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G. V. PIGULEVSKII and V. I. KOVALEVA

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Abstract

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G. V. PIGULEVSKII and V. I. KOVALEVA

ON A NEW SESQUITERPENE HYDROCARBON, DAUCENE

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In studying the essential oil of wild carrot, *Daucus carota* L., we encountered a great variety in the composition of the oil depending on the place where the carrot grew ([1]). The essential oil isolated from the fruits of wild carrot growing in the Caucasus (Armenia) consists mainly of carotol (80%). From the sesquiterpene fraction of the oil, by repeated chromatography on alumina (activity 1–2), we isolated the sesquiterpene hydrocarbon daucene, of bicyclic structure, $C_{15}H_{24}$ ($a_D + 23.32^\circ$), whose properties are given in Table 1.

Upon exhaustive hydrogenation, 2 moles of hydrogen were absorbed and a hydrocarbon of composition $C_{15}H_{28}$ was obtained. The IR spectrum (Fig. 1) of the hydrocarbon tetrahydrodaucene, $a_D + 2.40^\circ$, is very close to the spectrum of daucan obtained by Shorm ([2]), but differs somewhat from it. Apparently, daucene has an azulene structure; it contains two double bonds. The nature of the double bonds follows from analysis of the spectrum of combination scattering of light. In the spectrum two lines were found with $\Delta\nu$ 1669 (8) cm^{-1}, 1653 cm^{-1}. The frequency 1669 cm^{-1} corresponds to a secondary-tertiary double bond. As for the line with $\Delta\nu$ 1653 cm^{-1}, it probably corresponds to a tertiary-tertiary double bond in a five-membered ring.

The IR spectrum of daucene (Fig. 2) contains absorption bands in the region of 1657 cm^{-1} (of low intensity) and 829 cm^{-1}. The latter band corresponds to the out-of-plane deformation vibration of $=CH$.

It should be noted that upon hydrogenation of daucene the secondary-tertiary bond disappears first and a hydrocarbon C_{15}—H_{26} ($a_D + 9.66^\circ$) is formed. The tertiary-tertiary double bond is hydrogenated considerably less readily. Daucene forms, with nitrosyl chloride, a nitrosochloride with m.p. 104°. In the formation of the nitrosochloride the tertiary-tertiary double bond of the five-membered ring takes part, since in the IR spectrum of the nitrosochloride there is no absorption band in the region of 1657 cm^{-1}.

The structure of daucene proposed by us follows from its identity with the hydrocarbon obtained from carotol by dehydration in the presence of traces of sulfuric acid ([3], ?).

The latter also forms a nitrosochloride (107°) and has an identical IR spectrum.

Experimental Part

The essential oil isolated from the fruits of wild carrot has the following constants: d_4^{20} 0.9272, n_D^{18} 1.4978, $a_D + 23.88°$; acid number 0.22, ester number 20.0, OH content 5.80%, MR 66.31, calculated $MR\ F_2$ 66.14.

Found, %: C 88.05, 88.22; H 11.8, 11.78
$C_{15}H_{24}$. Calculated, %: C 88.16; H 11.84

Combination scattering of light, $\Delta\nu$: 257 (2), 296 (1), 369 (1), 385 (2), 431 (1), 506 (3), 595 (1), 635 (4), 658–683 (2), 846 (4), 887 (1), 948 (2), 977 (1), 1067–1169 (7), 1192 (6), 1306 (3), 1341 (3), 1375 (3), 1432–1463 (8), 1653 (8), 1669 (8), 2847–2966 (4).

Table 1

	B.p., °C/mm	d_4^{20}	n_D^{20}	α_D
Daucene	96°/4	0,8936	1,4918	+23,32°
Hydrocarbon from carrotol	95–96°/5	0,8945	1,4903	+44,00°

Hydrogenation of daucene $C_{15}H_{24}$. Charge: 6.08 g of substance, 0.6 g Pt (Adams), 20 ml glacial acetic acid. Absorbed H_2, 688 ml (calculated for one double bond, 662 ml). The isolated hydrocarbon has: b.p. 112°/17 mm, n_D^{20} 1,4778, d_4^{20} 0,8733, α_D +9,66°.

Fig. 1. Infrared spectrum of daucan

Fig. 2. Infrared spectrum of daucene

Found, %: C 87,27, 87,43; H 12,72, 12,75
$C_{15}H_{26}$. Calculated, %: C 87,29; H 12,71

Combination-scattering spectrum of light, $\Delta\nu$: 345 (2), 640 (3), 841 (3), 1061–1103 (6), 1122–1158 (6), 1182 (6), 1343 (5), 1345 (1), 1397 (1), 1430–1461 (6).

Hydrogenation of dihydrodaucene $C_{15}H_{26}$. Charge: 1.8014 g, 10 ml glacial acetic acid, 0.2 g Pt. Hydrogenation was complete after 20 h. During hydrogenation, 0.8 g Pt was added. Absorbed H, 187 ml (calculated 198 mm). The isolated hydrocarbon $C_{15}H_{28}$ has b.p. 103°/5 mm; n_D^{20} 1,4731; d_4^{20} 0,8772; α_D +2,40°.

Found, %: C 86,61, 86,51; H 13,39, 13,42
$C_{15}H_{28}$. Calculated, %: C 86,45; H 13,54

Analysis of the nitrosochloride of daucene with m.p. 104°:

Found, %: C 66,56, 66,57; H 8,99, 9,11
$(C_{15}H_{24}NOCl)_2$. Calculated, %: C 66,80; H 8,90

From the essential oil of the fruits of wild carrot (*Daucus carota* L.) growing in Armenia, we have isolated a new sesquiterpene hydrocarbon of composition $C_{15}H_{24}$—daucene, belonging to the daucan type.

Komarov Botanical Institute
Academy of Sciences of the USSR

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.