Chemistry of Natural Compounds, Vol. 29, No. 6, 1993

A NEW TERPENE KETONE, A COMPONENT OF THE ESSENTIAL OIL OF *Elsholtzia ciliata*

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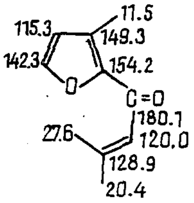
UDC 547.913.001.2

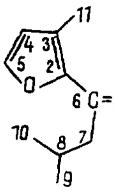
A new terpene ketone which has been called dehydroelsholtsia ketone has been isolated from the essential oil of Elsholtzia ciliata *(Thumb.) Hyl. The structure of dehydroelsholtsia ketone as 3-methyl-2-(3-methylbut-2-enoyl)furan has been proposed on the basis of a study of its IR, PMR, mass and ^{13}C spectra and has been confirmed by its conversion into elsholtzia ketone.*

Substance (I) with the composition $C_{10}H_{12}O_2$ (M^+ 164) has been isolated by preparative GLC from the essential oil of the epigeal part of *Elsholtzia ciliata* (Thumb.) Hyl. (*E. patrinii* (Lepech.)), *Lamiaceae* growing in the environs of Tomsk and collected in the flowering phase. It was a areddish readily mobile liquid with a peculiar pronounced pleasant odor. Its IR spectrum showed strong absorption bands (1580, 1618, 1658 cm^{-1}) relating to the stretching vibrations a double bond and a carbonyl group conjugated with one another. The presence of intense absorption bands (773 and 812 cm^{-1}, and also of one absorption band (850 cm^{-1}) in the region of deformation vibrations of C−H bonds permitted the assumption of the presence of a cis-substituted C=C bond in the molecule. A strong absorption band in the 1270 cm^{-1} region showed that the second oxygen atom in the molecule was present in the form of an ether bond.

In the PMR spectrum of substances (I) ($CDCl_3$, HMDS, δ, ppm) there were six signals: 1.92 (3H, d, J = 1 Hz, H-9), 2.20 (3H, d, J = 1 Hz, H-10), 2.37 (3H, s, H-11), 6.31 (1H, d, J = 2 Hz, H-4), 6.74 (1H, m, J = 1 Hz, H-7), 7.30 (1H, d, J = 2 Hz, H-5). Double resonance confirmed that the one-proton multiplet at 6.74 ppm was due to interaction with protons of the signals of the 1.92 and 2.20 ppm methyl groups. Analysis of the chemical shifts of the signals of the protons of substance (I) permit the assumption for this compound of the most probable structure of 3-methyl-2-(3-methylbut-2-enoyl)furan (I).



I



II

Such a structure of the ketone explains the difference in the chemical shifts of the protons of the isopropylidine group, the rotation of which is hindered as a result of conjugation.

The ^{13}C NMR spectrum of (I) consisted of 10 signals: three quartets at 11.5, 20.4, and 27.6 ppm ($-CH_3$); three doublets at 115.3, 114. 3, and 149.3 ppm (−CH=), and four singlets at 120.0, 128.9 (>C=), 154.2 (−O−C<), and 180.1 (>C=O). The assignment of the signals is shown in the formula of the compound.

When the ketone was hydrogenated over Adams platinum in acetic acid by Willstätter's method [1], the absorption of a mole of hydrogen led to a substance in the PMR spectrum of which the following signals were observed: 0.95 (6H, d, J = 7 Hz, H-9, 10) 2.30 (1H, m, J = 7 Hz, H-8); 2.50 (3H, s, H-11); 2.70 (2H, d, J = 7 Hz, H-7); 6.32 (1H, d, J = 1 Hz, H-4); 7.30 (1H, d, J = 1 Hz, H-5). The PMR spectrum, on the one hand, showed that the multiple bond of the isopropylidene group had been hydrogenated, and, on the other hand, it confirmed the assignment of the signals of the initial ketone made above.

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According to its IR spectum, the hydrogenated product was identical with a component isolated from the same essential oil corresponding in its constants and structure with the elsholtzia ketone described in the literature — substance (II) [1]. In the IR spectrum of elsholtzia ketone only the intense absorption band at 1620 cm^{-1} had disappeared, which is connected with the hydrogenation of one conjugated multiple bond.

Thus, the terpene compound isolated from the essential oil can be called dehydroelsholtzia ketone.

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer, PMR spectra on a Tesla 487.80 MHz spectrometer ^{13}C spectra on a Bruker WP-80 instrument, and mass spectra on a MKh-1310 spectrometer.

Substances (I) and (II) were isolated from the essential oil by preparative GLC on a 7 mm × 0.27 m column filled with Chromaton N 0.25-0.30 mm containing 20% of polyethyleneglycol 20 M. The carrier gas was hydrogen at 80 ml/min. The column temperature was 190°C.

Dehydroelsholtzia ketone (I) — $C_{10}H_{12}O_2$, n_D^{20} 1.4865, d_{20}^{20} 0.9674, $[\alpha]_D^{20}$ 0°. Its amount in the essential oil (GLC) was 85.00%.

Mass spectrum of dehydroelsholtzia ketone, m/z (%): 28(33), 29(29), 39(33), 41(15), 43(6), 65(5), 69(10), 77(10), 82(13), 83(100), 84(7), 91(12), 93(19), 95(7), 97(9), 107(10), 109(24), 121(24), 136(19), 147(14), 149(10), 164(58), 165(7).

Hydrogenation of Substance (I). The Willstatter hydrogenation of 0.85 g (0.05 mole) of the ketone in 10 ml of glacial acetic acid was performed in the presence of PtO_2 until the absorption of hydrogen slowed down. After the appropriate working up, the main substance (II) of the mixture was isolated with the aid of PGLC under the same conditions as (I).

Elsholtzia ketone (II) — $C_{10}H_{14}O_2$, n_D^{20} 1.4879, d_{20}^{20} 0.9815, $[\alpha]_D^{20}$ 0°. Amount in the esential oil (GLC) 6.50%.

REFERENCES

1. M. I. Goryaev and I. Pliva, Methods of Investigating Essential Oils [in Russian], Alma-Ata (1962).