FILIPENDULOL — A NEW TERPENE ALCOHOL

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In an investigation of the essential oil of Achillea filipendulina Lam. (fernleaf yarrow) obtained from flowering plants growing in the lower reaches of the R. Dzhabagly close to the Aksu-Dzhabagly reserve, from the fraction boiling at 88-96°C/10 mm we have isolated by preparative gas-liquid chromatography an alcohol with bp 91-92°C/10 mm, n_D^{20} 1.4907, d_{20}^{20} 0.9694, $[\alpha]_D^{20}$ 25.2°, with the composition $C_{10}H_{16}O$ (M^+ 152), which we have called filipendulol [1]. In the essential oil, this alcohol is present mainly in the form of its acetate with bp 90-91°C/10 mm, n_D^{20} 1,4680, d_{20}^{20} 0,9794, $[\alpha]_D^{21}$25', which can be isolated by fractional distillation.

Oxidation of filipendulol with chromic acid and also its boiling in benzene in the presence of acetone and of aluminum isopropanolate (Oppenauer method) [2] led to a ketone [IR spectrum: 1778 cm^{-1} (C=O). 1658, 3043 cm^{-1} (—CH=C)] with bp 80-81°C/10 mm, n_D^{20} 1,4772, d_{20}^{20} 0,9596, $[\alpha]_D^{20}$ 118°. This shows that the alcohol is secondary.

On hydrogenation over platinum oxide in methanol or in acetic acid, filipendulol added 1 mole of hydrogen, giving an alcohol with mp 71-72°C (subl.). On oxidation (by the Oppenauer method) dihydrofilipendulol gave a ketone which, when heated with hydrazine hydrate and caustic soda in triethyleneglycol (Huang-Minlon reaction) [3], gave a hydrocarbon having bp 80-81°C/50 mm, n_D^{20} 1,4613, d_{20}^{20} 0,8606, $[\alpha]_D^{19}$ 23,8° which was identified by its IR and mass spectra as cis-pinane [4, 5].

The reduction of filipendulol tosylate with lithium tetrahydroaluminate in ether gave d-α-pinene and its isomer with bp 66.5°/50 mm, n_D^{20} 1,4565, d_{20}^{20} 0,8599, $[\alpha]_D^{19}$ 104, 5°, M^+ 136.

Filipendulol and also its acetate, on being heated in ethanolic caustic soda, were converted into an optically active aldehyde (1725, 2730 cm^{-1}, H—C=0) with bp 76°C/10 mm, n_{20}^{20} 1.4704, d_{20}^{20} 0.9289, M^+ 152, mp of the 2,4-dinitrophenylhydrazone 153-154°C (corr.). Reduction of the aldehyde (by the Huang-Minlon method) [3] followed by hydrogenation of the resulting hydrocarbon over platinum oxide (according to Adams) gave a substance with mp 157-157.5°C/686 mm, n_D^{20} 1.4412, d_{20}^{20} 0.8033, which, according to its mass and PMR spectra was a tetramethylcyclohexane. This shows that the isomerization of filipendulol into the aldehyde was accompanied by cleavage of a bridge bearing the hydroxy group.

IR spectrum of filipendulol, cm^{-1}: 3360 (OH), 790, 1653, 3048 (—C=CH—), 1180, 1268, and a characteristic doublet at 1365-1383 [$-C(CH_3)_2$] [4].

PMR spectrum of filipendulol in CCl_4 (ZKR-60, ppm): 0.85 and 1.52 [3 H, singlets, $-C(CH_3)_2$], 1.65 (3 H, doublet, J = 3 Hz, $-HC{=}C{-}CH_3$), 1.90 (2 H, multiplet, $>CH{-}\underline{CH_2}{-}CH$), 2.17 (2 H, broadened singlet, $-CH<$), 3.91 (1 H, singlet, $\underline{H}{-}C{-}OH$), 4.81 (1 H, multiplet, OH), and 5.20 (1 H, multiplet, $-\underline{H}C{=}C{-}CH_3$).

Thus, on the basis of the results obtained it may be concluded that the compound isolated is an unsaturated secondary bicyclic alcohol and has the structure of 2,7,7-trimethylbicyclo[3,1,1]hept-2-en-6-ol.

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ESSENTIAL OIL OF Thymus rariflorus

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The genus Thymus (thyme) is one of the largest of the Labiateae family. Its representatives are also widely distributed in Azerbaidzhan (21 species) [1]. Thymes have long been used in medicine as popular antiseptics, analgesics, and expectorants [2]. Out of 136 species known in the flora of the USSR, only two have so far been used in medicine: Th. vulgaris L. (common thyme), and Th. serpyllum L. (mother-of-thyme), which are used in perfumery and the food industry [3-5]. We set ourselves the aim of investigating the amount and chemical composition of the essential oil of Th. rariflorus C. Koch. and its useful properties. The species has hitherto been scarcely studied in the chemical respect.

In addition, Th. rariflorus was grown in the Botanical Garden in 1969.

The material for analysis was collected in 1975 in the environs of the village of Leninkend, Shamkhorskii region. The amount of essential oil was determined by steam distillation as 0.3-0.7% of oil at a moisture content of the raw material of 13.81% (0.35-0.81% on the absolutely dry weight) and it had the following constants: d_{20}^{20} 0.9541; n_D^{20} 1.5055; acid No. 2.90, ester No. 15.73; ester No. after acetylation 218.84.

In addition, Th. rariflorus was grown in 1969 in the Botanical Garden at Baku. The material used was live shrubs brought from the Shamkhorskii region. The plant is growing and developing well at Apsheron and is giving a good epigeal mass with a yield of oil of 0.79-1.44% at a moisture content of 69.29% (2.27-4.44% on the absolutely dry weight).

The essential oil of Th. rariflorus is a liquid with a sharp odor of thymol which crystallizes at −7°C. The presence of 25 components in the oil has been shown by the GLC method (LKhM-8MD). Conditions of performing the analysis: carrier gas helium, rate of flow 6 ml/min. Carbowax 20 and PEG, mol. wt. 20,000. Length of the capillary column 50 m, internal diameter 0.25 mm, temperature of the evaporator 200°C, and of the column 70-180°C at 2 deg/min. The weight of the oil sample was 0.1 ml, discharge ratio 1/60, recorder 1 mV, speed of the paper 240 mm/h, FID, $V - 10^{-11}$ A. The components were identified by the introduction of known substances and from the retention times. It was possible to identify α-pinene, camphene, β-pinen, sabinene, myrcene, limonene, p-cymene, terpinene, terpineol, caryophyllene, linalool, boreneol, thymol, and carvacrol. The main substances (thymol and carvacrol) were isolated individually and were identified from their NMR and IR spectra.

It was found that the essential oil, on subcutaneous injection and administration per os, leads to a gradual and prolonged lowering of the arterial pressure which is accompanied by an intensification of the cardiac contractions. It was found that in the first 30-60 min after parenteral and enteral administration of the essential oil the intraocular pressure decreases.

The essential oil is also recommended as a product for perfumery and cosmetics.

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