NMR SPECTRA OF NATURAL COUMARIN DERIVATIVES

III. DIHYDROFUROCOUMARINS AND DIHYDROPYRANOCOUMARINS*

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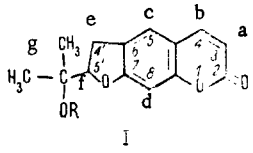
UDC 541.6 + 547.64

Recently, a considerable number of dihydrofurocoumarins and dihydropyranocoumarins having a number of common structural elements as a consequence of a common biosynthetic pathway have been isolated from plant materials. Consequently, it is desirable to consider the NMR spectra of these substances together, concentrating attention on their differences: in practice the problem frequently arises of assigning a new compound to one of these groups.

The bulk of the dihydrofurocoumarins and dihydropyranocoumarins known at the present time can be represented by the structural types shown below.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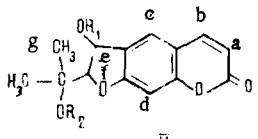
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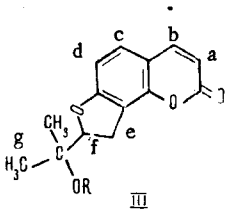
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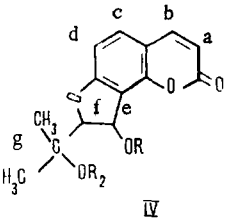
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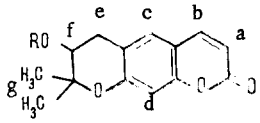
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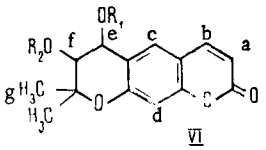
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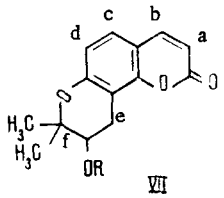
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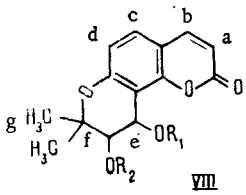

VIII

* For Communications I and II, see [1, 2].

All-Union Scientific-Research Institute of Medicinal Plants. S. Ordzhonikidze All-Union Chemical and Pharmaceutical Scientific-Research Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 712-721, November-December, 1971. Original article submitted July 12, 1971.

TABLE 1. NMR Spectra of Dihydrofurocoumarins and Dihydropyranocoumarins*

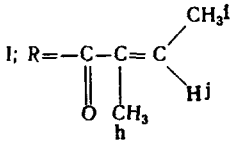
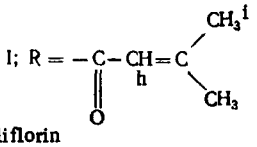
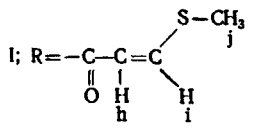
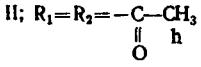
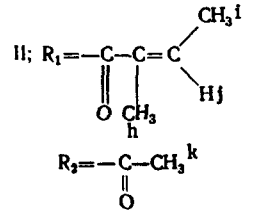
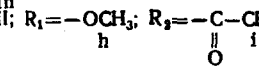
Compound†	Solvent	Chemical shift, δ, ppm; multiplicity,† J, Hz
Marmesin I; R = Hh	$CDCl_3$	a 6,17 (d; 10,0) e 3,24 (d; 9,1) b 7,58 (d; 10,0) f 4,74 (d; 9,1) c 7,17, s g 1,23, s d 6,65, s 1,37, s h 2,08 br
Deltoin  I; R = –C(=O)–C(h)=C(–CH_3 i)–Hj	$CDCl_3$	a 6,19 (d; 9,6) f 5,05 (t; 8,6) b 7,60 (d; 9,6) g 1,62, s c 7,22, s h 1,66, us d 6,71, s i 1,89 (q; 7,9; 1,5) e 3,28 (d; 8,6) j 5,99, m
Pranchimgin  I; R = –C(=O)–CH(h)–C(–CH_3 i)=CH_2	$CDCl_3$	a 6,08 (d; 10,0) f 5,09 (t; 8,0) b 7,56 (d; 10,0) g 1,48, s c 7,18, s 1,53, s d 6,66, s h 5,46, us e 3,18 (d; 8,0) i 1,79, us 2,04, us
Seseliflorin  I; R = –C(=O)–C(H h)=C(H i)–$S–CH_3$ j	CCl_4	a 6,05 (d; 9,8) f 5,19 (t; 8,8) b 7,41 (d; 9,8) g 1,48, s c 7,07, s 1,64, s d 6,64, s h 5,63 (d; 10,0) e 3,20 (d; 8,8) i 6,36 (d; 10,0) j 2,36, s
Smyrniorin  II; R_1=R_2=–C(=O)(h)–CH_3	CCl_4	a 6,10 (d; 9,6) f 5,14 (d; 5,5) b 7,51 (d; 9,6) g 1,62, s c 7,41, s 1,70, s d 6,71, s h 1,97, s e 6,29 (d; 5,5) 2,03, s
Smyrnioridin  II; R_1=–C(=O)(h)–C(–CH_3 i)=CHj R_2=–C(=O)–CH_3 k	CCl_4	a 6,11 (d; 9,1) g 1,62, s b 7,50 (d; 9,1) 1,71, s c 7,46, s h 1,84, m d 6,75, s i 1,98, m e 6,41 (d; 6,3) j 6,08, m f 5,19 (d; 6,3) k 1,95, s
5'-(1-Acetoxy-1-methylethyl)-4'-methoxy-4',5'-dihydro-3',2':6,7-coumarin  II; R_1=–OCH_3; R_2=–C(=O)(h)–CH_3 i	CCl_4	a 6,18 (d; 9,8) f 4,79 (d; 3,5) b 7,57 (d; 9,8) g 1,64, s c 7,42, s 1,49, s d 6,78, s h 3,40, s e 5,01 (d; 3,5) i 1,97, s

TABLE 1. (Continued)

Compound†	Solvent	Chemical shift, δ, ppm; multiplicity,‡ J, Hz
Zosimol III; R=H h	$CDCl_3$	a 6,14 (d; 9,6) e 3,31 (d; 8,4) b 7,55 (d; 9,6) f 4,74 (d; 8,4) c 7,20 (d; 8,2) g 1,25, s d 6,67 (d; 8,2) 1,35, s h 1,83, br
Libanoridin III; R=—C(=O)—CH_3 h	$CDCl_3$	a 6,17 (d; 10,0) e 3,30 (t; 8,5) b 7,62 (d; 10,0) f 5,14 (t; 8,5) c 7,25 (d; 8,5) g 1,49, s d 6,72 (d; 8,5) 1,56, s h 1,97, s
Zosimin III; R=—C(=O)—C(—CH_3 h)=C(—H j)—CH_3 i	CCl_4	a 6,05 (d; 10,0) f 5,12 (t; 8,5) b 7,54 (d; 10,0) g 1,62, s c 7,18 (d; 8,0) h 1,62, us d 6,57 (d; 8,0) i 1,85, m e 3,33 (d; 8,5) j 5,92, m
Libanorin III; R=—C(=O)—CH=C(—CH_3)—CH_3 i, h	$CDCl_3$	a 6,17 (d; 9,3) f 5,13 (t; 8,6) b 7,62 (d; 9,3) g 1,51, s 1,59, s c 7,26 (d; 8,7) h 5,55, us d 6,72 (d; 8,7) i 1,84, us e 3,32 (d; 8,6) 2,08, us
Athamantin IV; R_1=R_2=—C(=O)—CH_2—CH(—CH_3)—CH_3 i, h	$CDCl_3$	a 6,29 (d; 10,0) f 5,50 (d; 7,0) b 7,70 (d; 10,0) g 1,63, s c 7,50 (d; 8,0) 1,74, s d 6,92 (d; 8,0) h 2,18, us e 7,03 (d; 7,0) i 0,97, br
Edultin IV; R_1=—C(=O)—C(—CH_3 h)=C(—H j)—CH_3 i R_2=—C(=O)—CH_3 k	$CDCl_3$	a 6,22 (d; 10,0) g 1,60, s b 7,64 (d; 10,0) 1,68, s c 7,44 (d; 8,3) h 1,85, us d 6,86 (d; 8,3) i 1,99 (q; 8,5; 1,5) e 7,08 (d; 6,5) j 6,06, m f 5,29 (d; 6,5) k 2,02, s
5'-(1-Acetoxy-1-methylethyl)-4'-methoxy-4',5'-dihydrofuro-2',3' : 7,8-coumarin IV; R_1=—OCH_3 h R_2=—C(=O)—CH_3 i	CCl_4	a 6,14 (d; 9,8) f 4,70 (d; 3,5) b 7,58 (d; 9,8) g 1,46, s c 7,28 (d; 8,4) 1,60, s d 6,71 (d; 8,4) h 3,58, s e 5,15 (d; 3,5) i 1,93, s
Agasyllin V; R=—C(=O)—C(—CH_3)=C(—H i)—CH_3 h	CCl_4	a 6,05 (d; 9,2) e 3,20 (q; 16,5; 4,9) b 7,43 (d; 9,2) 2,83 (q; 16,5, 5, 7) c 7,06, s f 5,05 (t; J_1+J_2= =10,6) d 6,64, s g 1,38, s h 1,8—2,0, m i 6,05, m

TABLE 1. (Continued)

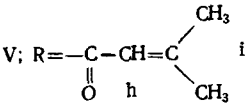
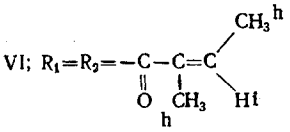
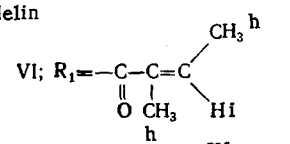
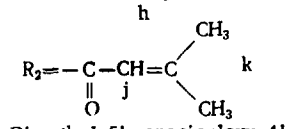
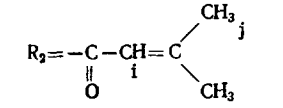
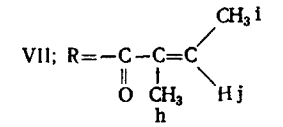
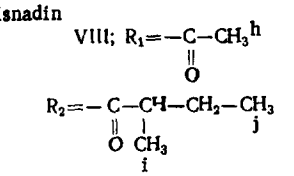
Compound†	Solvent	Chemical shift, δ, ppm, multiplicity,‡, J, Hz
Decursin  V; R=—C(=O)—CH=C(CH$_3$)$_2$ (i, h)	CCl_4	a 6,02 (d; 9,5) f 4,98 (t; 5,1) b 7,42 (d; 9,5) g 1,35, s c 7,05, s 1,40, s d 6,59, s h 5,57, us e 2,83 (q; 17,0; 5,1) i 1,88, us 3,18 (q; 17,0; 5,1) 2,16, us
Xanthalin  VI; R_1=R_2=—C(=O)—C(CH$_3$)=C(CH$_3$)$_2$ (h, h, i)	$CDCl_3$	a 6,23 (d; 10,0) f 5,52 (d; 4,5) b 7,62 (d; 10,0) g 1,46, s c 7,36, s 1,49, s d 6,79, s h 1,6—2,1, m e 6,34 (d; 4,5) i 6,10, m
Andelin  VI; R_1=—C(=O)—C(CH$_3$)=C(CH$_3$)$_2$ (h, h, i)  R_2=—C(=O)—CH=C(CH$_3$)$_2$ (j, k)	CCl_4	a 6,11 (d; 9,8) g 1,37, s 1,44, s b 7,55 (d; 9,8) h 1,84, us c 7,34, s 1,99 (q; 6,9; 1,3) d 6,66, s i 6,04, m e 6,01 (d; 5,7) j 5,64, us f 5,24 (d; 5,7) k 1,90, us 2,14 us
6'6'-Dimethyl-5'-senecioyloxy-4',methoxy-4',5'-dihydropyrano-3'2':6,7-coumarin VI; R_1=—OCH$_3$ (h)  R_2=—C(=O)—CH=C(CH$_3$)$_2$ (i, j)	CCl_4	a 6,11 (d; 9,3) g 1,37, s b 7,47 (d; 9,3) 1,42, s c 7,33, s h 3,50, s d 6,70, s i 5,65, us e 4,22 (d; 4,4) j 1,92, us f 5,19 (d; 4,4) 2,19, us
Xanthogalol VII; R=H (h)	$CDCl_3$	a 6,21 (d; 10,0) f 3,91 (t; 5,1) b 7,61 (d; 10,0) g 1,36, s c 7,23 (d; 8,8) 1,41, s d 6,77 (d; 8,8) h 2,18, s e 2,96 (q; 17,9; 5,1) 3,15 (q; 17,9; 5,1)
Xanthogalin  VII; R=—C(=O)—C(CH$_3$)=C(CH$_3$)$_2$ (h, i, j)	CCl_4	a 6,24 (d; 10,0) f 5,21 (t; 5,5) b 7,64 (d; 10,0) g 1,39, s c 7,27 (d; 8,0) h 1,87, us d 6,79 (d; 8,0) i 1,92, m e 2,96 (q; 18,0; 5,5) j 6,10, m 3,20 (q; 18,0; 5,5)
Visnadin  VIII; R_1=—C(=O)—CH$_3$ (h) R_2=—C(=O)—CH(CH$_3$)—CH$_2$—CH$_3$ (i, j)	CCl_4	a 6,09 (d; 9,5) f 5,21 (d; 4,8) b 7,47 (d; 9,5) g 1,41, s c 7,28 (d; 8,5) h 2,06, s d 6,67 (d; 8,5) i 1,17 (d; 7,0) e 6,38 (d; 4,8) j 0,91 (t; 7,5)

TABLE 1. (Continued)

Compound†	Solvent	Chemical shift, δ, ppm, multiplicity,‡ J, Hz
Dihydrosamidin VIII; R_1=—C(=O)—CO₃ h R_2=—C(=O)—CH₂—C(CH₃)(CH₃) i, j	$CDCl_3$	a 6,25 (d; 10,0) g 1,41, s b 7,63 (d; 10,0) 1,44, s c 7,38 (d; 8,2) h 2,14, s d 6,81 (d; 8,2) i 2,18 (d; 7,5) e 6,55 (d; 5,4) j 0,96 (d; 6,9) f 5,34 (d; 5,4)
Pteryxin VIII; R_1=—C(=O)—C(CH₃ h)=C(H j) R_2=—C(=O)—CH₃ k	$CDCl_3$	a 6,23 (d; 9,3) g 1,45, s b 7,62 (d; 9,3) 1,47, s c 7,39 (d; 8,6) h 1,86, us d 6,82 (d; 8,6) i 1,97 (q; 7,2; 2,0) e 6,63 (d; 4,9) j 6,00, m f 5,35 (d; 4,9) k 2,10, s
Anomalin VIII; R_1=R_2=—C(=O)—C(CH₃ h)=C(H i)(CH₂ j)	$CDCl_3$	a 6,21 (d; 10,0) f 5,43 (d; 5,1) b 7,62 (d; 10,0) g 1,46, s c 7,39 (d; 8,2) 1,50, s d 6,81 (d; 8,2) h 1,84, us e 6,69 (d; 5,1) i 6,08, m j 1,97 (q; 8,3; 1,8)
Floroselin VIII; R_1=—C(=O)—C(h H)=C(H i)(S—CH₃ j) R_2=—C(=O)—C(CH₃ k)=C(H l)	$CDCl_3$	a 6,19 (d; 10,0) g 1,44, s b 7,58 (d; 10,0) 1,49, s c 7,35 (d; 8,5) h 5,77 (d; 10,0) d 6,79 (d; 8,5) i 7,08 (d; 10,0) e 6,65 (d; 5,0) j 2,37, s f 5,43 (d; 5,0) k 1,8—2,0, m l 6,05, m
6,6'-Dimethyl-5'-angeloyloxy-4'-methoxy-4',5'-dihydropyrano-2',3':7,8-coumarin VIII; R_1=—OCH₃ h R_2=—C(=O)—C(CH₃ i)=C(H j)	$CDCl_3$	a 6,25 (d; 9,9) g 1,46, s b 7,61 (d; 9,9) 1,50, s c 7,32 (d; 9,0) h 3,80, s d 6,79 (d; 9,0) i 1,76—1,96, m e 4,50 (d; 2,0) j 6,10, m f 5,29 (d; 2,0)

* Spectra obtained on HA-100D and JNM-4H-100 instruments; 0—TMS.
† The Roman numerals denote one of the structural types shown above.
‡ s — singlet; d — doublet; t — triplet; q — quartet; m — multiplet; br — broad signal; us — unresolved or weakly resolved signal appearing in the form of a singlet.

The chemical shifts (CSs) and spin—spin coupling constants (SSCCs) in the spectra of the compounds that we have studied are given in Table 1. An analysis of the figures of Table 1 enables a number of conclusions of interest for the structural analysis of the compounds studied to be drawn.

The linear dihydrofurocoumarins and dihydropyranocoumarins can easily be distinguished from their angular analogs by analyzing the region of aromatic protons. In the spectrum of the linear compounds there are two singlets from the protons at C_5 and C_8, and in the spectra of the angular analogs there are two doublets from the protons at C_5 and C_6 with SSCCs of 8.2-9.0 Hz.

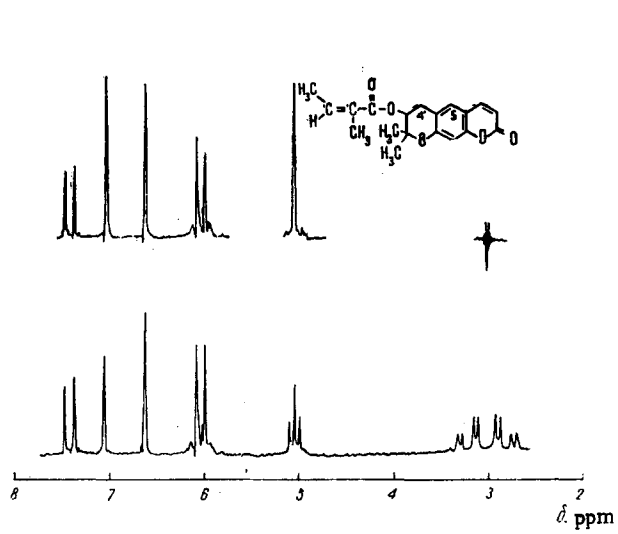


Fig. 1

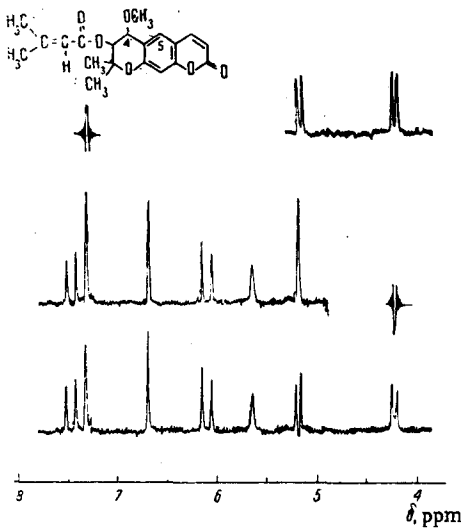


Fig. 2

Fig. 1. Fragment of the NMR spectrum of agasyllin in CCl_4, HA-100D. (The double-resonance spectrum is given at the top; it shows long-range SSC between the proton at C_5 and the protons of the methylene group at $C_{4'}$.)

Fig. 2. Fragment of the NMR spectrum of 6',6'-dimethyl-5'-senecioyloxy-4'-methoxy-5',6'-dihydropyrano-3',2' : 6,7-coumarin in CCl_4, HA-100D. (Parts of the double-resonance spectrum are shown at the top; they demonstrate long-range SSC between the protons at C_5 and $C_{4'}$.)

In the linear dihydrofurocoumarins and dihydropyranocoumarins long-range spin–spin coupling (SSC) between the C_5–H and the protons at $C_{4'}$ of the dihydrofuran and dihydropyran rings, shown up by means of double resonance, is found. Consequently, the signal from C_5–H is somewhat broadened as compared with the signal from C_8–H; for compounds of types (I) and (V) the peak intensity of the signal from C_5–H is 70-74% of the corresponding intensity for C_8–H. In compounds of types (II) and (VI)the broadening of the signal C_5–H is somewhat less (peak intensity 80-90% of that of the C_8–H signal). At the same time, in the latter case a broadened signal from $C_{4'}$–H is clearly seen, which is eliminated when the singlet from C_5–H is irradiated. As examples, parts of the spectra of agasyllin and of 6',6'-dimethyl-5'-senecioyloxy-4'-methoxy-5',6'-dihydropyrano-3',2' : 6,7-coumarin are shown in Figs. 1 and 2. Information on long-range SSC can also be used in structural studies of the compounds under consideration.

Dihydrofurocoumarins with a hydroxyisopropyl group in position 5' (types I and III; R = H) and the isomeric dihydropyranocoumarins (V and VII; R = H) can be differentiated from the positions and multiplicities of the signals of the protons of dihydrofuran and dihydropyran groupings. For the former, the signal of the methyl proton at $C_{5'}$ is at 4.74 ppm, and for the latter the corresponding $C_{6'}$–H signal is located at 3.90 ppm.

The proton at $C_{5'}$ is deshielded, since the coumarin nucleus exhibits an acceptor influence [3, 4] with respect to the substituent in position 7. In (V) and (VII), the deshielding influence of the hydroxy group is smaller, and the signal from $C_{3'}$–H is found in the stronger field.

Furthermore, for these types of compounds differences are found in the multiplicity of the signals of the protons of the methylene group. In the spectra of (I) and (III) (R = H) the methylene group appears in the form of a doublet at 3.24-3.31 ppm with J = 8.4-9.1 Hz. In this case, the protons of the dihydrofuran ring probably gives a degenerate ABX spectrum, in which the CS between the AB protons and the ratio $(J_{AX}-J_{BX})/2J_{AB}$ are substantially smaller than J_{AB}. Consequently, the SSCC found of 8.4-9.1 Hz is the average for J_{AX} and J_{BX}. A similar situation has been reported, for example, in the spectrum of 2-furfural [5].

In the spectra of dihydrocoumarins of types (V) and (VII) (R = H), the methylene protons have two quartets: at 2.96 and 3.15 ppm, J_1 = 17.9 and J_2 = 5.1 Hz.

TABLE 2. Average Increments for Calculating the Positions of the Signals of the Protons in the NMR Spectra

Substituent	Increment, ppm			
	linear		angular	
	through 2 bonds	through 3 bonds	through 2 bonds	through 3 bonds
At $C_{4'}$ and $C_{5'}$ for the dihydrofurocoumarins				
—OH, OAlk	+1,75	+0,05	+1,87	+0,05
—O—C—R (O)	+3,13	+0,33	+3,77	+0,39
At $C_{4'}$ and $C_{5'}$ for the dihydropyranocoumarins				
—OH, —OAlk	+2,20	+0,15	+2,12	+0,17
—O—C—R (O)	+3,20	+0,20	+3,36	+0,20

TABLE 3

Compound	Assignment accord. to [6]		Calculated values		Correct assignment	
	$H_{3'}$	$H_{4'}$	$H_{3'}$	$H_{4'}$	$H_{3'}$	$H_{4'}$
R_1=—C(O)—C(CH$_3$)=CH—CH$_3$, R_2=H	6,38	4,02	4,17	6,44	4,02	6,38
R_1=H, R_2=—C(O)—C(CH$_3$)=CH—CH$_3$	5,08	5,32	5,38	5,23	5,32	5,08
cis- R_1=CH_3, R_2=H	4,71	3,88	4,14	5,20	3,88	4,71
trans- R_1=CH_3, R_2=H	4,65	3,92	4,14	5,20	3,92	4,65

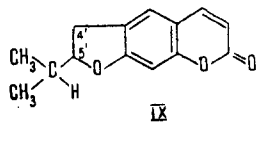
In the spectra of the acylated derivatives (R = Ac) of the compounds considered, the positions of the methine protons are similar. (In both cases, the signals are in the range from 4.98 to 5.21 ppm.) The differentiation of types (I) and (III) and of (V) and (VII) can be performed in the first place from the multiplicity of the signal of the CH_2 group, which is retained on passing from the hydroxy to the acyloxy derivatives and, in the second place, from the position of the signal of the gem-dimethyl grouping: for (I) and (III) at least one of the singlets is in the 1.53-1.64 ppm range, while for (V) and (VII) the CSs of these signals do not exceed 1.40 ppm.

In the spectra of compounds of types (II, IV, VI, and VIII), the protons of the dihydrofuran and dihydropyran rings give two characteristic one-proton doublets, which distinguishes these types of structures from compounds (I, III, V, and VII), each of which has the signal of a cyclic methylene group in its spectrum. The assignments of these doublets given in Table 1 were made by taking into account the influence on the CSs of the R_1 and R_2 radicals, the magnetic anisotropy of the benzene ring, and also information on the long-range SSC observed with the aid of double resonance.

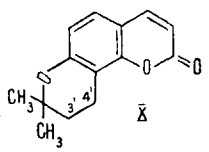
In order to distinguish the diacyloxydihydrofurocoumarins from the diacyloxydihydropyranocoumarins [types (II and IV) from (VI and VIII), R_1 = Ac_1, R_2 = Ac_2], it is most convenient to use the CS values of the protons of the gem-dimethyl grouping. In the first case, the spectrum contains two singlets: one in the 1.60-1.66 ppm range and the other at 1.68-1.74 ppm. In the spectra of the diacyloxydihydropyranocoumarins, the gem-dimethyl group gives one or two signals in the 1.37-1.50 ppm range. In addition to this, some differences must be noted in the position of the doublet of the proton at $C_{4'}$: for (II) it is at 6.29-6.41 ppm, for (IV) at 7.03-7.08 ppm, for (VI) at 6.01-6.34 ppm, and for (VIII) at 6.33-6.69 ppm.

Thus, the doublet mentioned appears in weaker fields for the angular compounds than for the linear compounds. Simultaneously, on comparing the CSs of the proton at $C_{4'}$ it can be seen that it is greater for the dihydrofurocoumarins than for the corresponding dihydropyranocoumarins.

To evaluate the positions of the signals from the atoms at $C_{4'}$ and $C_{5'}$ in the dihydrofurocoumarins and in the dihydropyranocoumarins it is possible to use the average increments calculated from the figures of Table 1 and shown in Table 2. The initial data in the calculation of the CSs are the values of the CSs of the corresponding protons in 5'-isopropyl-4',5'-dihydrofuro-3',2': 6,7-coumarin (IX) and dihydroseselin (X)



IX



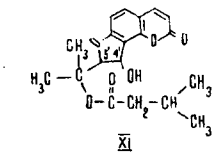
X

[for (IX): 4' – 3.28 ppm; 5' – 4.70 ppm; for (X): 4' – 2.91 ppm; 3' – 1.85 ppm].*

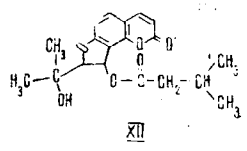
The use of the increments given in Table 2 will enable a number of erroneous assignments given in the literature to be corrected. Thus, Bohlmann and Rode [6] have given the NMR spectra of a number of khellactone derivatives of the general formula (VIII).

Table 3 shows the assignments for the $H_{3'}$ and $H_{4'}$ signals given by Bohlmann and Rode [6], the CS values calculated for these compounds by means of the increments of Table 2, and the correct assignments made on the basis of the results of the calculation.

An erroneous assignment of the signals of the protons of the dihydrofuran ring may lead to incorrect ideas of the structure of a new compound. Thus, Seshadri and Sood [7] proposed structure (XI) for vaginidin, a new dihydrofurocoumarin from the roots of Selinum vaginatum.



XI



XII

The position of the isovaleryloxy group was established on the basis of the NMR spectrum, in which the 4'- and 5'-protons gave two doublets at 7.0 and 4.5 ppm (J = 7 Hz). Seshadri and Sood [7] assigned the doublet at 7.0 ppm to $H_{5'}$ and that at 4.5 ppm to $H_{4'}$.

An evaluation of the CSs of the $C_{4'}$–H and $C_{5'}$–H with the aid of the increments of Table 2 shows that for structure (XI) both signals should be found at about 5.15 ppm. If, however, it is assumed that vaginidin has the structure (XII), the calculated CSs for $C_{4'}$–H and $C_{5'}$–H will be 7.05 and 5.14 ppm, which are much closer to the experimental values. Thus, vaginidin must have the structure (XII).

CONCLUSIONS

1. The NMR spectra of 27 dihydrofurocoumarins and dihydropyranocoumarins have been studied.

2. A number of laws have been found which are of interest for the purposes of the structural analysis of the dihydrofurocoumarins and dihydropyranocoumarins.

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* The CSs for (IX) were calculated indirectly from the figures for compounds of similar structure; for (X) the CSs were measured experimentally in $CDCl_3$.