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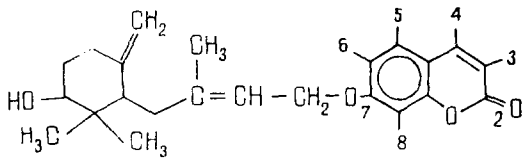
STEREOCHEMISTRY OF LATILOBINOL

A. Z. Abyshev

UDC 577.15/17.582.89

The results are given of a study of the stereochemistry of a coumarin terpenoid derivative — latilobinol — by nuclear magnetic resonance spectroscopy using lanthanoid shift reagents. On the basis of the results obtained, it has been established that the hydroxy group in the cyclohexane ring occupies the equatorial position.

In a study of the coumarin composition of *Prangos latiloba*, we previously isolated a new terpenoid coumarin — latilobinol (I) [1]. On the basis of chemical and spectral characteristics, the following structure was proposed for it:



However, stereochemical questions remained unsolved. In the present paper we report the results of a study of the stereochemistry of (I) by the methods of nuclear magnetic resonance (NMR) spectroscopy, using lanthanoid shift reagents (LSRs).

To determine the paramagnetic shift caused by the addition of LSRs we used a simplified form of the McConnel–Robertson formula [2]

$$\Delta\delta = K\frac{1}{r^3},$$

here $\Delta\delta$ is the induced chemical shift in the proton NMR spectra caused by the addition of an LSR; and r is the radius vector from the center of complex-formation to the observed proton, K being a constant for a given LSR and given temperature.

The task consisted in selecting the geometric parameter r that would give the best agreement of the induced chemical shift calculated from it and that found by experiment [3]. The comparison of theoretical and experimental values was made by the graphical method [4]. The method consists in the plotting of lines in the coordinates log $\Delta\delta$ = f(log r). Such a stereochemistry of the molecule was selected as the most probable in which the NMR parameters $\Delta\delta$ and the radius vector r permit the plotting of a straight line in these coordinates with an angle of slope tan $\alpha = -3$.

Figure 1 shows graphically the changes in the chemical shift of the protons as a function of the molar ratios of LSR and substrates $\delta = f(\rho)$. From the graphical results the change in the chemical shifts of the protons due to the addition of the LSR was determined.

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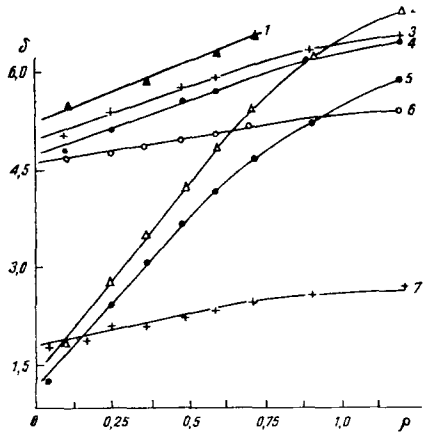


Fig. 1

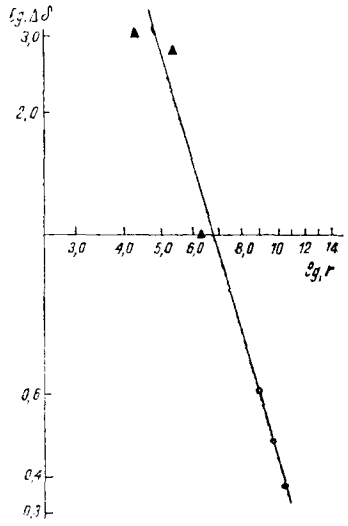


Fig. 2

Fig. 1. Dependence of the change in the chemical shift δ on the molar ratios of LSR to substrate for various protons: 1) methane proton; 6) methylene protons and 7) methyl protons of the aliphatic part of the molecule; 2 and 5) methyl protons; and 3 and 4) methylene protons at the double bond of the cyclohexene ring.

Fig. 2. The relation log Δδ = f(log r) for the latilobinol molecule.

The molecule of (I) can be divided into three parts: an aliphatic part linking the more rigid cyclohexane and the 7-hydroxycoumarin nuclei. We first studied the possible stereochemistry of the cyclohexane part of the molecule of (I). This was favored by the fact that complex-formation takes place at the hydroxylic oxygen of the cyclohexane nucleus to a considerably greater degree than that at the oxygen atoms in the coumain ring in positions 1, 2, and 7 [5]. We studied the protons of the methyl groups and of the methylene group of the double bond.

The table shows the results of calculations of the radius vector r of possible stereoisomers of the cyclohexane part of the latilobin molecule. For each stereoisomer the distance R_{O-Eu} from the center of complex-formation to the oxygen atom at which complex-formation took place was varied from 1 to 3 Å in 1-Å steps. Of the stereoisomers given, two — 1 and 6 — were selected since in them the angle of slope of the straight line plotted in the coordinates log Δδ = f(log r) agreed most closely with the value tan α = −3. Furthermore, it is known that the most suitable in the energetic respect is the "chair" stereoisomer [6]. On this basis it is possible to assume stereoisomer 1 for the cyclohexane moiety.

Figure 2 shows the relation log Δδ = f(log r) for the selected stereoisomer. From this graph we determined the distance from the center of complex-formation to the methine, methylene, and methyl protons of the aliphatic part of the molecule of (I): r_{CH} = 9.0 Å, r_{CH_3} = 9.7 Å, r_{CH_2} = 10.4 Å.

Thus, for latilobinol (I) a conformation has been established in which the hydroxy group of the cyclohexane nucleus occupies the equatorial position. As is well known [7], in a stereoisomer of latilobinol — farnesiferol B — this group occupies the axial position.

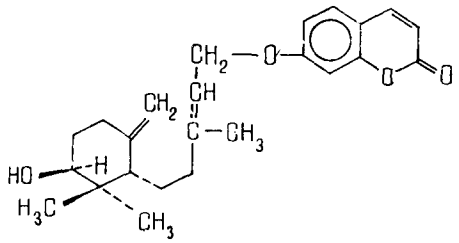


TABLE 1.

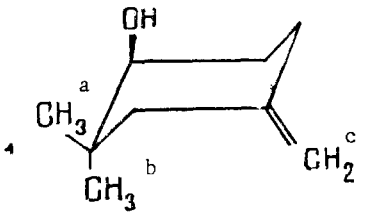
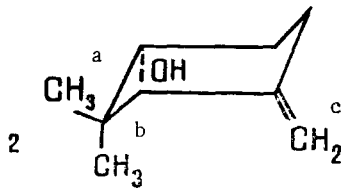
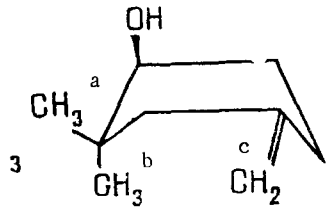
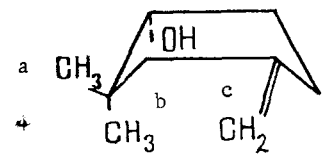
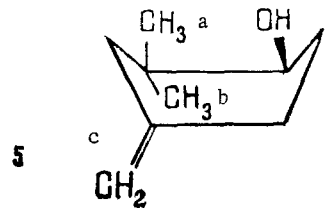
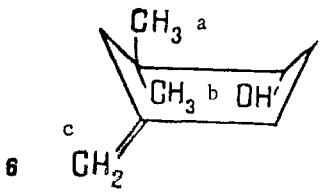
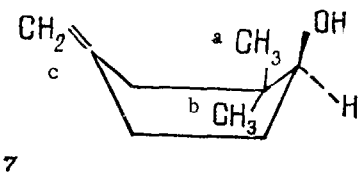
	R_{O-Eu}(Å)	r (Å)		
		a	*b*	*c*
 1	1	3,6	4,9	6,0
	2	.	5,4	6,3
	3	5,2	6,9	7,5
 2	1	—	—	—
	2	4,1	4,4	7,7
	3	6,0	6,0	9,6
 3	1	—	—	—
	2	4,0	6,0	5,9
	3	—	.	—
 4	1	—	—	—
	2	4,4	4,4	8,0
	3	—	—	—
 5	1	—	—	—
	2	3,5	5,5	7,4
	3	—	—	—
 6	1	—	—	—
	2	3,6	5,3	6,0
	3	4,4	6,0	6,7
 7	1	—	—	—
	2	4,3	6,0	3,0
	3	—	—	—

TABLE 1. (Continued)

1	—	—	—
2	4,4	4,4	7,2
3	—	—	—

EXPERIMENTAL

NMR spectra were taken on HX-90 Bruker spectrometer (in $CDCl_3$, 0 — TMS). Eu(dpm)$_3$ in CCl_4 solution was used as the lanthanoid shift reagent. The radius vectors r from the center of complex-formation to the observed protons of the cyclohexane part of the latilobinol molecule were calculated on a HP-2100S computer using a Dreiding model.

SUMMARY

The absolute configuration of a natural terpenoid coumarin — latilobinol — has been determined on the basis of its NMR spectra using lanthanoid shift reagents.

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COMPOSITION OF THE ESSENTIAL OIL OF *Tanacetum vulgare*

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UDC 547.913.001.2

The essential oil of the common tansy obtained from a population growing in the Dzhungarain Ala-Tau has been investigated. More than 50 substances have been detected, of which 39, including the main ones, have been identified.

The plant *Tanacetum vulgare* L. (common tansy) is found in almost all the regions of Kazakhstan, apart from the southern deserts. It grows in the forest and steppe zones in forest glades, on the banks and in the flood-plains of rivers, in the foothills, and in the valleys between mountains, and, as a weed, on roads and on the edges of fields and pastures.

This plant is widely used in folk medicine. A decoction of tansy flowers and fruit is an effective agent for expelling roundworms, pinworms, and tapeworms and is also used in jaundice, as a sedative in cases of rheumatism, headache, and epilepsy. In scientific

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