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^{13}C NMR CHEMICAL SHIFTS AND CARBON-PROTON COUPLING CONSTANTS OF SOME FUROCOUMARINS AND FUROCHROMONES*

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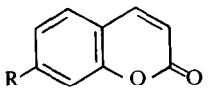
Key Word Index—^{13}C NMR; furocoumarins; dihydrofurocoumarins; furochromones.

Abstract—The ^{13}C NMR spectra of a variety of furocoumarins, dihydrofurocoumarins and furochromones are reported. The signals were assigned using carbon-proton coupling constants, ring annullation shifts, nuclear Overhauser effect considerations and shift effects caused by monothioester formation. Substituent effects on ^{13}C chemical shifts and carbon-proton coupling constants are discussed. Methoxyl induced shifts of 5- and 8-substituted furocoumarins are additive, but their effects cannot be transferred to the furochromone system.

INTRODUCTION

Furocoumarins and furochromones have attracted considerable interest due to their biological activity. Although their chemical, physical and physiological properties have been investigated extensively [1–8], only a few publications on their ^{13}C NMR spectra have appeared [9–11]. The naturally occurring furocoumarins and furochromones in this study were isolated from *Ficus platyphylla* (**2**), *Ficus carica* (**4**), *Ammi majus* (**6**, **7**, **9**, **10** and **14**) and *Ammi visnaga* (**15** and **16**) which grow in Egypt. The ^{13}CNMR spectra of these compounds may be used with advantage in the structure elucidation of unknown compounds since reliable assignments of various carbon atoms and functional groups could be made.



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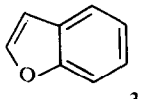

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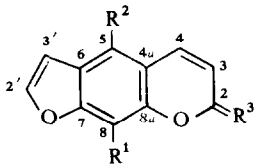
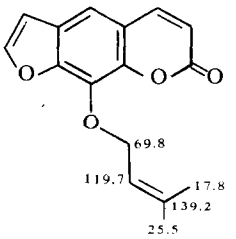


	R^1	R^2	R^3
4	H	H	O
5	OH	H	O
6	OCH_3	H	O
7	H	OCH_3	O
8	H	OCH_3	S
9	OCH_3	OCH_3	O



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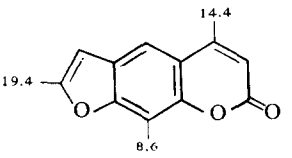

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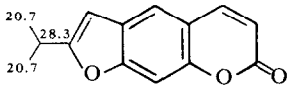

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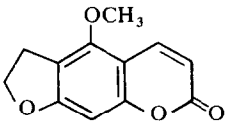

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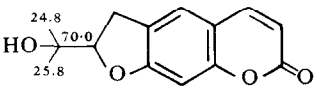

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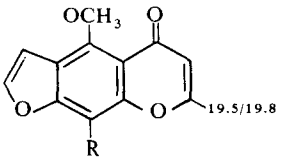

15 R = H
16 R = OCH_3

* Part XI in the series "Carbon-13 Nuclear Magnetic Resonance Spectra"; for part X see H. Duddeck, F. Hollowood, A. Karim and M. A. McKervey (1978) *J. Chem. Soc. Perkin Trans. 2 in press.*

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Table 1. ^{13}C NMR chemical shifts of furocoumarins, furchromones and related compounds*

	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-2′	C-3′	Others
1	160.4	116.4	143.6	118.8	128.1	124.4	131.8	116.4	153.9	—	—	
2	160.8	112.7	143.3	112.3	128.7	112.1	162.6	100.6	155.6	—	—	OCH_3: 55.5
3‡	—	—	—	122.4	120.9	127.2	154.7	111.1	123.9	144.5	106.5	
4	161.1	114.7	144.2	115.6	120.0	125.0	156.6	99.9	152.2	147.0	106.6	
4†	160.0	113.9	144.7	115.2	120.4	124.4	155.6	99.1	151.4	147.7	106.5	
5†	160.0	113.7	145.3	116.2	110.1	125.2	145.3	130.1	139.8	147.2	106.9	
6	160.4	114.5	144.4	116.5	113.1	126.2	147.6	132.7	142.9	146.6	106.8	OCH_3: 61.2
6†	159.6	114.0	144.9	116.2	113.9	125.8	146.8	131.8	142.3	147.5	106.9	OCH_3: 60.8
7	160.3	112.8	139.4	106.7	149.6	113.0	158.5	94.0	152.7	145.0	105.3	OCH_3: 60.3
7†	159.8	112.2	139.4	105.6	149.3	112.0	157.6	93.0	152.0	145.8	105.8	OCH_3: 60.2
8†	197.2	125.3	131.2	107.4	149.4	113.1	157.9	92.7	154.2	146.4	105.6	OCH_3: 60.1
9	160.5	112.8	139.5	107.7	144.4	114.9	149.9	128.3	143.7	145.3	105.3	OCH_3: 60.9/61.7 (at C-5/8)
9†	159.4	112.3	139.5	106.7	144.2	114.3	149.2	127.1	142.9	146.1	105.5	OCH_3: 60.6/61.1 (at C-5/8)
10	160.2	114.2	144.3	116.2	113.2	125.7	148.3	131.2	143.5	146.4	106.6	see Formulae Chart
11	161.6	112.9	155.7	109.3	112.3	125.6	153.4	116.2	149.1	157.6	102.9	see Formulae Chart
12	161.1	114.1	144.2	115.0	118.8	126.5	156.3	99.1	151.5	167.3	99.5	see Formulae Chart
13	161.5	110.5	139.2	110.4	152.7	105.9	165.5	92.9	156.6	72.4	28.3	OCH_3: 59.4
14†	160.5	111.2	144.6	121.1	123.8	125.5	163.3	96.7	155.1	91.0	28.7	see Formulae Chart
15	163.5	110.4	177.6	112.1	157.4	116.7	153.1	94.7	155.5	144.9	104.9	OCH_3: 61.3
16	163.9	110.3	177.8	113.5	147.0	119.2	148.6	129.7	146.8	145.4	104.9	OCH_3: 61.1/62.0 (at C-5/8)
17§	159.6	132.8	138.1	115.7	119.4	124.4	155.6	98.5	151.1	146.4	106.1	see ref. [10]
18§	162.9	126.6	138.1	117.7	118.7	124.5	155.5	99.1_5	150.7	146.4	106.2	see ref. [10]
19¶	160.9	114.3	144.0	114.7	116.5	121.6	153.5‖	99.8	151.5	152.5‖	136.3	see ref. [9]
20¶	160.5	112.7	138.9	107.0	147.5	113.2	157.5	94.5	152.1	145.1	103.8	see ref. [9]
21§	159.6	130.4	137.7	112.8	122.8	123.7	161.9	96.7	154.2	88.2	29.7	see ref. [10]

* Chemical shifts in ppm relative to TMS. Solvent $CDCl_3$, if not otherwise noted.
† Solvent DMSO-d_6.
‡ Numbering of the carbon atoms according to that of psoralene for better comparison.
§ Data taken from ref. [10] (reassigned).
¶ Data taken from ref. [9].
‖ May be interchanged.

RESULTS AND DISCUSSION

General

The ^{13}C NMR spectra of coumarin (**1**) [9–18], herniarin (**2**) [10, 11, 13, 16], benzo[b]furan (**3**) [9, 19] and some of the furocoumarins [9–11] have been reported previously. The data given in Tables 1 and 2 for these compounds were obtained in this laboratory and agree, apart from some reassignments, with the previous findings. The assignments of the ^{13}C NMR signals are mainly based on carbon-proton coupling information, and even when it was not possible to extract all coupling constants from a given carbon signal due to its complexity, the corresponding signal in the spectrum of a related compound could often be identified by its similarity ('finger-print'). Furthermore, substituent effects on the chemical shifts were useful for unambiguous assignment.

Several compounds were measured in two solvents to allow comparisons with related derivatives which were soluble either in $CDCl_3$ or DMSO-d_6 only. It turned out that not only chemical shifts but also one-bond coupling constants may be changed significantly by an alteration of the solvent. For example, the C-2′/H-2′ coupling constant in bergapten (**7**) was 204.3 Hz in $CDCl_3$, but 207.5 Hz in DMSO-d_6. This must be kept in mind when one-bond couplings are used for peak assignments.

Furocoumarins

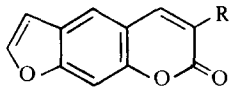
The signals of the protonated carbons of psoralene (**4**) can easily be assigned by comparison of the chemical shifts and the coupling pattern of the C-3, C-4, C-5 and C-8 signals with those of coumarin (**1**) and herniarin (**2**) and those of the C-2′ and C-3′ signals with the corresponding ones of benzo[b]furan (**3**). C-2 can be attributed by looking for its nicely resolved proton-coupled four-line signal with equal intensities due to the two- and

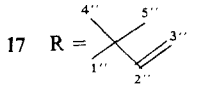
Table 2. Typical ^{13}C–^1H coupling constants (Hz) of furocoumarins and furochromones

C-2	H-3*:	4–5
		6–7 for **15** and **16**
	H-4:	11–12
C-3	H-3:	172.5–174
		ca 177 for **15** and **16**
C-4	H-4:	162–164 ($CDCl_3$)
		165–167 (DMSO-d_6)
	H-5:	5–6
C-4a	H-3:	6–8
C-5	H-5:	163–166 ($CDCl_3$)
		166–168 (DMSO-d_6)
	H-4:	*ca* 4
C-8	H-8:	170–172 for **7** and **8**
		166–167 for **12** and **14**
		168–169 for **13** and **15**
C-2′	H-2′:	204–205 ($CDCl_3$)
		206–208 (DMSO-d_6)
	H-3′:	10.5–11.5
C-3′	H-3′:	179–180
		ca 176 for **11** and **12**
	H-2′:	13–14

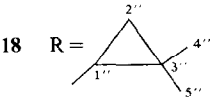
* Denotes the proton participating in the coupling. For substitution dependence see text.

three-bond couplings with H-3 and H-4. This is also valid for all other furocoumarins (**5**–**14**) except **11** which bears a methyl group at C-4. The C-4a and C-6 signals could be assigned by comparison with the corresponding signals of anhydromarmesin (**12**). Only the downfield signal of **4** (125.0 ppm) is affected significantly by the isopropyl substitution at C-2′ so that this signal was attributed to C-6. This sequence is in agreement with the assignment of the C-4a and C-6 signals of **5**, **6** and **10** reported by Wenkert *et al.* [9]. The differentiation of C-7





17 R =



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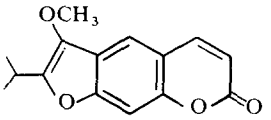

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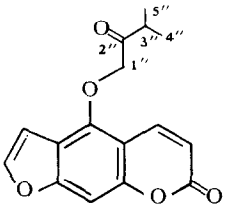

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and C-8a, however, was not so obvious. Looking at the (reassigned) data reported by Reisch *et al.* [10] none of the signals in question of chalepensin (**17**) and clausindin (**18**) is shifted remarkably with respect to **4**, since in both cases the isoprenoid substituents are in the *para* position relative to C-8a and even more remote of C-7. Also the data of anhydromarmesin (**12**) do not allow a clear decision; those of peucedanin (**19**) [9], however, clearly reveal that only C-7 is affected by the introduction of the methoxyl group at C-3′. The same sequence of the C-7 and the C-8a signals as for **4** was adopted for all other coumarins. Further evidence for the assignment above was obtained by estimation of the chemical shifts on the central benzene ring. The effects of the furan-annullation in **3** on the chemical shifts of the benzene carbons were added to those of **1** in the appropriate manner. The discrepancies of the calculated values from the experimental ones do not exceed 2–3 ppm and are even negligible for C-5 and C-8.

The spectra of xanthotoxol (**5**) , xanthotoxin (**6**) and imperatorin (**10**) correspond to those published by Wenkert *et al.* [9], but for C-7, C-8 and C-8a of **6** and C-8 and C-8a of **10** we came to somewhat different results.

The signals of bergapten (**7**) were assigned with the help of the reported data of isooxypeucedanin (**20**) [9]. This was corroborated by the spectrum of thiobergapten (**8**). Replacement of the carbonyl oxygen by sulphur causes characteristic shifts of the lactone ring carbon signals. C-2 is deshielded by 37.4 ppm which is in fair agreement with earlier findings for thio acid derivatives [20, 21]; the α positioned C-3 is also deshielded by 13.1 ppm. The two β positioned carbons C-4 and C-8a behave differently. Whereas C-4 is shielded by 8.2 ppm, the signal of C-8a is shifted downfield by 2.2 ppm. C-4a is deshielded by 1.1 ppm, but the remaining carbons which do not belong to the lactone ring are not affected. Also, the carbon-proton coupling constants are sensitive to the thiocarbonyl formation. The coupling of C-2 with H-3 increases from 4.9 to 7 Hz and that of H-4 decreases from 11.7 to 10.2 Hz. The one-bond coupling constant of C-3 is enhanced by 2.9 Hz and that of C-4 diminished by 3.7 Hz which is in analogy to the changes of the chemical shifts of these carbons. Even for C-8 the direct coupling constant is enhanced significantly. Preparation of the monothioester therefore appears to be a valuable aid for the assignment of ^{13}C NMR signals for such compounds.

In the spectrum of isopimpinellin (**9**) the signals due to C-2, C-3, C-4, C-2′ and C-3′ can easily be identified by the comparison of their chemical shifts and couplings with those of **4**, **6** and **7**. Of the remaining carbon signals those at highest field (114.9 and 107.7 ppm) were attributed to C-6 and C-4a, respectively, because their chemical shifts correspond well to those of C-6 and C-4a of **7**; it is known [22] that methoxyl shifts on *meta* positioned carbons are small. Furthermore, the C-6 signal in the proton-coupled spectrum appears as the characteristic double doublet which was observed in **5**, **6** and **10**. The C-4a signal is a somewhat broadened doublet due to a 6–7 Hz coupling with H-3. Analogously, C-7 and C-8a were assigned by the similarities of their chemical shifts with those of the corresponding carbons of **6**. The C-7 signal is a double doublet due to two couplings with H-2′ and H-3′, whereas that of C-8a appears as a diffuse doublet probably by coupling with H-4. The signals of the remaining methoxylated carbons C-5 and C-8 are *ca* 16 ppm apart from each other. Since the chemical shift difference of C-5 and C-8 in **4** is similarly large (*ca* 20 ppm), the assignment is obvious. The differentiation between the close-lying signals of C-5 and C-8a (144.4 and 143.7 ppm in $CDCl_3$) was accomplished by the shape of their proton-coupled signals. Whereas the C-8a signal is a diffuse doublet (*vide supra*), that of C-5 is a badly resolved triplet probably due to similar couplings to the two *peri* positioned hydrogens H-4 and H-3′. Furthermore, the signal at 143.7 ppm attributed to C-8a is extremely small in the proton-decoupled spectrum due to the absence of nuclear Overhauser enhancement by nearby protons [23] thus causing an extremely large longitudinal relaxation time of that carbon. For the larger signal of C-5, however, H-4 and H-3′ may contribute to the relaxation process shortening its T_1. The two methoxyl carbon signals are assigned considering the chemical shift difference of the corresponding carbons of the monomethoxyl derivatives **6** and **7**. Although the numerical values are a little larger in **9**, the sequence is believed to be unchanged.

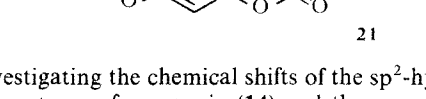
The signals of the protonated carbons C-3, C-5 and C-3′ of trimethylpsoralene (**11**) and of C-2 are easily recognized by their chemical shifts and their coupling patterns. The signal at 112.9 ppm is attributed to C-3, because under proton-coupling conditions it is a doublet of quartets (5.8 Hz coupling to the protons of the methyl group at C-2′), whereas the signal at 112.3 ppm is a doublet of somewhat broadened singlets representing C-5. The signal at 109.3 ppm belongs to C-4a; compared

to **4** it is shifted upfield due to its *ortho* position with respect to the methyl group at C-4. That at 116.2 ppm therefore belongs to C-8. C-6 is expected not to be affected seriously by the methyl substitutions, the methyl groups are either in the *meta* position or remote. Consequently, it was assigned to the signal at 125.6 ppm. The extremely small signal at 149.1 ppm was again attributed to C-8a (*vide supra*) and that at 153.4 ppm to C-7 because of its similar upfield shift of *ca* 3 ppm with respect to **4** caused by the *ortho* position of the methyl at C-8. For the assignment of C-2′ and C-4 the same sequence as in **4** was adopted. The assignment of the three methyl signals at 19.4, 14.4 and 8.6 ppm is routine. That at lowest field corresponds to the methyl at C-2′, the signal of the methyl at C-4 appears 5 ppm at higher field due to one γ interaction with C-5 and that of the methyl at C-8 a further 6 ppm at higher field, since two coplanar γ oxygens are present.

The peak assignment of anhydromarmesin (**12**) is obvious. The chemical shifts of the carbons in the coumarin part of the molecule agree well with those of **4**, C-3′ is recognized by the *ortho*-isopropyl shielding effect and its characteristic coupling pattern, and the C-2′ signal appears at lowest field because of the 20 ppm downfield shift of the α positioned isopropyl group [22].

Dihydrofurocoumarins

An inspection of the chemical shifts of chalepensin (**17**) and psoralene (**4**) shows that introduction of the isoprenyl group at C-3 affects only the shieldings of C-2, C-3 and C-4. Knowing this, a comparison of the ^{13}C chemical shift data of marmesin (**14**) and rutamarin (**21**) [10] led to a reassignment of the rutamarin signals (Table 1). The data of **14** [9] are also confirmed, apart from an apparent misprinting, by the coupling information given in Table 2.



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Investigating the chemical shifts of the sp^2-hybridized carbon atoms of marmesin (**14**) and the corresponding coumarin carbons of anhydromarmesin (**12**) one obtains shifts for these carbons which are essentially due to the hydrogenation of the C-2′/C-3′ double bond. The effects of the substituents at C-2′ upon these carbon atoms are rather small for both compounds and may be neglected in this context.

By adding these 'hydrogenation shift' values to the corresponding carbon atom shifts of bergapten (**7**) calculated chemical shifts for dihydrobergapten (**13**) are obtained which agree well with those observed by the assignment of its spectral data using proton-coupled signal information. The only exceptions are the signals of C-4a and C-6 which are both in the *ortho* position with respect to the methoxyl group at C-5. The signal of C-4a appears *ca* 6 ppm at higher field and that of C-6 *ca* 6 ppm at lower field than expected. This example again demonstrates how carefully substituent effects have to be treated in unsaturated compounds.

Furochromones

The C-2′ and C-3′ signals in the ^{13}C NMR spectrum of khellin (**16**) are easily identified by their couplings which agree with those of **9**. The signal at lowest field (177.8 ppm) must be due to the C-4 carbonyl and C-2 and C-3 are recognized by their undecoupled signals which reveal couplings with the protons of the methyl at C-2. Of the benzene carbon signals those at highest field (113.5 and 119.2 ppm) are attributed to C-4a and C-6, respectively; C-4a only couples with H-3 (3.8 Hz), whereas the C-6 signal is a double doublet due to couplings with H-2′ (7.0 Hz) and H-3′ (3.5 Hz). The C-8 signal appears at 129.7 ppm. The remaining signals at 148.6, 147.0 and 146.8 ppm were attributed to C-7, C-5 and C-8a, respectively. C-7 gives rise to a double doublet (7.6 and 5.7 Hz couplings with H-2′ and H-3′ which cannot be assigned safely), C-5 to a diffuse quartet (couplings with methoxyl protons) and C-8a to a singlet since no considerable coupling constant can be envisaged.

Based on these data, and considering the methoxyl group shifts (*vide infra*), the assignment of visnagin (**15**) signals is straightforward, particularly for C-8 and C-8a. Furthermore, the coupling patterns are helpful (Table 2).

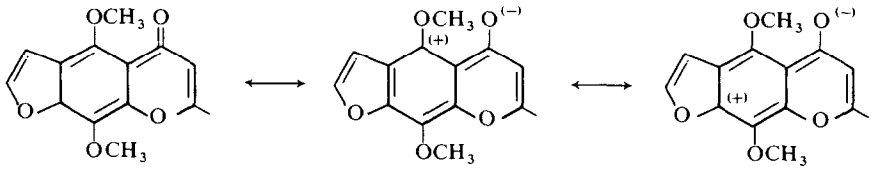
Substituent effects

It is interesting to check the methoxyl group substituent effects (SCS) on the ^{13}C chemical shifts of the central benzene ring of the furocoumarins and furochromones. Comparing the shifts of **6** and **4** the SCS of a methoxyl group at C-8 in furocoumarins ($\Delta\delta^8$) and by analogy those of such a group at C-5 ($\Delta\delta^5$) may be obtained (Table 3). The SCS on the directly substituted as well as the *meta* and *para* carbon signals correspond fairly well to those in anisole [22] whereas the *ortho* shifts are smaller by *ca* 3 ppm in most cases. The combined SCS of the two methoxyls in **9** ($\Delta\delta^{5+8}$) agree extremely well with those calculated by adding $\Delta\delta^5$ and $\Delta\delta^8$ (values in parentheses in Table 3). If, however, the molecular system is changed the methoxyl SCS may vary

Table 3. Substituent effects (SCS) of methoxyl groups at C-5 and C-8 of furocoumarins and furochromones on ^{13}C NMR chemical shifts of the benzene ring carbons*

	C-4a	C-5	C-6	C-7	C-8	C-8a
$\Delta\delta^8 = \delta$(**6**) $- \delta$(**4**)†	+0.9	−6.9	+1.2	−9.0	+32.8	−9.3
$\Delta\delta^5 = \delta$(**7**) $- \delta$(**4**)†	−8.9	+29.0	−12.0	+1.9	−5.9	+0.5
$\Delta\delta^{5+8} = \delta$(**9**) $- \delta$(**4**)†	−7.9	+24.4	−10.1	−6.7	+28.4	−8.5
	(−8.0)‡	(+22.1)	(−10.8)	(−7.1)	(+26.9)	(−8.8)
$\Delta\delta^{8'} = \delta$(**9**) $- \delta$(**7**)†	+1.0	−5.2	+1.9	−8.6	+34.3	−9.0
$\Delta\delta^{8''} = \delta$(**16**) $- \delta$(**15**)†	+1.4	−9.6	+2.5	−4.5	+35.0	−8.7

* In ppm; downfield shifts correspond to deshielding.
† For explanation see text.
‡ The values in parentheses are calculated by adding $\Delta\delta^5$ and $\Delta\delta^8$.



Scheme 1

considerably. The $\Delta\delta^{8'}$ values in Table 3 represent SCS observed when a methoxyl group is introduced at C-8 in bergapten (**7**). The same operation is done when going from **15** to **16** leading to the $\Delta\delta^{8''}$ values in Table 3. The SCS in the two frameworks agree well except for C-5 and C-7. This may be a consequence of different perturbances of the mesomeric systems by the methoxyl substituents at C-8 (Scheme 1). This clearly shows how carefully SCS effects have to be taken as aids for assignment in aromatic and olefinic systems, particularly when these systems are highly substituted. If, however, the molecular frameworks regarded are closely related or identical additivity may be observed even for such highly substituted rings.

Methoxyl substitution at C-5 and/or C-8 in the furocoumarin series also affects coupling constants but only those over one bond. C-5 substitution in psoralene (**4**) enhances the coupling constants of C-4 and C-8 by *ca* 3 Hz, whereas C-3′ is affected only slightly. C-8 substitution, however, increases the coupling constant $^1J_{CH}$ at the *para* positioned C-5 only by 1–1.5 Hz and those of C-4 and C-3′ are left nearly unchanged. This example reveals that coupling constants of differently substituted compounds of this type can successfully be used for peak assignment. Only the one-bond coupling constants may be dependent on the nature and the site of substituents.

EXPERIMENTAL

Compounds. **1** and **3** are available commercially. They were used without further purification. The naturally occurring compounds were isolated according to known procedures from the following plants: **2** from *Ficus platyphylla* [1–6]; **4** from *Ficus carica* [24]; **6**, **7** and **10** from *Ammi majus* [25, 26]; **9** from *Ammi majus* [27]; **14** from *Ammi majus* [28]; **15** and **16** from *Ammi visnaga* [3–6, 29–32]. Compound **5** was prepared from **10** [27, 33], **11** according to refs. [34–36], **12** from **14** [28] and **13** from **7** [37, 38]. Compound **8** was prepared from **7** according to the following procedure. **7** (1.75 g) was mixed with phosphorus pentasulphide (3.5 g) and the mixture was heated for 2 hr in dry xylene (75 ml) under reflux. The reaction mixture was filtered and the filtrate evapd under red. press. till dryness. The product (1.7 g) was crystallized from glacial HOAc, mp 146–148°. UV λ_{max} nm (log ε): 235 (4.06), 270 (3.5), 380 (3.8); MS *m/e*: 232 (M^+, base peak), 217, 188, 173.

Spectra. The ^{13}C NMR spectra were obtained at 22.64 MHz using a Bruker WH-90 spectrometer. The samples were run at concentrations of *ca* 1–2 M in $CDCl_3$ and/or DMSO-d_6 with TMS as internal standard. Proton-coupled spectra were recorded under 'gated decoupling' condition.

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