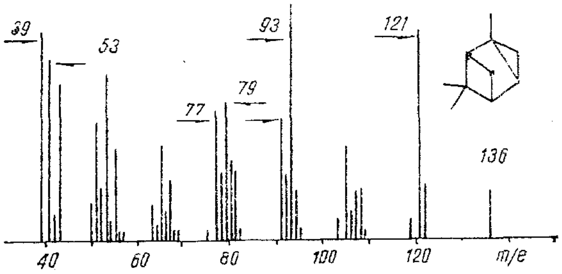


Fig. 2. Mass spectrum of cyclopinene (MKh 1303 mass spectrometer, 100°C, energy of the ionizing electrons 20–70 eV; the intensities of the marked ion peaks are halved).

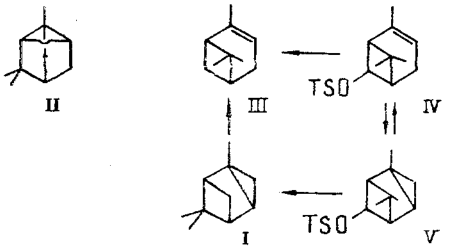
Thus, the composition and spectral characteristics permit the conclusion that the hydrocarbon is a tricyclic compound.

In its composition and constants, the compound obtained resembles cyclofenchene (II) (bp 145°C/764 mm, d_{20}^{20} 0.8600, n_D^{20} 1.4548, $[\alpha]_D^{20}$ –1.83° [6]. However, the structure of this compound does not agree with the presence of a three-membered ring having geminal protons.

The most probable structure corresponding to the spectral characteristics of our compound is (I). The molecular refraction calculated for this, 43.01, practically coincides with the value found, 42.96.

Such a structure for the hydrocarbon (I) was also confirmed by its chemical transformations. When it was heated with cation-exchange resins in a hydrocarbon medium, a mixture was obtained which, according to the results of GLC analysis, consisted of several substances the main one of which proved to be α-pinene (III), which was identified by the results of mass spectrometry. The catalytic hydrogenation of this hydrocarbon over platinum oxide was accompanied by a slow addition of hydrogen, giving a substance with n_D^{20} 1.4617 identified by its IR spectrum as pinane [5].

The formation and transformation of hydrocarbon (I) apparently take place in the following way:



Under the conditions of the reaction [3] filipendulol tosylate (IV) isomerizes into the tosylate of a tricyclic alcohol (V), giving the hydrocarbon (I). The three-membered ring in the latter isomerizes to a multiple bond, converting the substance into α-pinene (III).

Thus, the most probable structure for the hydrocarbon obtained is that of 2,7,7-trimethyltricyclo[3.1.1.$0^{2,4}$]heptane. We have called it cyclopinene.

EXPERIMENTAL

NMR spectra were taken on a B 487 C/80 MHz instrument, IR spectra on a UR-20 spectrometer and mass spectra on a standard MKh-1303 instrument at 100°C with an energy of the ionizing electrons of 20–70 eV.

The substances were isolated by distillation and preparative TLC (UKh-2 instrument; 250 × 0.8 cm; PEG-2000, 25% on treated INZ-600, 0.30–0.40 nm; temperature 150°C). The amounts of the substances in mixtures were determined by the standardization method.

Preparation of Cyclopinene (I) [3]. Filipendulol tosylate, obtained by a standard method [7] (colorless crystals, rapidly darkening in the air and decomposing explosively when heated in bulk) (22 g) was dissolved in 100 ml of dry ether. The solution was poured into a flask with a stirrer and a reflux condensor containing 5 g of $LIAlH_4$ in 200 ml of ether, and the mixture was heated for 5 h. The excess of $LiAlH_4$ was decomposed with moist ether, and then a 10% solution of H_2SO_4 was added until the solid matter had dissolved completely. The ethereal layer was separated off, washed free from acid, dried, and distilled. This gave 7.8 g of a mixture of hydrocarbons containing 66% of cyclopinene (I), 28% of d-α-pinene, and 4% of p-cymene.

Isomerization of Cyclopinene. To a solution of 1.6 g of the substance in 5 ml of hexane was added 0.02 g of KU-21 sulfonated cation-exchange resin that had previously been treated with 5% HCl, washed to neutrality with water, and then washed with ethanol. The mixture was boiled (70°C) in a flask with a reflux condenser and a magnetic stirrer for an hour. Analysis showed that it contained 12% of cyclopinene, 76% of α-pinene, 4% of β-pinene, and 3% of camphene, p-menth-2-ene, limonene, and p-cymene.

It must be mentioned that the isomerization of cyclopinene takes place partially in a preparative column in the region adjacent to a metering device having an elevated temperature. When the pure substance was rechromatographed, the peak of α-pinene was observed, in addition to its own peak.

SUMMARY

A new hydrocarbon $C_{10}H_{16}$, which has been called cyclopinene, has been obtained. On the basis of spectral characteristics and chemical transformations it has been suggested that its most probable structure is that of 2,7,7-trimethyltricyclo[3.1.1.$0^{2,4}$]heptane.

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