NMR SPECTRA OF COUMESTANS

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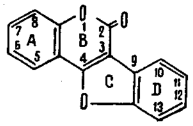
At the present time, spectral methods are of great importance in the structural investigations of many classes of natural compounds, including coumarins.

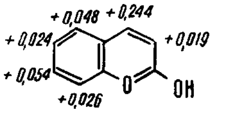
We have studied the NMR spectra of the coumestans, compounds structurally close to the coumarins, in order to determine the dependence between the structures of these substances and their spectral characteristics.

Coumestans consist of a closed benzofurocoumarin system with the following generally accepted sequence of numbering of the basic skeleton:



The spectra were obtained on an HA-100D NMR spectrometer. In view of the exceptionally low solubility of the coumestans in the majority of suitable solvents, the spectra were measured of their solutions in trifluoroacetic acid with tetramethylsilane as internal standard, its signal being taken as 0. For comparison of the spectral results, the spectrum of 7-methoxycoumarin was recorded under the same conditions (Table 1). The assignment of the signals was performed on the basis of their multiplicity, the results of the successive consideration of the spectra of compounds of similar structure, and ideas on the distribution of the π-electron density in the molecule of a protonated coumarin.

The figures in Table 1 show that in the protonated coumestans the chemical shifts of the protons of the benzene ring of the coumarin part of the molecule are in the same ratios as in the spectra of the neutral molecules of coumarin derivatives [1]. In actual fact, the signals of the protons at C_5 and C_7 are in a weaker field than those of the protons at C_6 and C_8. This is in complete harmony with the distribution of the effective π-electronic charges on the secondary carbon atoms in protonated coumarin shown below [2].



At the same time, in the coumestans the signal of the proton at C_5 is located approximately 0.35-0.40 ppm downfield in comparison with the corresponding coumarins. This is due to the influence of the oxygen atom at C_4. An analogous influence on C_4–H is observed [3, 4] in coumarins with alkoxy groups in position 5.

The assignment of the signals of the protons of ring D is conveniently performed by using, 7,12-diacetoxycoumestan as example, since the absence of a substituent in position 11 enables their multiplicity

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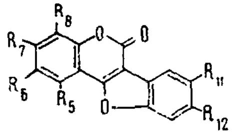
TABLE 1. Characteristics of the NMR Spectra of the Coumestans

Compound 	Chemical shifts and coupling constants (δ, ppm; multiplicity; J, Hz)									
	H_5	H_6	H_7	H_8	H_{10}	H_{11}	H_{12}	$OCOCH_3$	CH_3	OCH_3
7,12-Diacetoxycoumestan $R_7=R_{12}=OCOCH_3$, $R_5=R_6=R_8=R_{11}=H$	8,21 (d 8,5)	7,38 (q 8,5 2,2)	— —	7,48 (d 2,2)	8,14 (s)	7,32 (q 8,5 2,2)	7,59 (d 2,2)	2,52 (s)	— —	— —
7,11,12-Triacetoxycoumestan $R_5=R_6=R_8=H$ $R_7=R_{11}=R_{12}=OCOCH_3$	8,24 (d 8,6)	7,42 (q 8,6) 2,2	—	7,51 (d 2,2)	8,04 (s)	—	7,74 (s)	2,53 (s)	—	—
11,12-Diacetoxycoumestan $R_5=R_6=R_7=R_8=H$ $R_{11}=R_{12}=OCOCH_3$	8,17 (m)	7,5	— Multiplet	7,9	8,02 (s)	—	7,73 (s)	2,52 (s)	—	—
11,12-Diacetoxy-6-methylcoumestan $R_5=R_7=R_8=H$; $R_6=CH_3$; $R_{11}=R_{12}=OCOCH_3$	8,00 (d 2,2)	—	7,64 (q 8,5; 2,2)	7,53 (d 8,5)	8,02 (s)	—	7,73 (s)	2,53 (s)	2,58 (s)	—
11,12-Diacetoxy-8-methylcoumestan $R_5=R_6=R_7=H$; $R_8=CH_3$; $R_{11}=R_{12}=OCOCH_3$	8,0 (m)	7,40–7,80 Multiplet		—	8,02 (s)	—	7,73 (s)	2,52 (s)	2,60 (s)	—
11,12-Diacetoxy-6,7-dimethylcoumestan $R_5=R_8=H$; $R_6=R_7=CH_3$ $R_{11}=R_{12}=OCOCH_3$	7,91 (s)	—	—	7,43 (s)	7,99 (s)	—	7,71 (s)	2,53 (s)	2,49 (s)	—

7,11,12-Triacetoxy-5-methylcoumestan $R_6=R_8=H$; $R_5=CH_3$; $R_7=R_{11}=R_{12}=OCOCH_3$	—	7,20 (ns)	—	7,34 (d 2,3)	8,05 (s)	—	7,76 (s)	2,51 (s)	3,03 (s)	—
7,11,12-Triacetoxy-5-methoxycoumestan $R_5=OCH_3$; $R_6=R_8=H$; $R_7=R_{11}=R_{12}=OCOCH_3$	—	6,84 (d 2,5)	—	7,08 (d 2,5)	8,00 (s)	—	7,72 (s)	2,50 (s)	—	4,15 (s)
11,12-Diacetoxy-7-methoxy-5-methylcoumestan $R_5=CH_3$; $R_6=R_8=H$; $R_7=OCH_3$ $R_{11}=R_{12}=OCOCH_3$	—	7,02 (s)	—	7,02 (s)	7,99 (s)	—	7,70 (s)	2,52 (s)	2,96 (s)	4,03 (s)
7,11,12-Trimethoxycoumestan $R_5=R_6=R_8=H$; $R_7=R_{11}=R_{12}=OCH_3$	8,00 (d 8,5)	7,17 (q 8,5; 2,1)	—	7,12 (d 2,1)	7,56 (s)	—	7,35 (s)	—	—	4,04 (s) 4,08 (s) 4,11 (s)
11,12-Diacetoxy-7-methoxycoumestan $R_5=R_6=R_8=H$; $R_7=OCH_3$; $R_{11}=R_{12}=OCOCH_3$	8,06 (d 8,5)	7,20 (q 8,5; 2,4)	—	7,15 (d 2,4)	7,94 (s)	—	7,66 (s)	2,49 (s)	—	4,02 (s)
11-Acetoxy-7,12-dimethoxycoumestan $R_5=R_6=R_8=H$; $R_7=R_{12}=OCH_3$; $R_{11}=OCOCH_3$	8,02 (d 8,5)	7,17 (q 8,5; 2,6)	—	7,12 (d 2,6)	7,74 (s)	—	7,38 (s)	2,51 (s)	—	4,02 (s)
7-Methoxycoumarin	7,64 (d 8,5)	7,14 (q 8,5; 2,6)	—	7,07 (d 2,6)	—	—	—	—	—	4,03 (s)

to be used for this purpose. A doublet at 8.14 ppm with a spin−spin coupling constant of 8.5 Hz is due to the proton in position 10, and a doublet at 7.59 ppm with a meta constant of 2.2 Hz is due to $C_{13}-H$. In agreement with this, in compounds with substituents in positions 11 and 12 the signal in the weaker field is assigned to $C_{10}-H$ and that in the stronger field to $C_{13}-H$.

SUMMARY

The NMR spectra of 12 coumestans in trifluoroacetic acid have been studied. The same features of the chemical shifts of the ring protons are found in the spectra of the coumestans as in the spectra of the coumarins.

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