A STUDY OF THE COUMARINS OF *Haplophyllum obtusifolium* BY ^{13}C NMR SPECTROSCOPY

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We have isolated a number of coumarins from *Haplophyllum obtusifolium* Ledeb., and have established their structures on the basis of chemical and spectral (IR, UV, ^{1}H NMR, mass) characteristics. The most interesting proved to be obtusiprenin and obtusiprenol, each containing four substituents in the benzene ring [1, 2]. The establishment of the structures of such compounds requires an accurate determination of the mutual positions of the substituents, which presents certain difficulties. For the unambiguous establishment of the structures of these coumarins we used ^{13}C NMR spectroscopy.

In the present communication we discuss the results of a study of the ^{13}C NMR spectra of fraxetin (I) [3], obtusiprenin (II) [1], obtusiprenol (III) [2], obtusidin (IV) [1], and obtusicin (V). Details of the ^{13}C NMR spectrum of daphnetin (7,8-dihydroxycoumarin) are given in the literature [4]. The assignment of the signals of the carbon atoms in the spectrum of (I) was made on the basis of a comparison of the values of the chemical shifts (CSs) of the carbon atoms with the analogous values for daphnetin by using the results on the α, ortho, meta, and para effects from $-OCH_3$ groups in the spectra of methoxycoumarins [4, 5]. The resonance lines in the spectra of (II–V) were identified by a mutual comparison of the ^{13}C NMR spectra obtained under the conditions of complete and incomplete decoupling (off-resonance) from protons, and also from the results of the analysis of the CSs of the carbon atoms of 1',1'- and 3',3'-dimethylallyl groups [6, 7] taking into account the increments of alkyl groups in the CSs of the carbon atoms of coumarin [8].

TABLE 1. Details of the ^{13}C NMR Spectra (DMSO-d_6, 0 — TMS)

Carbon atom	7,8-Dihydroxy-coumarin	Compound					Multiplicity
		I	II	III	IV	V	
C-2	161,1	159,8	159,3	159,3	158,5	159,3	s
C-3	111,7	111,4	111,0	111,0	129,2 s	113,8	d
C-4	145.4	144,9	142,7	142,7	145,0	143,8	d
C-5	119,4	100,0	121,9 s	121,7 s	99,9	99,8	d
C-6	113,0	144,7	142,4	142.4	144,7	143,8	s
C-7	150,0	138,8	141,4 (a)*	141.4 (a)	141.4 (a)	140.4	s
C-8	132,6	132,3	130,8 (b)	130,9	131,8	137,9	s
C-9	144,2	138,8	140.7 (a)	140,5 (a)	138,4 (a)	137,9	s
C-10	112,7	110,0	108,6	108,6	110,0	113,8	s
CH_3O-		56,1	60,3	60,5	56,1	56,0	q
C-1'			23,8	23,3	40,0 s	59,6	t
C-2'			122,9	121,8	145,0	121,3	d
C-3'			130,5 (b)	134,9	111,2 t	149,2	s
C-4'			18,0	14,0	27,3	21,3	q
C-5'			25,5 q	65,9	27,3 q	68,1	t

*The assignments in the vertical columns with similar pairs of letters may be interchanged.

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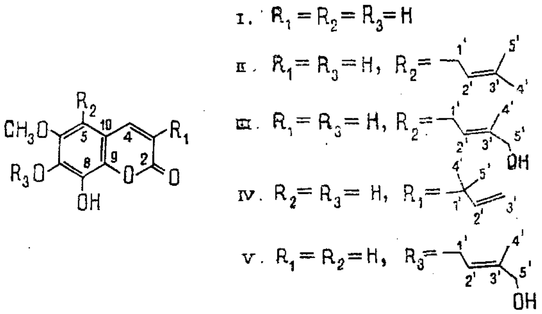

Details of the spectra are given in Table 1. A comparison of the values of the CSs of the ^{13}C nuclei of the coumarin ring shows that when a prenyl substituent is introduced into the coumarin nucleus, the C-5 signals in the spectra of obtusiprenin and obtusiprenol are shifted downfield by 2.17—2.19 ppm in comparison with the corresponding signal in the spectrum of fraxetin. The signals of the ^{13}C nuclei at C-6, C-8, and C-10 (ortho and para positions relative to C-5) undergo upfield shifts in the range of 0.3—1.6 ppm, while the signals of the ^{13}C nuclei at C-7 and C-9 (meta position) shift downfield by 1.7—2.6 ppm. This fact is in harmony with the presence of a side chain at C-5 in the molecules of (II) and (III).

The spectra of obtusiprenin and obtusiprenol (see Table 1) each contain the signals of all 15 carbon atoms. A comparison of the spectra of (II) and (III) showed that a hydroxy group at C-5' has a substantial influence on the CSs of the neighboring cation atoms. In the spectrum of (III), unlike that of (II), a weak-field triplet appears at 65.6 ppm which is due to the C-5' carbon atom bearing a hydroxy group. The C-3' signals in the spectrum of (II) appears at 130.2 ppm, while the analogous signal in the spectrum of (III) undergoes a weak-field shift through the β-hydroxy effect and is found at 134.6 ppm. It must be mentioned that in the spectrum of (II) and (III) the CSs of the carbon atoms of the $-OCH_3$ group are shifted downfield by 4.2—4.5 ppm as compared with the spectra of (I), (IV), and (V). This is due to the sterically hindered position of the $-OCH_3$ group in the benzene ring [9, 10]. Thus, the structures of the coumarins (II)-(V) are completely confirmed by their ^{13}C NMR spectra.

The ^{13}C NMR spectra were taken on a Varian XL-100 instrument at 25.2 MHz in DMSO-d_6 (0 — TMS) by A. A. Pashchenko (V. I. Lenin Tashkent State University).

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