THE COUMARIN TAVICONE FROM THE ROOTS OF FERULA KARATAVICA

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 6, pp. 591–592, 1969
UDC 577.15/17;582.29

By the chromatographic separation of the neutral fraction of the resin of the roots of Ferula karatavica Rgl. et Schmalh. on Al_2O_3 we have isolated a coumarin with the composition $C_{23}H_{26}O_4$ (M^+ 366), mp 141–142° C (ethanol), $[\alpha]_D^{26}$ −77° (benzene), which we have called tavicone. Yield 1%. IR spectrum in paraffin oil, cm^{-1}: 1730 (ketonic CO group in a five-membered ring), 1705 (CO of a lactone), 830 (double bond). On acid hydrolysis, tavicone formed umbelliferone.

The exhaustive hydrogenation of tavicone in CH_3COOH over PtO_2 yielded the nonumbelliferone part of the substance in the form of a saturated liquid ketol. IR spectrum in CCl_4 solution, cm^{-1}: 3500 (OH) and 1740 (ketonic CO group in a five-membered ring); UV spectrum (λ_{max}, mμ): 290 (log ε 1.58).

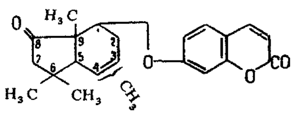
Reduction of the ketol with $LiAlH_4$ in diethyl ether yielded two isomeric diols with the composition $C_{14}H_{26}O_2$ (M^+ 226), mp 125–126° C and 162–163° C (petroleum ether and diethyl ether). The signals of an olefinic proton (5.68 ppm)* and the protons of a vinylmethyl group (δ 1.77 ppm) in the NMR spectrum of tavicone showed the presence of a secondary-tertiary double bond in it.

The presence of a $>CH{-}CH_2{-}O{-}$ grouping in tavicone is confirmed by a triplet (3.98 ppm) and a quartet (δ 4.29 ppm) corresponding to each of the protons of the $-CH_2{-}O-$ group. Under double-resonance conditions (the frequency of the strong radio frequency field corresponded to the chemical shift of the methine proton at 2.72 ppm), the signals of the protons of the methylene group in $-O{-}CH_2-$ were converted into doublets ($|J_{gem}|$ = 11 Hz).

It follows from this that the nonumbelliferone part of tavicone is attached to its coumarin part by the grouping $>CH{-}CH_2{-}O-$ probably at $C_{(1)}$.

The half-width of the signal of the methine proton ($C_{(1)}$—H) is about 30 Hz. On considering the $-O{-}CH_2-$ signals, we found that the sum of their coupling constants with the methine proton was 16 Hz. Then the sum of the coupling constants of the methine proton with the other vicinal protons is ~14 Hz. This figure is in good agreement with the sum of the coupling constants $J_{ea} + J_{aa}$ (≈13 Hz) [1] and is considerably greater than that expected for a $>CH{-}CH{=}$ fragment [2]. Consequently, the double bond is present at $C_{(3)}$—$C_{(4)}$ as is confirmed by the absence from the mass spectrum of tavicone of strong peaks due to retrodiene decomposition [3]. In the 2.2–2.7 ppm region of the NMR spectrum of tavicone ($CDCl_3$ solution) there are the signals of two protons of a methylene group. In benzene solution, the same signals appear in the form of a well-defined AB quarted (2.06 and 2.48 ppm, J = 17.5 Hz). These results show the presence of a cyclopentane ring in tavicone. On passing from solution in $CDCl_3$ to solution in benzene, the signals of the protons of the gem-dimethyl and the angular methyl groups of tavicone shift in the strong-field direction by 0.11 and 0.23 ppm, respectively. The greater shift of the signal of the protons of the angular group shows that the CO group is adjacent to the angular methyl group.

Thus, on the basis of what has been said above the following structure may be proposed for tavicone:



The mass spectra were taken on a MKh-1303 instrument at an energy of 40 eV.

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*The chemical shifts are given relative to the signal of TMS (0 δ, ppm).

REFERENCES

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8 October 1968

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