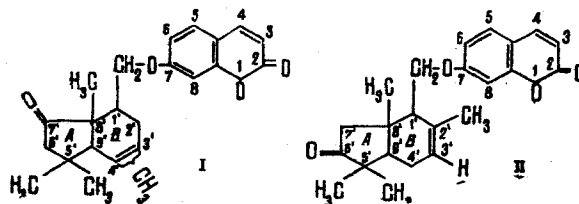


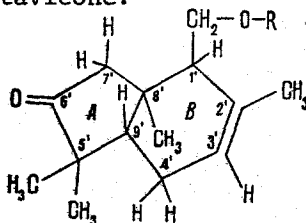
On the basis of investigations performed previously [1], structure (I) was proposed for tavicone:



However, as a result of a study of the PMR spectra of this compound with additions of the shift reagent $\text{Eu}(\text{FOD})_3$, we have obtained additional information enabling the structure of tavicone to be refined (Fig. 1). Thus, the relatively larger shift of the signals of the gem-dimethyl grouping than of the signal of the angular methyl group ($\Delta\delta_{\text{CH}_3-\text{C}_5'}/\Delta\delta_{\text{CH}_3-\text{C}_8'} = 1.5$), shows the location of the ketone group at C_6' . The signal of the proton at $\text{C}_9'-\text{H}$ is a quartet ($J_{9',4'a} = 12 \text{ Hz}$; $J_{9',4'e} = 4 \text{ Hz}$), which shows the presence of a methylene group in position $4'$. Since there is a proton in the $1'$ position, the double bond is located at $\text{C}_2'=\text{C}_3'$. It follows from double-resonance results that the width of the signal of the olefinic proton is determined by its interaction with the protons of the methylene group in position $4'$ and the protons of the methyl group on the double bond. The $\text{H}_{1'}$ proton does not interact with the olefinic proton. The smallest value of the $^3J_{\text{CH}-\text{CH}=\text{}}$ constant is 2 Hz [2, 3] and, consequently, the closeness of the value of the $J_{\text{H}_1, \text{H}_{\text{olefin}}}$ to zero shows the presence of a methyl group at C_2' . Thus, tavicone is represented by structure (II).

The large value of the constant $J_{9',4'a} = 12 \text{ Hz}$ in itself does not show the trans linkage of rings A and B in tavicone, since if the cyclohexene ring were present in the "boat" conformation a high value of $J_{9',4'a}$ would also be possible with the cis linkage of the rings. However, in the "boat" conformation the expected value of the sum of the constants $J_{4'a,3'}$ and $J_{4'e,3'}$ is more than 8 Hz [2, 3], while for the "half-chair" conformation it is 6.3 Hz . The observed value of 6.5 Hz is very close to the latter value. This value of the $J_{9',4'a}$ constant coincides with the corresponding constant in cyclohexenes present in the "half-chair" conformation [2]. The allyl constant $J_{3',1'}$, which is close to zero, shows [2, 4] the closeness of the dihedral angle between the proton and the double bond to 45° , which is observed in the "half-chair" conformation for a quasi-equatorial proton.

Thus, from a consideration of the coupling constants it follows that the cyclohexene ring is present in the "half-chair" conformation with an axial substituent at C_1' . In this case, the linkage of the rings is transoid. The facts given above permit the following spatial formula to be proposed for tavicone:



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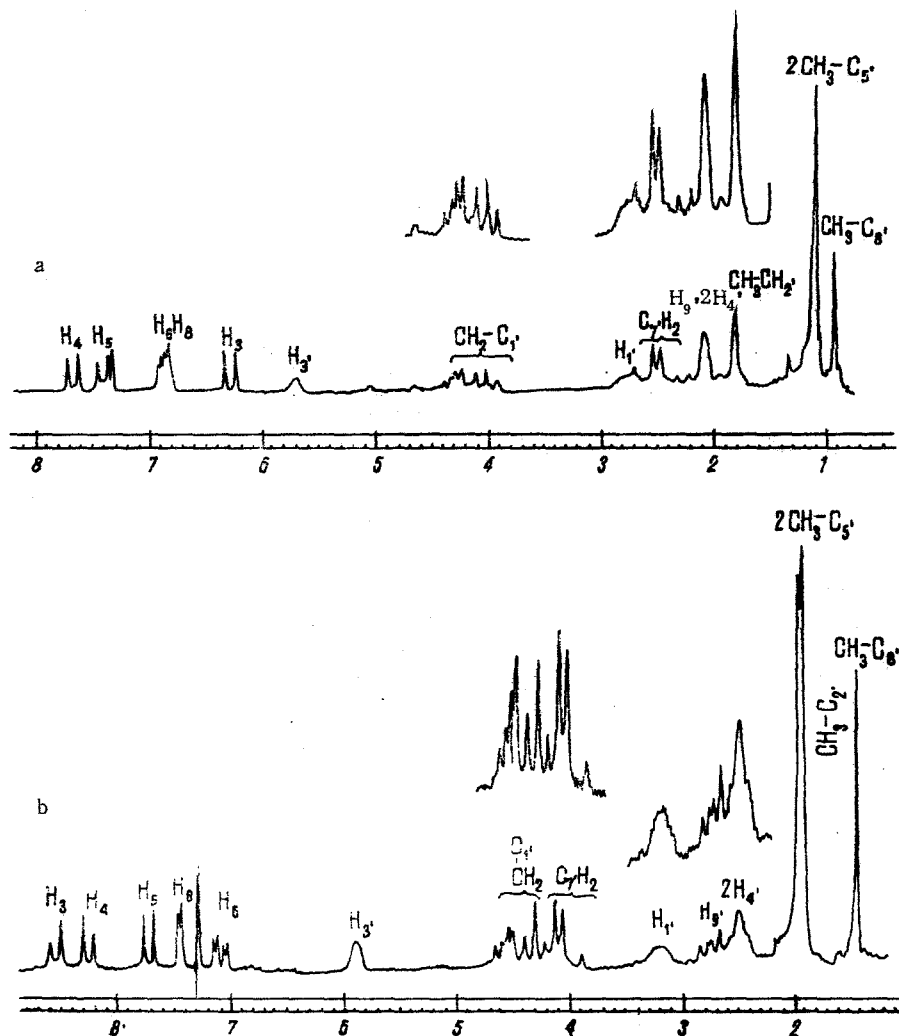


Fig. 1. NMR spectrum of tavicone in CDCl_3 in the absence of a reagent (a) and with the reagent $\text{Eu}(\text{FOD})_3$ (b).

where R is the coumarin residue.

The results of the application of the chemical shift reagent are in harmony with the proposed structure. It follows from the basic formula for the displacement of the signals under the action of a chemical shift reagent [5, 6] that for two protons (i and j) at distances r_i and r_j from the heteroatom the shifts $\Delta\delta_i$ and $\Delta\delta_j$ are connected by the following equation:

$$\log \frac{\Delta\delta_i}{\Delta\delta_j} = n \log \frac{r_j}{r_i}.$$

If the distance r_0 from the center of complex-formation to one of the protons in the molecule is known, the other values of r can be found from the value of $\Delta\delta$ in two spectra of the substance with the shift reagent. No information is required on the concentration of the substance and of the shift reagent in the solution, which excludes errors connected with their determination.

Below we give the values of $\Delta\delta$, r , and n found from the formula given above in the molecule of tavicone with the transoid linkage of the rings and the quasi-axial orientation of the substituents at C_1' : (See table at top of following page.)

The identical values of $\Delta\delta$ for the two protons at C_7' shows the symmetrical arrangement of these protons relative to the ketone group, which enables us to determine the distance between the oxygen atom of the ketone group and the protons at C_7' from Dreiding models ($r_{7'} = 2.75 \text{ \AA}$). Using this value, we determined the value of n . For different

Proton	$\Delta\delta$	$\frac{\Delta\delta_{7'}}{\Delta\delta}$	$\log \frac{\Delta\delta_{7'}}{\Delta\delta}$	r (Å)	$\frac{r}{r_{7'}}$	$\log \frac{r}{r_{7'}}$	n
H _{1'}	0,20	4,2	0,6232	5,4	1,97	0,2945	2,12
CH ₃ -C _{2'}	0,09	9,34	0,9703	8,3	3,01	0,4786	2,03
H _{3'}	0,12	7,00	0,8451	7,0	2,55	0,4065	2,04
H _{4'a}	0,23	3,65	0,5623	5,0	1,82	0,2601	2,15
H _{4'e}	0,19	4,23	0,6263	5,4	1,97	0,2945	2,12
CH ₃ -C _{5'}	0,47	1,77	0,2480	3,7	1,35	0,1303	1,90
H _{7'} and H _{7''}	0,84	1	0	2,75	1	0	0
CH ₃ -C _{8'}	0,31	2,71	0,4330	4,7	1,71	0,2330	1,84
CH ₂ -C _{1'}	0,16	5,25	0,7202	5,7	2,07	0,3160	2,24
H _{9'}	0,38	2,21	0,3444	4,0	1,45	0,1614	2,13

protons in the proposed configuration the values of n proved to be extremely similar, which is evidence in favor of the structure given for tavicone.

EXPERIMENTAL

The NMR spectra were obtained on an HA-100D instrument; the measurements with additions of Eu(FOD)₃ from E. Merck, Darmstadt, were performed at 20°C.

SUMMARY

It has been established from H¹ NMR spectra in CDCl₃ with additions of Eu(FOD)₃ as paramagnetic shift reagent that tavicone must be ascribed the structure of 7-(1,1,3a,5-tetramethyl-2-oxo- Δ^5 -hexahydroinden-4-ylmethoxy)coumarin. The stereochemistry of this compound has been determined.

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