THE STRUCTURE AND STEREOCHEMISTRY OF CONFERIN

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The most probable structure (I), without taking relative configurations into account, has been proposed for conferin, isolated from Ferula conocaula Korov. [1]. A study of the PMR spectrum of dihydroconferin (II), $C_{26}H_{32}O_6$, M^+ 440, obtained by reducing (I) with sodium tetrahydroborate has enabled proposed structure (I) to be confirmed, and an investigation of the PMR spectra of (II) with additions of the paramagnetic shift reagent $Eu(DPM)_3$ has shown the relative configurations of (I) and (II).

PMR spectrum of (II) ($CDCl_3$; 20°C; 0 – TMS; HA-100D), δ, ppm: 0.98 (s 3 H, $C_{9'}-CH_3$), 1.01, 1.09 [singlets, 3 H each, $C_{5'}(CH_3)_2$],1.75 (HC, 3 H, $C_{2'}-CH_3$); 2.07 (s, 3 H, $O-COCH_3$); 3.30 (q, 1 H, $J_{a,a}=8.5$ Hz, $J_{a,e}=5.0$ Hz, $C_{6'}-H$); 4.12 (m, 2 H, $C_{1'}-CH_2-O-$), 5.41 (ur, 1 H, $W_{1/2}=7.0$ Hz, $C_{3'}-H$); 5.60 (m, 1 H, $\Sigma J=18.5$ Hz, $C_{4'}-H$), 6.25 (d, 1 H, J=9.5 Hz, C_3-H), 6.80 (m, 2 H, C_6-H, C_8-H), 7.37 (d, 1 H, J=8.5 Hz, C_5-H), 7.62 (d, 1 H, J=9.5 Hz, C_4-H).

The values of the spin–spin coupling constants of the signal of the proton geminal to the hydroxy group show the equatorial orientation of the hydroxyl in (II) and witness the presence of a methylene group in positon 7'. The latter conclusion is confirmed by the results of double-resonance spectra – the absence of spin–spin coupling between the protons geminal to the hydroxy and acetoxy groups, i.e., of the two positions 4' and 7' in which the acetoxy group may be present in the molecules of the (I) and (II) the only possible one is position 4'. The sum of the coupling constants of the signal of the proton at $C_{4'}$ (18.5 Hz) shows the equatorial orientation of the acetoxy group and the axial orientation of the proton at $C_{10'}$, which is in harmony with an hypothesis based on biogenetic considerations of the trans linkage of the rings in the decalin nucleus. To confirm the structure of (II) and to determine the relative configuration at C_1 we measured the PMR spectra of (II) with additions of $Eu(DPM)_3$. Figure 1 shows the dependence of the value of ΔEu (the shift of the signals at an equimolar ratio of the substance and the reagent) on r (the distance in Å from the oxygen atom of the hydroxy group to the protons concerned) in logarithmic coordinates. It can be seen that the points corresponding to the protons of the methyl groups at $C_{2'}$, $C_{5'}$, and $C_{9'}$ lie on the same straight line. The location of the points corresponding to the equatorial orientation of the $C_{1'}-CH_2$ group shows that

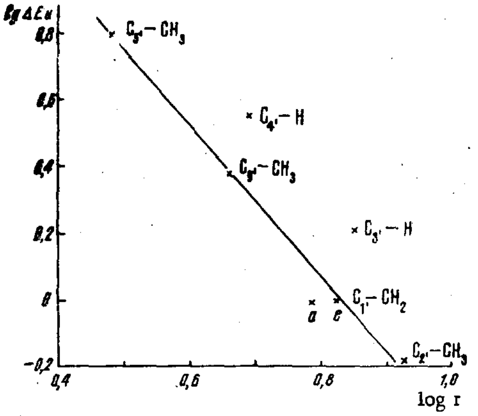

Fig. 1. Dependence of log ΔEu on log r for some protons of dihydroconferin.

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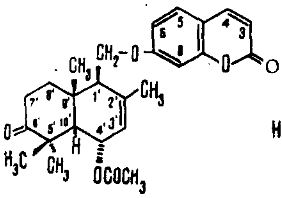
this group is equatorial. The deviation from the straight line of the points corresponding to $C_{4'}-H$ and $C_{3'}-H$ is probably due to partial complex-formation at the oxygen atoms of the acetoxy group. The tangent of the angle of slope of the straight line is 2.2, which is in harmony with the value found by Demarco et al., [2].

Thus, the arrangement of the hydroxyl with respect to the groups shown in Fig. 1., i.e., the correctness of structure (I) for conferin and of structure (II) for dihydroconferin, is confirmed:



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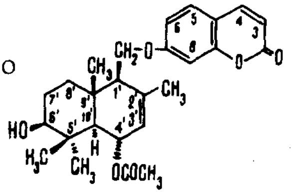

II

LITERATURE CITED

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2. P. V. Demarco, T. K. Elsey, R. B. Levis, and E. Wenkert, J. Amer. Chem. Soc., 92, 5734 (1970).