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# 3,7,7-TRIMETHYLCYCLOHEPTA-1,3,5-TRIENE — A COMPONENT OF THE TURPENTINES FROM *Pinus sylvestris*

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UDC 547.9:547.517

A previously unknown component has been isolated from the oleoresin turpentine of *Pinus sylvestris* L. It has been established by chemical and spectral methods that it is 3,7,7-trimethylcyclohepta-1,3,5-triene. It has been shown by the GLC method that this hydrocarbon is present in all the main types of turpentines in amounts of from 0.1 to 0.7%.

In industrial samples of the turpentines obtained from the pine *Pinus sylvestris* L. the presence of 15 terpene hydrocarbons, of one oxide, and of five to 10 components of undetermined nature have been established [1-4]. In the present paper we consider the establishment of the structure of an unknown component having a boiling point close to that of β-pinene, which made its isolation by fractional distillation difficult. When GLC analysis is performed on the widely used liquid phase (LP) tricresyl phosphate (TCP) this component has a relative retention time (RRT) with respect to car-3-ene of 1.04 [3], and appears indistinctly when the concentration of the latter is appreciable.

We succeeded in achieving a good separation of this component from the others of the turpentine by using as LP diethyleneglycol adipate (DEGA). Under these conditions, the RRT of the component in relation to that of car-3-ene was 1.28. The amount of the component under investigation in industrial samples of pine oleoresin turpentine [5] does not exceed 0.1%.

As a result of two successive fractional distillations of the turpentine we obtained a concentrate containing 16.1% of the component. By preparative GLC we isolated from the concentrate in 99.7% purity a substance with the composition $C_{10}H_{14}$, bp 62-63°C (20 mm); $d_4^{20}$ 0.8530; $n_D^{20}$ 1.4962; $[\alpha]_D^{20}0°$.

The UV spectrum [$\lambda_{max}^{C_2H_5OH}$ 270 nm (log ε 3.70)] was characteristic for a conjugated system of endocyclic double bonds.

The IR spectrum had the following characteristic absorption bands ($cm^{-1}$): 1358, 1375 ($-CMe_2$); 1440, 1452, 1469 ($-CH_3$); 1557, 1613, 1630 (three conjugated double bonds).

In its properties, the compound under investigation corresponded to 3,7,7-trimethylcyclohepta-1,3,5-triene (I). The following properties are given for this compound in the literature: bp 53-55°C (13 mm); $d_4^{20}$ 0.8559; $n_D^{20}$ 1.4965. UV spectrum: $\lambda_{max}$ 269 nm (log ε 3.577) [6].

To confirm the structure of (I) we studied its PMR spectrum, including spectra taken with the use of double resonance. The spin—spin coupling constants for (I) were: $J_{1-2} = J_{5-6} = 10$ Hz, $J_{4-5} = 6.8$ Hz, which agrees well with literature information given for cycloheptatriene derivatives [7]. The constants mentioned permit the doublet of doublets to be assigned to the protons at $C_1$ and $C_6$, the low-field doublet to the proton at $C_4$, and the unresolved multiplet to the protons at $C_2$ and $C_5$. The chemical shifts of the signals of the individual protons obtained with the use of double resonance were as follows: 4.90 (H-1), 4.85 (H-6), 5.67 (H-2), 5.71 (H-5), 6.00 (H-4), which corresponds to literature information [8].

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Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 783-785, November-December, 1979. Original article submitted August 20, 1979.

On exhaustive hydrogenation, 3 moles of hydrogen added to 1 mole of compound (I). From its physical and spectral properties, the product of the hydrogenation of (I) corresponded to 1,1,4-trimethylcycloheptane (II) [9, 10].

Compound (I) gave an adduct with maleic anhydride.

We have shown by the GLC method that 3,7,7-trimethylcyclohepta-1,3,5-triene is present in industrial samples of pine turpentines of the sulfate type (traces), of the extraction type (0.3%), and of the dry-distillation type (0.7%), and also in the native oleoresin (traces) of some individual trees of the species *Pinus sylvestris* L.

## EXPERIMENTAL

Fractional distillation of pine oleoresin turpentine was carried out successively in columns with efficiencies of 50 and 100 theoretical plates at reflux numbers of 50 and 100, respectively.

GLC analysis was performed on a Vyrukhrom instrument with a flame-ionization detector using a column with dimensions of 6000 × 3 mm filled with deactivated INZ-600 diatomite brick (grain size 0.25-0.50 mm) impregnated with DEGA (15%), at a thermostat temperature of 90°C with a rate of flow of carrier gas (nitrogen) of 50 ml/min.

Compound (I) was isolated by the PGLC method on a PAKhV-05 instrument in a column with dimensions of 8000 × 4 mm filled with Chromaton (grain size 0.250-0.316 mm) impreganted with DEGA (20%) at 80°C with a rate of flow of carrier gas (helium) of 80 ml/min.

IR spectra were recorded on a UR-20 spectrophotometer, UV spectra on a Specord-UV, and PMR spectra on JNCS-100 and Tesla-60 instruments with tetramethylsilane as internal standard. The analyses of the substances corresponded to calculated values.

*3,7,7-Trimethylcyclohepta-1,3,5-triene (I).* IR spectrum ($cm^{-1}$): 615 m, 640 m, 674 m, 722 s, 750 s, 770 m, 819 s, 860 m, 882 w, 941 w, 967 w, 1038 m, 1071 m, 1143 m, 1169 w, 1194 s, 1230 w, 1242 w, 1358 s, 1375 s, 1417 m, 1440 s, 1452 s, 1469 s, 1557 m, 1613 m, 1630 m, 2874 s, 2962 s, 2943 s, 2966 s, 2989 s, 3010 s.

By boiling 0.50 g of (I) with 0.37 g of maleic anhydride in 1 ml of diethyl ether at 50°C for 6 h, 0.65 g (75.6% yield) of an adduct was obtained which, after three crystallizations from ethanol, had mp 103-104°C.

The hydrogenation of 0.2145 g of compound (I) was carried out over platinum black in absolute hexane at 20°C. The amount of hydrogen added was 100.4 ml (STP), which corresponds to 93.3% of the theoretical amount required for the hydrogenation of three double bonds.

The 1,1,4-trimethylcycloheptane (II) obtained in the hydrogenation of (I) had the composition $C_{10}H_{20}$, $d_4^{20}$ 0.8040, $n_D^{20}$ 1.4417.

## SUMMARY

It has been established that oleoresin turpentine from *Pinus sylvestris* L. contains 3,7,7-trimethylcyclohepta-1,3,5-triene.

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