THE STEREOCHEMISTRY OF NEVSKIN

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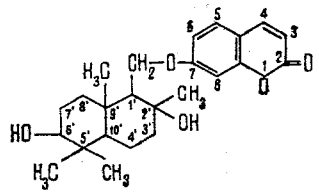
The terpenoid coumarins samarcandin and nevskin are stereoisomeric compounds [1]. The following structure has been proposed for the latter on the basis of the investigations performed:



From a consideration of the parameters of the NMR spectrum of acetylnevskin it follows that the acetyl substituent at C_6' occupies the equatorial position $J_{6a,7a}$ = 9.5 Hz; $J_{6a,7e}$ = 6.0 Hz) [2]. Below we give the chemical shifts and coupling constants of the signals in the spectrum of acetylnevskin (Varian HA-100D, t = 20°C, $CDCl_3$, 0 — TMS):

Proton	δ, ppm; J, Hz, multiplicity
$\mathbf{CH_3}$—$C_{2'}$	1.16; s
$\mathbf{CH_{3e}}$—$C_{5'}$	0.89; s
CH_{3a}—$C_{5'}$	0.89; s
CH_3—$C_{9'}$	1.14; s
$C_{6'}$—OCO$\mathbf{CH_3}$	2.03; s
H—$C_{6'}$	4.50; q, $J_{6a,7a}$=9.5; $J_{6a,7e}$=6.0
$\mathbf{CH}$—$C_{1'}$	4.15; q, J_{gem}=10.0; J_{vic}= 3.0
$\mathbf{CH}$—$C_{1'}$	4.36; q, J_{gem}=10.0; J_{vic}= 4.0
$\mathbf{H_3}$	6.25; d, J_{ortho}= 9.2
H_4	7.63; d, J_{ortho}= 9.2
H_5	7.35; d, J_{ortho}= 8.5
H_6	6.81; q, J_{ortho} = 8.5; J_{meta} =2.0
H_8	6.85; d, J_{meta}=2.0

The single of the angular methyl group in acetylnevskin is shifted downfield by 0.21 ppm as compared with that in acetylsamarcandin (0.95 ppm), which shows the axial position of the hydroxy group at C_2'. To determine the configuration of the substituent at C_1' in nevskin, we used the chemical shift reagent $Eu(FOD)_3$. The values of ΔEu in the spectra of the acetyl derivatives of nevskin and samarcandin are as follows (ppm): (See table at the top of following page.)

The closeness of the values of ΔEu for the acetyl groups and the coincidence of ΔEu for the protons at C_4 and C_5 of the coumarin nucleus show the approximately similar associating capacities of the centers at C_6' and of the oxygen atoms of the lactone ring. At the same time, it can be seen from the values of ΔEu for CH_3—C_2' and the OH groups in these compounds that the associating capacity of the center at C_2' in acetylsamarcandin is considerably higher than that for acetylnevskin. Since the values of ΔEu for CH_3—C_2' in samarcandin and deacetylkellerin, in which the hydroxy groups at C_2' have different configurations, are close, the fall in the value of ΔEu(OH) in acetylnevskin cannot be due solely to the 1—3 coupling of the OH and CH_3—C_9' groups. The cause of the decrease in the associating capacity

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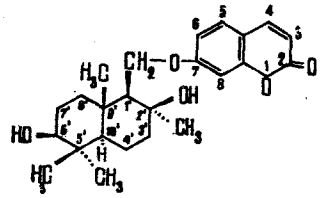
Proton	Acetylnevskin	Acetylsamarcandin
$CH_{3a}-C_{5'}$	2,5	1,9
$CH_{3e}-C_{5'}$	3,0	2,8
$CH_3-C_{2'}$	1,6	3,3
$OH-C_{2'}$	7,3	29,0
$CH_3-C_{9'}$	2,0	1,5
$CH-C_{1'}$	1,6	3,1
$CH-C_{1'}$	1,9	4,4
$H-C_{6'}$	10,0	7,8
$H-C_{1'}$	—	7,3
$-O-COCH_3$	7,5	6,3
H_3	4,8	4,0
H_4	1,3	1,3
H_5	0,7	0,7
H_6	0,6	1,4
H_8	1,7	2,6

of the center at C_2' may be considered to be the steric influence of the voluminous substituent at C_1'. It follows from this that the OH group at C_2' and the substituent at C_1' are present in the cis position, i.e., the substituent at C_1' has the equatorial and the OH group at C_2' the axial orientation. Thus, nevskin has the following relative configurations of the substituents:



It follows from the facts given that nevskin differs from isosamarcandin [3] only by the configuration of the substituent at C_2'. Then the structure of acetylnevskin should be identical with that of colladocin [4]. However, these compounds differ from one another in their physicochemical constants in the same way as acetylnevskin differs from acetylisosamarcandin. Consequently, the terpenoid coumarin colladocin is, in all probability, the acetyl derivative of isosamarcandin.

EXPERIMENTAL

The NMR spectra were obtained on an HA-100D instrument; the measurements with the addition of $Eu(FOD)_3$ from E. Merck, Darmstadt, were performed at 20°C.

SUMMARY

The relative configurations of the substituents in nevskin have been determined from the H^1 NMR spectra in $CDCl_3$ with additions of $Eu(FOD)_3$ as paramagnetic shift reagent.

LITERATURE CITED

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4. V. N. Borisov et al., Khim. Prirodn. Soedin., 247 (1975).