^{13}C NMR SPECTRA AND STRUCTURE OF SOME COUMARIN DERIVATIVES

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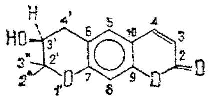
The results are given of a study of the ^{13}C NMR spectra of (—)-3(R)-decursinol, obtusifol, bergapten, isoimperatorin, and oxypeucedanin and its hydrate. The possibility has been shown of using the principle of additive contributions in the assignment of the signals of the carbon atoms in the compounds under investigation.

Previously, in a study of the coumarin composition of *Seseli grandivittatum* Schischk, and *Haplophyllum schelkovnikovii* Grossh. we isolated the coumarin derivatives (—)-3'(R)-decursinol (I) and obtusifol (II). The main results of an investigation of their structures with the aid of PMR spectra have been given previously [1-4].

In the present paper we discuss the results of a study of the ^{13}C NMR spectra of (I) and (II), and some known linear furocoumarins (III-VI) that are widely distributed in plants of the genus *Prangos*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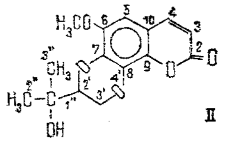
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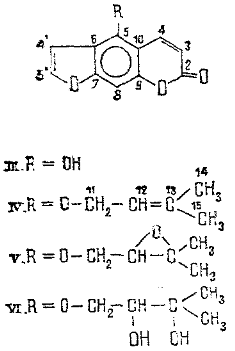

The assignment of the signals in the ^{13}C NMR spectra was made with allowance for the degree of hybridization of the carbon atoms and the number of protons attached to the corresponding carbon atoms [5, 6], and also using literature information on the ^{13}C spectra of analogs of the compounds under investigation. To determine the chemical shifts (CSs) of the signals, the spectra of compounds (I-VI) were taken under the conditions of complete decoupling from protons, and the spin-spin coupling constants (SSCCs) were determined from spectra obtained in the pulsed scanning regime. This regime permitted a considerable decrease in the time of accumulation because of the action of the Overhauser effect [5, 7]. The multiplicities of the protonated carbon atoms and the positions of the quaternary carbon atoms were confirmed in spectra taken under the conditions of stationary off-resonance suppression.

The signals of the carbon atoms of bergaptol (III) in the ^{13}C NMR spectra (Fig. 1a) were readily assigned by comparison of the CSs and SSCCs of the corresponding carbon atoms in it with those of linear furocoumarins studied previously — psoralen and bergapten [8] —, and also by taking into account the contribution of the hydroxy group in position 5 to the change in the CSs of the signal of the carbon atoms in the ^{13}C NMR spectrum [9]. Thus, the signal at 139.5 ppm was assigned to C-4, and that at 144.7 ppm to C-5', since $J_{C-4'} = 160$ Hz < $J_{C-5'} = 200$ Hz. A long-range spin-spin coupling constant of C-5' with H-4' of J = 11 Hz was observed [8] (Fig. 2). The C-8 and C-4' signals were assigned similarly, since $J_{C-8} = 174$ Hz < $J_{C-4'} = 180$ Hz, and a long-range spin-spin coupling constant of C-4' with H-5' having J = 14 Hz was observed. The remaining doublet at 110.8 ppm was assigned to C-3. By using the values of the contributions of hydroxy groups in the ortho, meta, and para positions of the benzene ring [9] it is possible empirically to find the values of the CSs of quater-

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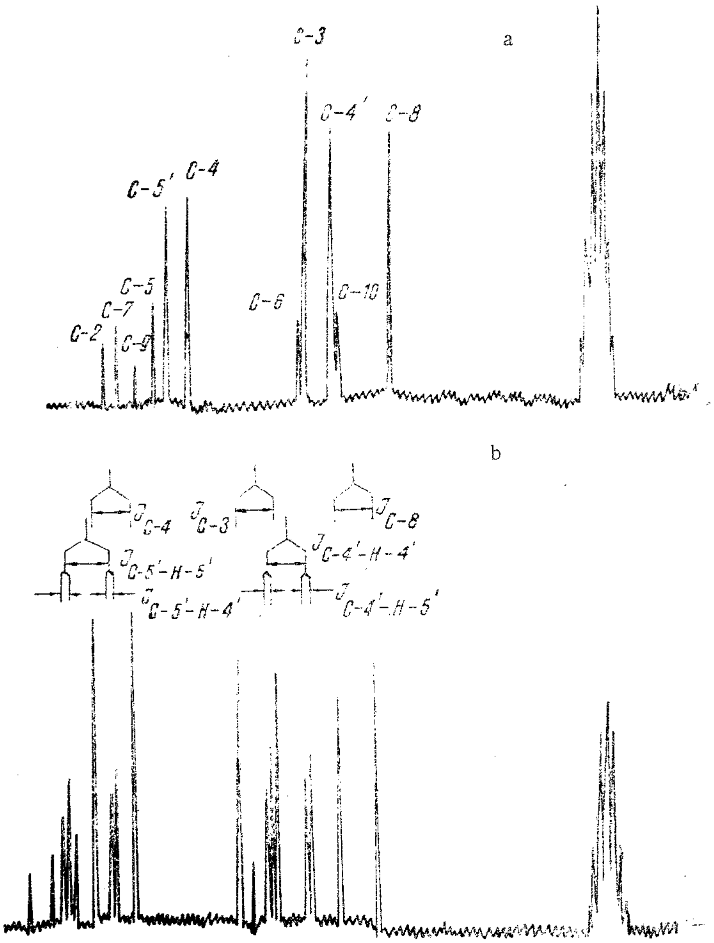

Fig. 1. ^{13}C NMR spectrum of bergaptol: a) with complete suppression of spin–spin coupling with protons; b) taken in the pulsed scanning regime.

nary C-2, C-5, C-6, C-7, C-9, and C-10 atoms. The results of a determination of the chemical shifts of some carbon atoms from the contributions made by a hydroxy group in position 5 are given below:

	C-2	C-5	C-6	C-7	C-8	C-9	C-10
Contribution of a hydroxy group in position 5	0.7	29.5	—12.6	1.1	—8.1	1.1	—12.6
Values d, ppm calculated empirically	160,7	149.9	111.8	156.7	91,0	152.5	102.6
Values of δ, ppm, found experimentally	160.1	147,7	112.4	156,8	90,9	152,6	103.7

A comparison of the CSs of the carbon atoms of compound (III) calculated empirically and obtained experimentally permits the use of the principle of additive contributions of substituents in the study of the structure of unknown coumarin derivatives by the ^{13}C NMR method.

The signals of the carbon atoms in the ^{13}C NMR spectrum of isoimperatorin (IV) (Fig. 2) were assigned by comparing their CSs and SSCCs with the corresponding signals for bergaptol (III) and isooxypeucedanin [10]. In the ^{13}C NMR spectrum of (IV), additional signals of the aliphatic chain in position 5 are observed: quartets at 25.8 and 18.3 ppm are assigned to the methyl carbons of the gem-dimethyl group C-14 and C-15, a triplet at 69.5 ppm is due to the C-11 methylene carbon atom attached to oxygen, and a doublet at 118.7 ppm is caused by C-12. The signal from the quaternary atom in the aliphatic part of the molecule (IV) does not appear in the ^{13}C NMR spectrum with complete decoupling from protons. Its CS apparently coincides with that of one of the other signals. This was confirmed in a study of the spectra taken in the regime of pulsed scanning and of stationary off-resonance decoupling. A singlet signal of this carbon atom appeared at 139.0 ppm. The positions of the signals of

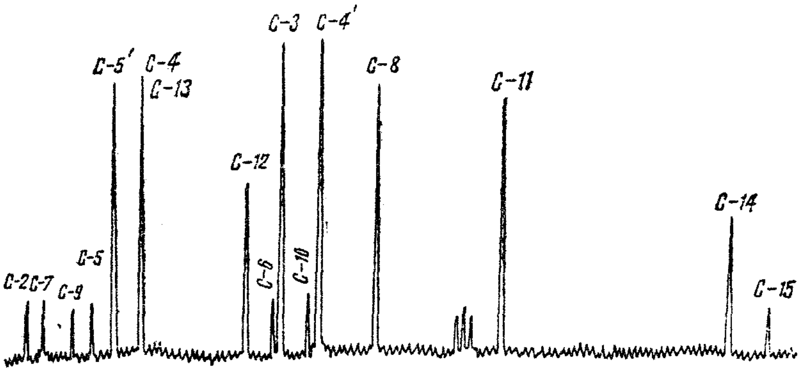

Fig. 2. ^{13}C NMR spectrum of isoimperatorin with complete suppression of spin–spin coupling with protons.

the carbon atoms of the aliphatic substituent in the ^{13}C NMR spectra of (IV) agreed completely with the assignment of the corresponding carbon atoms in imperatorin [8].

The signals of the carbon atoms of the cyclic part of the oxypeucedanin molecule (V) and of its hydrate (VI) also correspond to the assignment for (IV) described above. A difference is observed only for the signals of the aliphatic substituent. These signals were assigned with a determination of their multiplicities.

The CSs and SSCCs of the ^{13}C NMR of the furocoumarins (III-VI) investigated are given in Table 1.

The signals of the protonated carbon atoms C-3, C-4, C-5, and C-8 in (I) were assigned on the basis of information obtained for (III-VI) taking the results of Elgamal et al. [8] into account. The remaining signals of the protonated carbon atoms of the 3',4'-dihydropyran ring were assigned on the basis of their multiplicities: two quartets in the strong field at 21.9 and 25.1 ppm were ascribed to the C-2", and C-3" methyl atoms, a triplet at 30.6 ppm corresponds to the C-4' methylene atom, and a doublet at 68.9 ppm is due to C-3'. The signals of the quaternary atoms C-2, C-6, C-7, C-9, and C-10 in (I) correspond to signals observed in the spectra of (III-VI), and a singlet at 78.0 ppm is due to C-2'. The results obtained are shown in Table 2.

The signals of the carbon atoms of the coumarin nucleus in the obtusifol molecule (II) (Fig. 3a) were assigned by the use of the CSs in the ^{13}C NMR spectrum of 7,8-dihydroxycoumarin [9] and in consideration of the contribution to the change in the CSs from the methoxy group in position 6. Below we give the results of a determination of the chemical shifts of the signals of the carbon atoms in the ^{13}C NMR spectrum of (II):

	C-2	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*
CSs of 7,8-dihydroxycoumarin [9]	161,1	111.7	145,4	119.4	113,0	150.0	132.6	144,2	112.7
Contribution from the methoxy group in position 6	—0.3	0	0,6	—20.0	32.7	—10.4	0.4	—6 4	—0.9
Values of δ calculated empirically, ppm	160.8	111,7	146,0	99 4	145,7	140.0	133,0	137,8	111.8
Values of δ found experimentally, ppm	159.6	113.0	144.3	100,7	145,0	136.3	131.7	137,9	111.1

The signals of the carbon atoms in the benzodioxane part and of the isopropoxy group in (II) were assigned on the basis of their multiplicities (Fig. 3b): a singlet at 69.3 ppm corresponds to the C-1" quaternary atom in the gem-dimethyl group (in an analogous manner to (VI)), a doublet at 78.7 ppm and a triplet at 64.8 ppm are caused by the C-2' and C-3' atoms, respectively, and quartets at 24.7 and 27.0 ppm correspond to the methyl carbons (C-2" and C-3") in the gem-dimethyl grouping. A quartet at 55.9 ppm corresponds to the carbon atom of the methoxy group in position 6.

The results of the assignment of the CSs and SSCCs are given in Table 2.

EXPERIMENTAL

The ^{13}C NMR spectra of compounds (I-VI) were obtained on a standard HX-90 spectrometer (Bruker) in the pulsed regime of accumulation with Fourier transformation. For recording the spectra we used saturated solutions: of (I) and (IV-VI) in $CDCl_3$, and of (II) and (III)

TABLE 1. Chemical Shifts (δ, ppm) and Spin—Spin Coupling Constants in the ^{13}C NMR Spectra of (III-VI)

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
III	160,1	110,8 J=172 Hz	139,5 J=160 Hz	147,7	112,4	156,8	90,9 J=174 Hz	152,6
IV	160,7	112,0 J=173 Hz	139,0 J=162 Hz	148,4	113,7	157,6	93,7 J=170 Hz	152,1
V	160,4	112,6	138,5	148,0	113,8	157,4	94,4	152,0
VI	160,9	112,5	138,9	148,0	112,9	157,7	94,8	152,0

Compound	C-10	C-11	C-12	C-13	C-14	C-15	C-4′	C-5′
III	103,7						104,6 J=180 Hz	144,7 J=200 Hz
IV	106,9	69,5 J=147 Hz	118,7 J=150 Hz	139,0	25,8 J=126 Hz	18,3 J=126 Hz	104,7 J=176 Hz	144,4 J=202 Hz
V	107,1	72,1	61,0	58,1	24,6	19,0	104,2	144,7
VI	107,0	74,3	76,5	71,6	25,3	24,6	104,6	144,9

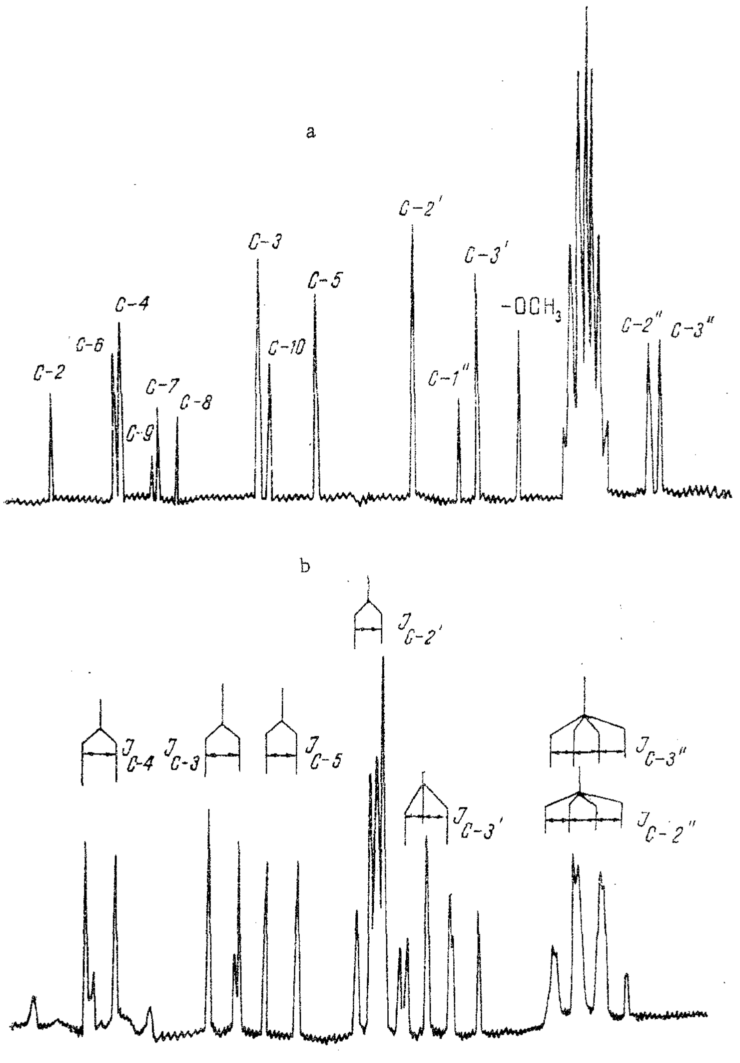

Fig. 3. ^{13}C NMR spectrum of obtusifol: a) with complete suppression of spin—spin coupling with protons; b) taken in the pulsed scanning regime.

TABLE 2. Chemical Shifts (δ, ppm) and Spin—Spin Coupling Constants in the ^{13}C NMR Spectra of (I) and (II)

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
I	161,0	112,7 J=173 Hz	142,7 J=168 Hz	128,6 J=164 Hz	116,4	156,2	104,8 J=164 Hz	153,6
II	159,6	113,0	144,3 J=161 Hz	100 7 J=161 Hz	145,0	136,3	131,7	137,9

Compound	C-10	C-2′	C–3′	C-4′	C-1″	C-2″	C-3″	OCH$_3$
I	112,5	78,0	68,9 J=149 Hz	30,6 J=138Hz		25,1 J=136, Hz	21,9 J=130 Hz	
II	111,1	78,7	64,8		69,3	24,7 J=149 Hz	27,0 J=144 Hz	55,9 J=144 Hz

in DMSO. The chemical shifts were measured with an accuracy of 0.1 ppm relative to the signal of the solvent with subsequent recalculation to the TMS scale from the formulas $\delta = \delta_{DMSO} + 39.6$ and $\delta = \delta_{CDCl_3} + 76.9$. The spin-spin coupling constants were determined with an accuracy of 3.0 Hz.

SUMMARY

A complete assignment of the signals of the carbon atoms in the ^{13}C NMR spectra of (-)-3'(R)-decursinol (I), obtusifol (II), bergaptol (III), isoimperatorin (IV), and oxypeucedanin (V) and its hydrate (VI) has been made. The possibility has been shown of using the principle of additive contributions in the assignment of the signals of carbon atoms in the compounds investigated.

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