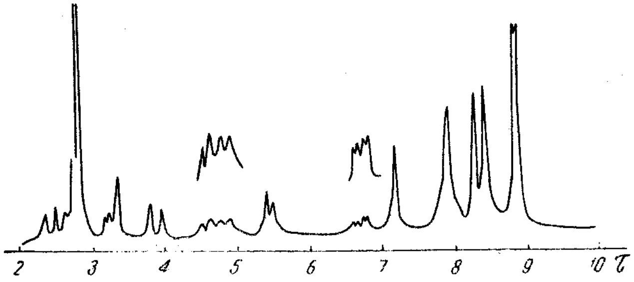
UDC 547–314

THE STRUCTURE OF KARATAVICINOL

N. P. Kir'yalov and V. Yu. Bagirov

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 4, pp. 225–227, 1969

From the resin of the roots of Ferula karatavica Rgl. et Schmalh. we have isolated a coumarin with the composition $C_{24}H_{32}O_5$, mp 52–53° C, $[\alpha]_D^{20}$ −12° (c 7.5; ethanol), which we have called karatavicinol. The acid hydrolysis of karatavicinol yielded umbelliferone. The UV, IR, and NMR spectra also show the coumarin nature of karatavicinol.

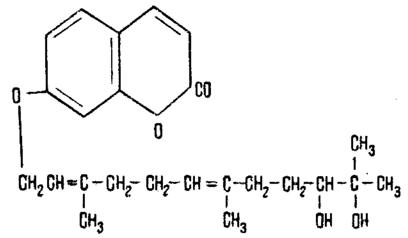


NMR spectrum of karatavicinol in chloroform.

Assuming on the basis of a study of the spectra that karatavicinol has two hydroxyl groups, one of which is secondary, we oxidized it with chromic anhydride in acetic acid and obtained a substance with the composition $C_{24}H_{30}O_5$, mp 59–60° C, identical with karatavicin [1]. On reduction with $NaBH_4$, karatavicin is readily reconverted into karatavicinol.

The results presented make it possible to propose for karatavicinol the structural formula I, which is also confirmed by the NMR spectrum (figure).

I



The signal with a center at τ 8.80 (6 H, J = 1.5 Hz) corresponds to the protons of a gem-dimethyl group. The doublet signals with centers at τ 4.63 (H, J = 6 Hz) and 4.90 (H, J = 9 Hz) apparently belong to olefinic protons. The vinylmethyl protons resonate at τ 8.24 (3 H) and 8.43 (3 H). The singlet signal at τ 7.18 (2 H) may be ascribed to the protons of the two OH groups. The quartet signal (half-width of the line ~15 Hz) with a center at τ 6.74 (H, J = 9 Hz) corresponds to a proton at a secondary hydroxyl group.

Experimental

Isolation of karatavicinol. A solution of 40 g of the neutral fraction of the resin of the roots of Ferula karatavica in 50 ml of chloroform was chromatographed on a column (800 g of Al_2O_3 of activity grade III). Elution was carried out with a mixture of petroleum ether and chloroform (1 : 9). The viscous oil was crystallized from a mixture of petroleum and diethyl ethers (1 : 3). This gave karatavicinol with mp 52–53° C, R_f 0.10 (Al_2O_3, activity grade III, chloroform). The yield was 2.5% of the neutral fraction of the resin.

UV spectrum: 324 μ(log δ 4.20). IR spectrum, cm^{-1}: 3370, 1725, 1615, 1404, 1135, 1027, 800, 855, 835, 794.

Found, %: C 72.15; H 8.10. Calculated for $C_{24}H_{32}O_5$, %: C 72.00; H 8.00.

Oxidation of karatavicinol. A solution of chromic anhydride (1 g) in 1 ml of water diluted with 5 ml of acetic acid was added to a solution of 0.6 g of karatavicinol in 20 ml of glacial acetic acid. The mixture was left for 1 hr and was then diluted with water, and the reaction product was extracted with diethyl ether. The ethereal extract was washed with water and dried over Na_2SO_4, and the ether was distilled off. The residue was crystallized from a mixture of petroleum and diethyl ethers (1 : 3). A substance with mp 59–60° C was obtained which gave no depression of the melting point in admixture with an authentic sample of karatavicin. Their IR spectra were also identical.

Reduction of karatavicin. A solution of 0.5 g of karatavicin in 20 ml of 92% ethanol was treated with 0.5 g of NaBH. The mixture was kept at room temperature for 1 hr. Then 15 ml of 2% H_2SO_4 was gradually added. The reaction product was extracted with diethyl ether. The ethereal extract was washed with water and dried over Na_2SO_4, and the ether was distilled off. The residue was crystallized from a mixture of petroleum and diethyl ethers (1 : 3). The substance had mp 52–53° C and gave no depression of the melting point in admixture with karatavicinol. Yield 30%. The IR and NMR spectra were also identical.

The microanalyses were carried out by E. A. Sokolva, the IR spectra were taken on a UR-10 instrment by A. M. Kutnevich, and the NMR spectra were obtained on a JNM-C-60 MG spectrometer.

Conclusions

The neutral fraction of the resin of the roots of Ferula karatavica Rgl. et Schmalh. has yielded a new coumarin with the composition $C_{24}H_{32}O_5$, mp 52–53° C, $[\alpha]_D^{20}$ −12° (c 7.5; ethanol) which has been called karatavicinol. It has been established that karatavicinol is an ether of umbelliferone and a sesquiterpene aliphatic triol. The structural formula **I** has been proposed for karatavicinol.

REFERENCE

1. N. P. Kir'yalov and V. Yu. Bagirov, KhPS [Chemistry of Natural Compounds], 3, 223, 1967.

1 April 1968 Komarov Botanical Institute AS USSR