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^{13}C-NMR Spectroscopy of Coumarins and their Derivatives : A Comprehensive Review

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1. INTRODUCTION

Coumarins constitute an important class in the realm of natural products with significant biological activity (1). Although many books and articles have appeared since 1970 containing ^{13}C NMR data of various classes of natural products, only a very few of them deal with coumarins derivatives, and these mainly cover the literature of the 1970s only (2,3). Since that time, however, the data of many more coumarins have been published and NMR spectroscopy has seen a revolution. Thus, we believe that it is time to update the earlier reviews.

Since the early 1970s, ^{13}C NMR spectroscopy has developed into one of the most valuable tools for structure elucidation of organic compounds and natural products because the ^{13}C NMR spectrum is a fingerprint of a given compound. Moreover, ^{13}C data of a derivative not yet reported can often be extrapolated from the chemical shifts of compounds with related structural features. Nevertheless, it is still mandatory to perform a safe ^{13}C signal assignment of unknown molecules in order to avoid misinterpretations which may lead to erroneous conclusions. Therefore, we present a brief overview of NMR methods (section 2.1) which can be divided into two parts: a) The classical procedures have already been summarized by us before (3); nevertheless we include some of them here for the sake of completeness. b) New one- and two-dimensional NMR experiments have been designed during the 1980s which make some of the classical methods obsolete.

The data in this review have been compiled in a data base using MDL ISIS-Base. Literature has been covered until spring 1995.

2. METHODS OF ^{13}C SIGNAL ASSIGNMENTS

In general, ^{13}C NMR spectra are recorded under proton broad-band decoupling in order to avoid the severe signal overlap which can easily occur because of the large one-bond carbon-hydrogen coupling constants $^{1}J(C,H) = 120\text{-}250$ Hz. This procedure results in a breakdown of all signal splittings due to such couplings. Owing to the low natural abundance of the ^{13}C isotope (ca. 1.1%), ^{13}C NMR signals appear as narrow singlets if no further NMR-active nuclei with high natural abundance (e.g. ^{19}F or ^{31}P) are present in the molecule.

This spectral simplification, however, produces a serious drawback in signal assignments since valuable coupling information is destroyed. Thus, a variety of assignment methods have been developed some of which are introduced in this chapter. There are five main areas: experimental NMR techniques, coupling constants, solvent effects, presence of auxiliaries and derivatization.

2.1 Experimental NMR Techniques

In the 1970s these techniques consisted mainly of ^{1}H decoupling methods, the most prominent ones of which were the ^{1}H broad-band (BB) decoupling and the single-frequency off-resonance decoupling (SFORD) techniques. In SFORD, the decoupler frequency is positioned outside the ^{1}H resonance range (off-resonance). Thus, all carbon-hydrogen couplings are reduced to such an extent that only the largest coupling constants, namely $^{1}J(C,H)$, give rise to small residual splittings, from which the number of hydrogens adjacent to the respective carbon atoms can be read directly; singlets correspond to quaternary carbons, doublets to methine, triplets to methylene and quartets to methyl groups. Nevertheless, in these spectra, signal overlap and second-order effects sometimes prohibit unambiguous interpretations in unfavourable cases.

After 1980, NMR spectroscopy saw a revolution due to the introduction of new one- and two-dimensional experiments, new superconducting magnets providing magnetic fields up to 17.6 T (^{1}H-resonance frequency: 750 MHz) and an enormous progress in computer technology. New techniques, such as the recording of J-coupled spin echoes (**A**ttached **P**roton **T**est), and INEPT and DEPT have been developed to circumvent these difficulties (4). By executing INEPT or DEPT involving polarization transfer from ^{1}H to ^{13}C, the information about the number of adjacent hydrogens is also no longer reflected in residual signal splittings as in SFORD but in signal phases and intensities; CH and CH_3 signals appear as positive and those of CH_2 as negative singlets (Fig. 1c). Alternatively, it is possible to suppress all signals except those of CH (Fig. 1b). Therefore, a comparison of these two DEPT spectra with the ^{1}H BB-decoupled spectrum (Fig. 1a) allows an unambiguous assignment of all four sorts of CH_n fragments ($n = 0\text{-}3$).

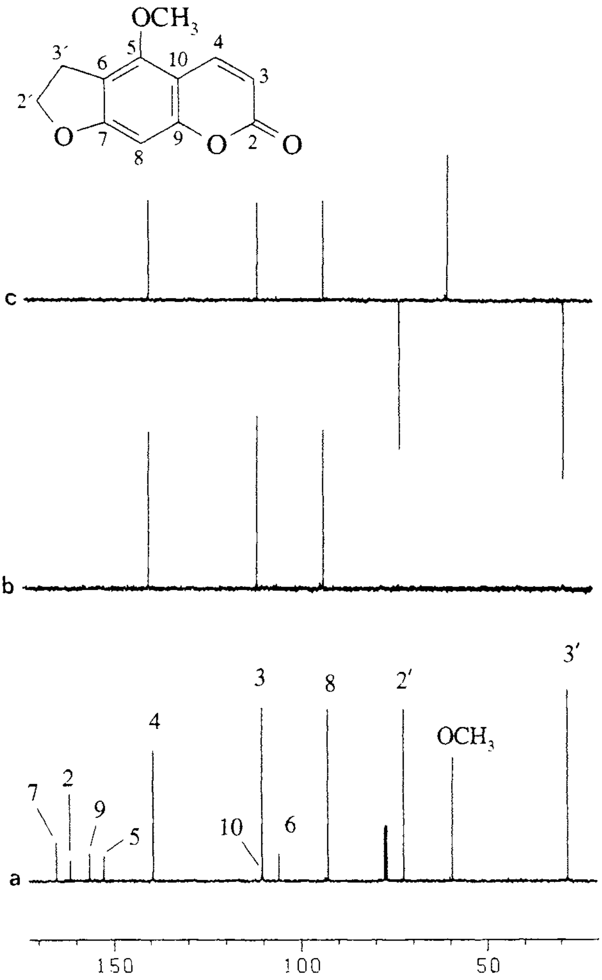


Fig. 1: (a) ^{1}H BB-decoupled ^{13}C NMR spectrum of dihydrobergapten (**G5-1**) and two DEPT spectra (b and c).

Signals of quarternary carbon atoms are often of very low intensity owing to saturation effects (long spin-lattice relaxation times, T_1) and/or low nuclear Overhauser enhancements (NOE). Hence, they might easily be hidden below much more intense signals corresponding to hydrogen-bearing carbon atoms. In such cases, it is advisable to perform a J-coupled spin echo experiment with a delay time of $1/[2 \cdot {}^1J(C,H)]$ leading to zero-intensities of protonated carbon signals and leaving only signals of quarternay carbons. Fig. 2b shows that C-10 of herniarin, which is hidden below the intense signals of C-3 and C-6 in the ^{1}H BB-decoupled spectrum (Fig. 2a), appears clearly in the APT spectrum whereas little residual peaks remain for C-3 (left, negative) and C-6 (right, positive) due to small deviations from the one-bond ^{13}C,^{1}H coupling constant used for the delay setting.

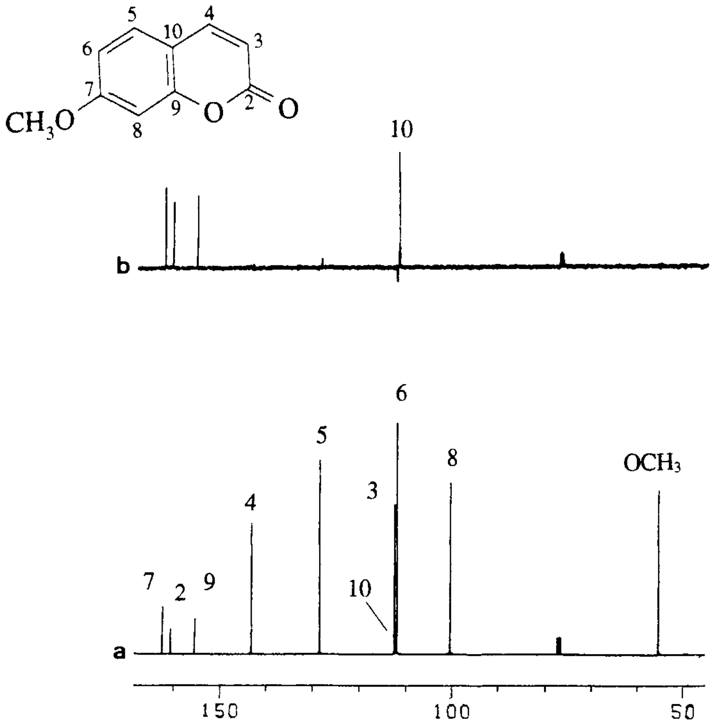


Fig. 2: ^{1}H BB-decoupled (a) and APT spectrum (b) of 7-methoxycoumarin (**B7-4**, herniarin)

Correlations between ^{1}H and ^{13}C nuclei via scalar couplings can be shown by two-dimensional COSY spectra (4-6). This is exemplified by a heteronuclear (^{1}H,^{13}C) COSY spectrum of 7-methoxycoumarin (**B7-4**, herniarin) shown in Fig. 3a (bottom). The cross-peaks connect the signals of hydrogen and carbon atoms directly attached.

Cross-peaks indicating couplings over more than one bond can be detected by long-range variants of ^{1}H,^{13}C COSY experiments or by COLOC (Fig. 3b) (7). It is interesting to note that C-7 bearing the methoxy group is identified by a COLOC peak due to a three-bond coupling between C-7 and the methoxyl protons. In addition, cross-peaks proving couplings between C-2/H-4, C-9/H-4, C-5/H-4, C-7/H-5, C-9/H-5, C-4/H-5, C-8/H-6, C-9/H-8, and C-6/H-8 can be identified; the coupling of C-10 with H-3 is not visible in this scale due to overlap by the cross-peak representing ^{1}J(C-3,H-3).

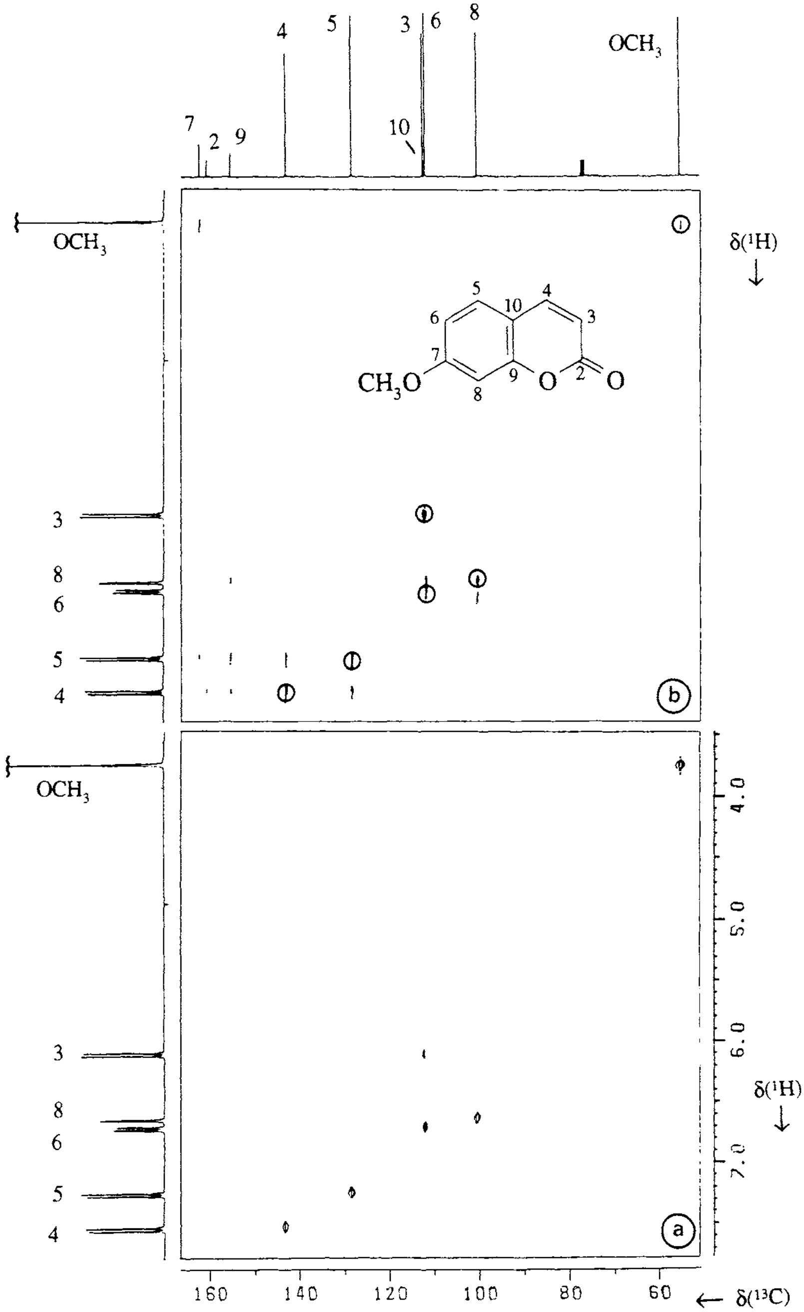


Fig. 3: (a) ^{1}H,^{13}C COSY and (b) COLOC spectra of 7-methoxycoumarin (**B7-4**, herniarin); the encircled signals in the COLOC spectrum correspond to one-bond ^{1}H,^{13}C correlations already depicted in the ^{1}H,^{13}C COSY spectrum.

If long-range heteronuclear couplings to only one single proton are required, it may be sufficient to record one-dimensional selective irradiation experiments, such as selective INEPT (8).

In recent years inverse techniques (HMQC, HMBC etc.) have been developed providing analogous spectra as shown in Fig. 3 which, however, require much less material and can often be performed in a much shorter spectrometer time (9).

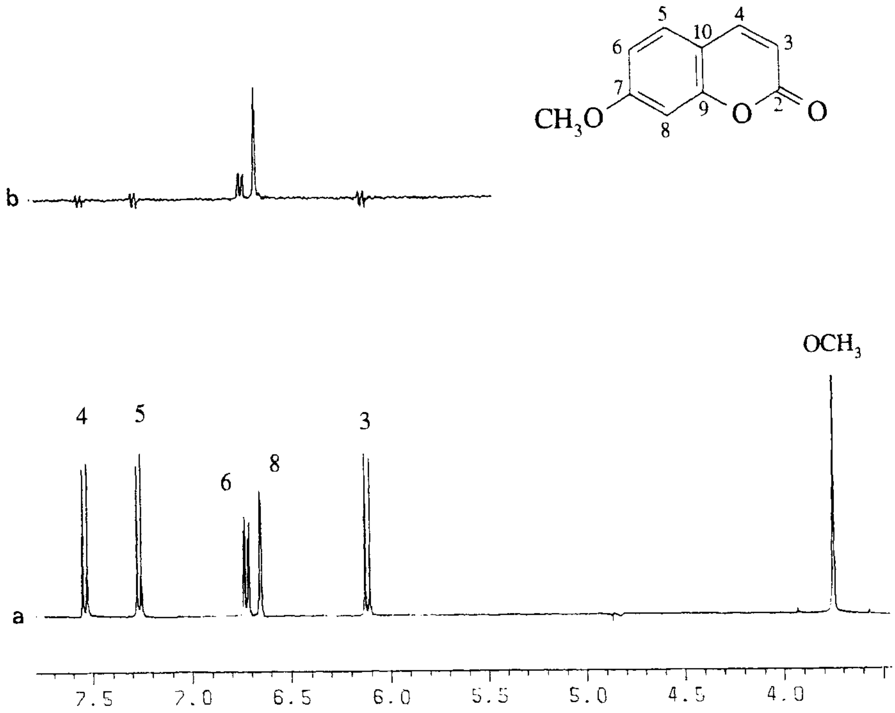


Fig. 4: (a) ^{1}H NMR spectrum of 7-methoxycoumarin (**B7-4**, herniarin); (b) NOE-difference spectrum with the methoxyl protons irradiated.

For heteronuclear correlations it is often mandatory to have an unequivocal ^{1}H signal assignment. Hydrogen atom distances in space can be monitored by various methods based on homonuclear NOE experiments. Among them are the one-dimensional NOE-difference technique (Fig. 4) and two-dimensional experiments such as NOESY and ROESY (10). Fig. 4b shows the NOE-difference spectrum of 7-methoxycoumarin (**B7-4**, herniarin) with the methoxyl protons irradiated, displaying responses of the H-6 and H-8 atoms which are close in space with respect to the methoxyl group rotating around the C^7-O bond. Heteronuclear NOE experiments irradiating protons and observing ^{13}C nuclei have proven to be useful as well (10, 11).

2.2 Coupling constants

Carbon-hydrogen coupling constants are useful aids for peak assignments in the ^{13}C NMR spectroscopy of coumarin derivatives. A simple train of consecutive FID recordings without decoupling is, however, disadvantageous. The gated-decoupling method (Fig. 5) is, rather, recommended. Here, delays are inserted between successive recordings during which the decoupler is switched on (12). This technique yields a considerable signal-to-noise ratio improvement, because the NOE is partly regained. Further, larger pulse durations (up to 90° pulses) are allowed which, at least in part, compensate the loss of time during the decoupling delays.

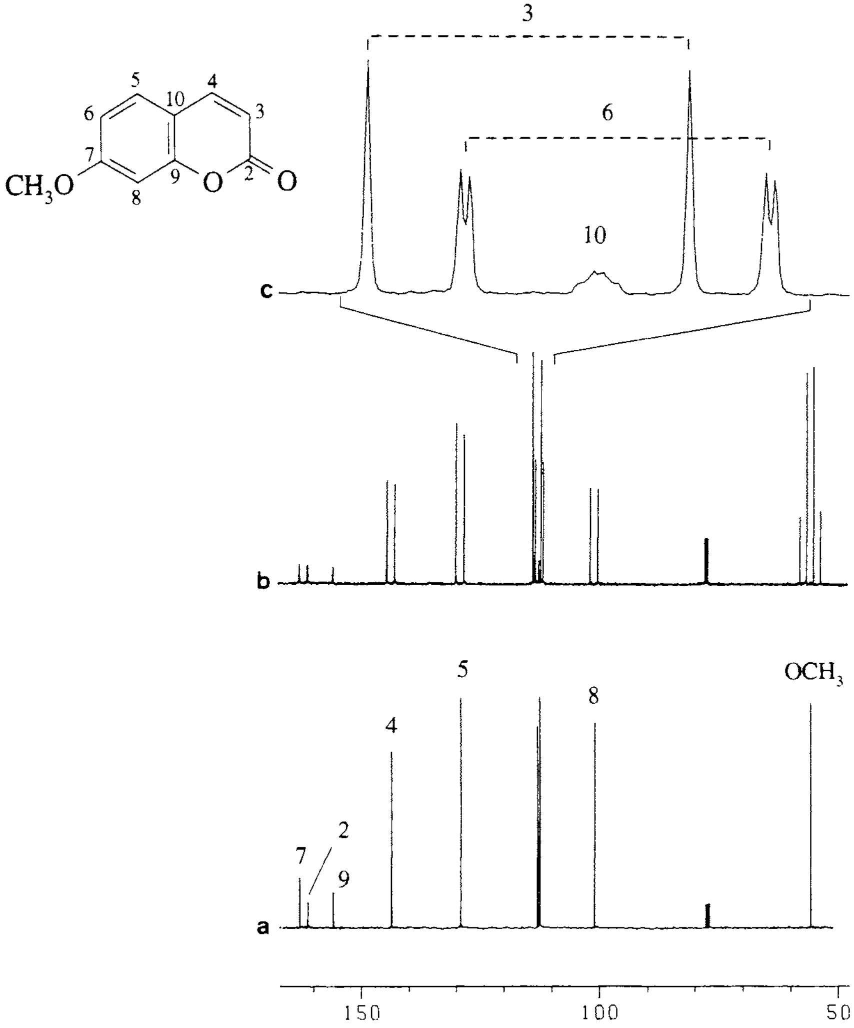


Fig. 5: (a) Broad-band and (b) gated decoupled ^{13}C NMR spectra of 7-methoxycoumarin (**B7-4**, herniarin), (c) expanded section of (b).

This experiment is not only useful for determining $^{13}C,^{1}H$ coupling constants but is an alternative for identifying quarternary carbon atoms overlapped by other signals of carbons with hydrogen atoms attached (see Fig. 5c).

Peak assignments by observing $^{13}C,^{1}H$ coupling constants (13) have been described in various publications dealing with the ^{13}C NMR of coumarins (2, 14-30). Fig. 6 shows some typical one-bond coupling constants [$^{1}J(C,H)$, in Hz] in coumarin (**A-1**) (21) and psoralen (**F-1**) (23).

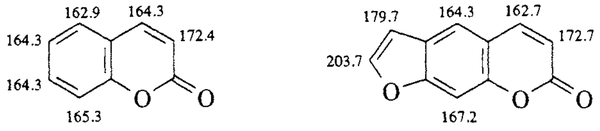


Fig. 6: One-bond coupling constants [$^{1}J(C,H)$, in Hz] in coumarin (**A-1**) and psoralen (**F-1**).

In coumarin itself all $^{1}J(C,H)$-values are within a small range (about 163-165.5 Hz) except for C-3, which has the only value larger than 170 Hz. This was used to differentiate between C-3 and C-8 (21). The same pattern was found for a variety of derivatives; for example, it was helpful in assigning C-3 and C-6 in some aminocoumarins (28); only for coumarins bearing a 4-hydroxy group is $^{1}J(C\text{-}3,H\text{-}3)$ considerably smaller (15, 19, 24). In furanocoumarins, the largest $^{1}J(C,H)$-values appear in the furan moiety, that for C-2' even exceeding 200 Hz (23, 26, 27, 31, 32).

Carbon-hydrogen couplings *via* more than one bond have also been investigated intensively, and have proved to be very useful for signal correlations (17, 19-21, 23). Three-bond couplings, $^{3}J(C,H)$ for example, depend on the geometry of the molecular moiety; they are generally larger in *transoid* than in *cisoid* orientations. Thus, the assignment of the C-2 and COOH signals of 3-carboxycoumarin (**B3-13**) was accomplished: $^{3}J(C^{2},H^{4}) = 10.3$ Hz (*transoid*); $^{3}J(COOH,H^{4}) = 5.4$ Hz (*cisoid*) (20, 21), as well as the assignment of the C-2 and C-α signals of some carbonyl and aromatic substituents at C-3 (28).

Even if the $^{n}J(C,H)$ values ($n > 1$) cannot be determined exactly owing to second-order effects, the signal shapes often give helpful hints (33). Günther *et al.* (34) established a fingerprint rule for *ortho*-disubstituted benzenes, by which α- and β-methine carbon signals can be distinguished. This rule can be employed successfully for the distinction of the C-5 and C-6 signals (16) and of the C-6 and C-8 signals (28) of coumarin derivatives.

Coupling pattern differences of the carbonyl carbon signals due to long-range couplings represent a helpful technique for the differentiation between benzocoumarins and benzochromones (30).

The influences on the ^{13}C,^{1}H couplings due the introduction of a methyl group in methyl-angelicins and other annulated furanocoumarins were highlighted (26, 27). The corresponding influence of a methoxy substituent in coumarins is discussed (29), and on this basis the previous assignment of C-2 and C-10 as well as C-2 and C-5 for the natural product citropten (**C57-4**) has been reversed.

In one instance the method of biosynthetic labelling (35) was applied to synthesize ^{13}C-enriched aflatoxin B_1, which contains a coumarin moiety (36-39). In these papers several assignments were assisted by the enhanced ^{13}C signal intensities and by one-bond ^{13}C,^{13}C coupling constants, $^{1}J(C,C)$.

2.3 Solvent effects

The ^{13}C shielding is not very sensitive to solvent changes. Although coumarins contain a polar lactone residue, the ^{13}C chemical shifts of coumarin and its derivatives remain constant within about ±1 ppm when the deuteriochloroform solvent is replaced by deuterated dimethyl sulphoxide (23, 40), despite the different complexing abilities of these two solvents. Thus, ^{13}C chemical shifts appear to be rather insensitive to solvent changes and only if small substituent effects on the ^{13}C chemical shifts (SCS) are to be discussed is it advisable to record all spectra in identical solvents. Basically, this also holds for protic organic solvents. Slight alterations of $^{1}J(C,H)$-values in the order of 3-5 Hz might occur on solvent changes (23).

Much more pronounced effects were reported by Sojka (15) who compared the ^{13}C chemical shifts of a number of coumarin derivatives in chloroform and in 96% sulphuric acid and by Yufit et al. (74) for some 4,7-diaminocoumarins in 10-25% and 40% sulphuric acid solutions. For coumarin itself the differences are: C-2, 13.2; C-3, -5.3; C-4, 16.5; C-5, 4.3; C-6, 7.1; C-7, 8.0; C-8, 3.4; C-9, 0.6; and C-10, 3.7 ppm, when the data of the chloroform spectrum are subtracted from those in sulphuric acid (15). Even the $^{1}J(C,H)$ values are sensitive, and vary up to 16 Hz. These dramatic effects are explained by protonation of the carbonyl group and by considering a different balance of mesomeric forms of the molecule. They are not constant in their magnitude, however, when coumarin is substituted in different positions.

2.4 Signal shifts in the presence of auxiliaries

Another possibility of producing explicable signal displacements is the addition of complexing reagents. Bose *et al.* (41) reported that titanium tetrachloride in deuteriochloroform can be used as a shift reagent in ^{1}H and ^{13}C NMR spectroscopy, and applied this method to coumarin and some angular furanocoumarins (42).

The use of lanthanide shift reagents (LSR) to simplify NMR spectra and for structure determinations was recognized in the early 1970s (43). Although it was shown that contact contributions are generally not negligible in ^{13}C NMR (44, 45), this complication can be overcome by using ytterbium complexes (44, 46). In this case, contact shifts are essentially restricted to carbon atoms directly bonded to the complexation site.

2.5 Derivatization

Another method is to compare the ^{13}C chemical shifts of a given compound with those of a derivative easy to prepare. Although this procedure is somewhat obsolete after the advent of modern one- and two-dimensional NMR techniques we include it due to its importance in the early years of coumarin ^{13}C NMR spectroscopy.

Structural information can be gained from signal displacements by derivatization which may be realized either *in situ* by adding a given reagent to the substrate solution in the NMR tube, or by a separate chemical reaction prior to the measurement.

The reaction of hydroxylated compounds (alcohols or phenols) and amines with trichloroacetyl isocyanate (TAI) (47) to form urethanes and ureas, respectively (48), can be performed within the NMR tube. This method, however, is restricted to compounds containing those functionalities and has not been applied widely.

Derivatization prior to the NMR experiment may be very valuable, e.g. when one or more hydrogen atoms can be replaced by deuterium at specific positions (49). Thereby, for example, a methine signal is split into a 1:1:1 triplet due to one-bond carbon-deuterium coupling (deuterium spin quantum number I = 1, cf. signal of deuteriochloroform). Further, its total intensity is decreased by less efficient spin-lattice relaxation and NOE. Thus, in practice, the signal of a deuteriated carbon almost disappears in the spectrum. For adjacent carbons slight line broadenings [^{n}J(C,D), n = [illegible] and isotope shifts of a few tenths of a ppm have to be expected (50). Selective deuteriation of coumarins has been used in some instances. 3-Deuterio- and 4-deuterio-coumarin have been investigated for signal assignments as well as 3-deuterio-4-hydroxycoumarin and 6,7-dideuterio-4-hydroxycoumarin (19, 47, 51, 52). In the latter case the C-5 signal was unambiguously identified and distinguished from that of C-6. Selective deuteriation, however, is depreciated since it is often, synthetically, a laborious procedure.

The preparation of coumarinic thionolactones and comparison of their ^{13}C NMR data with those of the parent compounds, has been used as a tool for spectral assignments, at least for the pyrone ring carbons (23, 40, 53, 54).

3. ^{13}C CHEMICAL SHIFTS AND SUBSTITUENT EFFECTS

3.1 General

Numerous publications have appeared for calculating ^{13}C chemical shifts by *ab initio* and semi-empirical MO methods (55-58) and correlating the experimental shielding data with the physico-chemical parameters and structural properties of the molecules (59, 60).

There have also been attempts to predict the ^{13}C chemical shifts of coumarins. The first to do so was Sojka (15), who found a fairly good correlation between the carbon shifts of coumarin and its protonated derivative with the π charge densities calculated by the CNDO/2 method (61). Shortly afterwards, Günther *et al.* (14) reported that substituent effects (SCS) in various mono- and di-methoxycoumarins correlate well with the HMO atom-atom polarizabilities, π_{ij} (62):

$$SCS = K\,\pi_{ij} \quad [K(OMe) = 80.13]$$

Furthermore, Günther *et al.* (14) found a result similar to Sojka's (15) when correlating coumarin shifts with π charge densities calculated by the Hückel MO method (63). This, however, fails for methoxylated coumarins (14) demonstrating that simple charge density - shift relationships are not generally applicable reliably. Ernst (20) reported a linear relationship between β-methyl substituent effects in unhindered methylated coumarins and the π bond order, P_π, of the C-α—C-β bond calculated by the INDO MO method (64):

$$\beta\ SCS = 13.49 - 19.80\,P_\pi$$

In a more rigorous way, Grigor and Webb (65) reproduced the ^{13}C shieldings of coumarin and some mono- and dimethoxycoumarins by refined INDO MO calculations and found that, in addition to atom-atom polarizabilities (14) and π bond orders (20), other factors such as excitation energies and electron-nucleus distances, $(r^{-3})_{2p}$, play an important role in the determination of the ^{13}C chemical shifts of these compounds.

The effect of the nature of the substituent in the pyrone ring on the electron structures of 3-amino- (**B3-11**), 3-hydroxy- (**B3-3**) and 3-carboxycoumarin (**B3-13**) was evaluated on the basis of quantum-chemical (CNDO/2) calculations and ^{13}C NMR data (66). The character and degree of the relationship between the chemical shifts and the electron densities on the carbon atoms were established by means of regression analysis.

Two studies correlate substituent-induced chemical shifts (SCS) with substituent parameters. Gottlieb *et al.* (33) investigated the SCS on the pyrone ring carbons C-2, C-3, C-4, C-9 and C-10 in 6- and 7-substituted coumarins, and found good correlations of the ring-junction atoms C-9 and C-10 with the Hammett constants σ_p^+ and of C-2 and C-4 with σ_m, and, separately, with σ_p. Moreover, the correlation of the C-3 chemical shifts with σ^+ is excellent. This behaviour is strongly reminiscent of related data for substituted styrenes (67) so that Gottlieb *et al.* concluded that the SCS are transmitted essentially via the -CH=CH-CO- moiety, the lactone group insulating the alternative transmission pathway.

Table 1. Substituent effccts (SCS) in various monosubstituted coumarins

Substituent	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**	**C-7**	**C-8**	**C-9**	**C-10**
3-Br	-4.1	-5.4	0.4	-1.2	0.1	-0.2	-0.4	-1.3	0.0
3-Cl	-3.9	4.4	-2.9	-0.2	0.5	0.0	-0.3	-1.7	0.0
3-OH	-1.9	25.3	-28.6	-1.8	0.1	-4.3	-0.8	-4.7	1.9
3-NH_2	-1.6	16.9	-18.2	?	0.1	-7.0	-0.9	-5.9	3.1
3-NMe_2	-2.4	20.9	-27.1	-2.7	-0.7	-5.2	-1.5	-4.7	1.5
3-Me	1.7	9.3	-4.4	-1.1	-0.1	-1.4	-0.1	-0.7	0.8
3-COOH	-3.2	1.8	4.9	2.2	0.5	2.6	-0.2	0.7	-0.7
4-OH	2.5	-25.1	22.4	-4.7	-0.9	0.3	-0.3	-0.2	-2.7
4-OMe	2.1	-26.4	22.6	-5.3	-0.7	0.4	0.1	-0.8	-3.3
4-Me	0.1	-1.3	8.7	-3.5	-0.2	-0.1	0.5	-0.4	1.2
5-OMe	0.7	-1.8	-4.8	28.4	-19.0	0.8	-7.2	1.5	-9.0
5-Me	0.2	-0.5	-3.2	8.2	1.3	-0.2	-1.7	0.7	-1.1
6-Br	-1.0	1.1	-1.8	1.8	-7.7	2.4	1.9	-1.2	1.4
6-Cl	-0.8	1.2	-1.7-	1.3	5.0	-0.4	1.6	-1.8	0.8
6-OH	-0.3	-0.3	0.2	-15.7	29.3	-12.1	0.5	-7.1	0.3
6-OMe	-0.3	0.7	-1.0	-18.3	31.5	-12.8	1.3	-5.5	0.3
6-OAc	1.3	1.0	0.4-	7.3	22.8	-5.8	1.7	-2.2	1.0
6-NH_2	2.4	0.0	1.0	-15.9	20.0	-11.3	1.1	-6.7	0.9
6-NO_2	-0.4	2.4	-0.2	-3.7	20.2	-4.8	2.0	4.0	0.7
6-Me	0.5	0.1	-0.2	-0.3	9.7	1.0	0.1	-1.7	-0.2
6-CHO	0.3	1.5	0.4	2.9	9.0	0.9	1.9	4.2	0.9
6-COOH	0.8	0.9	0.7	2.6	3.4	1.8	0.9	3.1	0.2
6-CN	-0.2	2.3	-0.4	5.2	-15.5	3.6	2.3	2.9	2.1
7-Br	-1.0	0.2	-1.2	0.5	3.2	-6.3	3.4	0.2	-1.2
7-Cl	0.6	0.1	0.1	1.2	1.1	6.3	0.9	0.6	-0.9
7-OH	0.3	-4.9	0.7	1.5	-11.1	29.8	-13.9	1.8	-7.3
7-OMe	0.4	-3.7	-0.3	0.6	-12.3	30.8	-15.8	1.7	-6.5
7-OAc	1.3	-0.4	0.6	1.2	-5.4	22.0	-5.7	1.0	-1.6
7-NH_2	3.2	-6.8	1.6	1.4	-11.8	20.7	-15.9	2.7	-8.5
7-NO_2	-0 3	3 7	-1.0	1.4	-4.9	16.4	-3.7	0.2	5.3
7-Me	0.5	-1.0	-0.2	-0.5	1.2	11.3	0.5	0.3	-2.3
7-COOH	1.2	1.6	0.2	0.5	1.5	2.8	2.1	0.0	3.8
8-OH	-0.4	-0.3	0.9	-9.7	0.0	-13.4	28.3	-11.5	0.9
8-OMe	-1.0	0.5	-0.6	-9.1	-0.5	-18.2	30.8	-9.1	0.5
8-Me	0.5	-0.1	0.2	-2.5	-0.4	1.4	9.9	-1.5	-0.2

Rabaron *et al.* (24) described a three-parameter correlation of the ^{13}C chemical shifts of various 3-substituted 4-hydroxy- and 4-hydroxy-7-methoxy-coumarins with $\mathcal{F}$, $\mathcal{R}$ and Q (68):

$$SCS = a\,\mathcal{F} + b\,\mathcal{R} + cQ + d$$

The use of Swain and Lupton's parameters $\mathcal{F}$ and $\mathcal{R}$ (69) alone does not yield satisfactory results (24).

Although the aforementioned calculations and correlations are of great merit by allowing deep insight into charge densities and SCS transmission mechanisms, practical applications are hampered by their inherent restrictions and limitations. Comparisons of SCS in coumarins with those in related molecular systems, such as substituted naphthalenes, also give interesting results which can be used diagnostically. In the following sections, the SCS of various substituted coumarins (Table 1) are discussed along these lines.

3.2 *ipso*/α Effects

In general, the α SCS are similar to those of corresponding 1- and 2-substituted naphthalenes (20, 49, 70-72). There are only a few exceptions. For example, the α-methyl effect in 7-methylcoumarin is considerably larger than for all other isomers (11.2 *vs.* 8.3-9.7 ppm) (20). Despite the similarity of the α-hydroxy effects in 4-hydroxycoumarin and 1-naphthol (22.4 and 23.4 ppm, respectively), the corresponding methoxy effects are quite different (22.6 and 27.6 ppm, respectively). In 6-cyano- and 7-nitrocoumarin the α SCS are smaller by *ca.* 3 ppm than in 2 cyano- and 2-nitronaphthalene. Again, there is no satisfactory explanation.

3.3 *ortho*/β Effects

By analogy with naphthalenes (72), the β SCS in coumarins depend strongly on the positions of the substituents and the affected carbons: for 4-, 5- and 8-substituted coumarins the substituents shield the neighbouring methine carbons to a greater extent than the quarternary carbons; for 6- and 7-substituted coumarins the differences of the β effects are smaller than in the corresponding naphthalenes. The averages of the two β SCS for a certain substituent in both systems, however, are approximately the same, showing that the β SCS reflect a subtle balance of canonical forms and electric field influences (72). This is demonstrated in Fig. 7 for 4-hydroxycoumarin: The electron density at C-3 is higher than at C-10, because the canonical structure **A** is much more favoured than **B**. The latter does not retain the π electron sextet of the benzene ring (72) and, further, it is tetraionic. The possible α-pyrone-γ-pyrone tautomerism (52, 73), however, is not involved in this discrepancy between the coumarinic and naphthalenic system, since methoxy derivatives reveal similar effects.

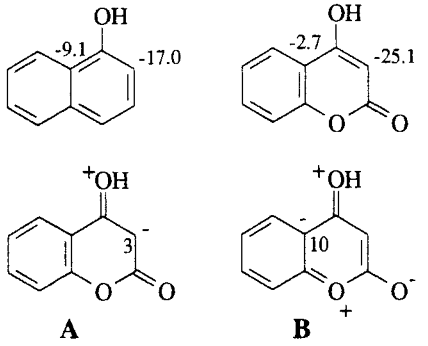


Fig. 7. β SCS in 1-naphthol and 4-hydroxycoumarin.

Abnormal β effects exist for substituents in the 3-position. This can be interpreted in terms of intramolecular interactions (electronic, steric and/or by hydrogen bridging) between the substituents and the neighbouring carbonyl group. Such interaction effects are discussed below.

It has already been noted that β-methyl effects at *ortho* carbons can be correlated to π bond orders (20).

3.4 *meta*/γ_{anti} Effects

Substituent effects at *meta*-positioned carbons are small, in agreement with those of naphthalene derivatives. Methyl and carboxyl SCS are negligible, whereas those of hetero substituents are generally deshielding (up to 2.5 ppm). An exception has been reported if the γ_{anti} carbon is C-2 (carbonyl). The effect of a C-4—NEt$_2$ group on C-2 in **C47-3** (as compared to **B7-37**) is +1.7 ppm (74). Some authors claimed that γ_{anti} effects of a 3-(1,1-dimethylallyl) group on C-10 can be used to distinguish between C-3 alkylated linear dihydrofurano- from dihydropyranocoumarins (75a). No such effect is observed in the corresponding angular derivatives. This fact is proposed as spectroscopic criterion for distinguishing between these isomers (75b).

3.5 γ_{syn} Effects

This type of molecular arrangement, which leads to the well known ("steric") diamagnetic γ SCS (59, 72), is represented only in a few cases among the available data for monosubstituted coumarins: 4-X···C-5 (X = Me, OH, OMe) and 5-Me···C-4. As expected, the SCS values are -3.2 to -5.3 ppm. Additionally, some γ_{syn} SCS can be estimated from the spectra of some di- and tri-substituted coumarins. The effect of the 4-phenyl group on C-5 in 4-phenyl-7-hydroxycoumarin, when compared with 7-hydroxycoumarin, is only -1.5 to -2.0 ppm if intramolecular interaction is permissibly neglected. The low value may be a consequence of the anisotropy of the phenyl group; this, however, is not observed in aliphatic molecules such as 2-phenyladamantane (76). Likewise, a 5-methoxyl γ_{syn} SCS of -5 to -6 ppm at C-4 may be deduced from the data for **C57-4**, **C58-1** and **D578-8**.

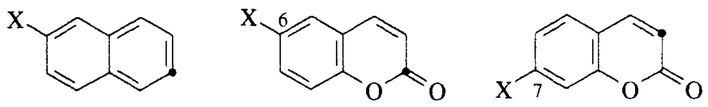
3.6 *para*/δ Effects

As has been shown by Ernst (71, 72) for naphthalene derivatives, *para* SCS can amount up to ±10 ppm, and can be correlated linearly with total charge density changes calculated by INDO MO methods. This also seems to hold for 6- and 7-substituted coumarins, because fairly good correlations exist between respective *para* effects in both molecular systems. Exceptions only occur for 3-carboxycoumarin and 3-hydroxycoumarin, which are probably due to intramolecular hydrogen bridging. Analogous observations are noted in connection with *ortho* effects.

γ_{syn} and *para* (δ) effects of alkyl and O-alkyl substituents in linear furanocoumarins can be used to distinguish between the substituent's position, C-5 or C-8 (77). Moreover, such effects of substituents at C-5 allow a differentiation between linear and angular furanocoumarins (77).

3.7 Long-range effects

Long-range effects differ in some cases from those of naphthalenes (20, 72), as demonstrated in Fig. 8.



X = COOH	+2.5	+0.8	+1.6
X = OH	-2.1	-0.3	-4.9

Fig. 8. Long-range SCS on carbon atoms marked by "•" ; naphthalenes compared with coumarins.

Apparently, in 6-substituted coumarins the effects cannot be transmitted to the carbonyl group, since the corresponding canonical form is highly unfavoured. On the other hand, in 7-hydroxycoumarin (**B7-3**, umbelliferone) the canonical form depicted in Fig. 9 is of exceptional importance:

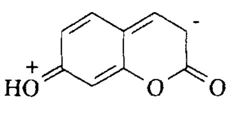


Figure 9. Canonical form of 7-hydroxycoumarin (**B7-3**, umbelliferone)

A similar value is observed by comparing the C-3 chemical shifts of 4-methylumbelliferone (**C47-6**, δ = 110.4) (19) and 4-methylcoumarin (**B4-12**, δ = 115.1) (20). An analogous comparison of δ(C-3) of **C47-12** (15) and **B4-12** (20) gives an SCS of -7.1 ppm for the diethylamino substituent, which is an even stronger electron-donating function than a hydroxy group (71b, 72).

Other long-range SCS are small, or even negligible, within the limit of experimental error and reproducibility.

4. EFFECTS OF INTRAMOLECULAR INTER ACTION ON SUBSTITUENT EFFECTS

It is a well known and often reported fact that individual SCS in molecules with more than one substituent are additive, unless there is an intramolecular interaction between them. This is also mentioned in a number of ^{13}C NMR studies on coumarinic compounds (18, 19, 24, 78, 79). A systematic investigation of the data in this review confirms these findings (see Table 2).

Table 2. Non-additivity effects (δ_{exp} - δ_{cal})[a] in di- and trisubstituted coumarins.

Substituents		**C-2**	**C-3**	**C-4**	**C-5**	**C-6**	**C-7**	**C 8**	**C-9**	**C-10**
3-Br, 4-OH	**C34-1**	-0.3	3.5	-4.1	1.3	0.6	0.8	0.6	-0.7	0.2
3-Cl, 4-OH	**C34-2**	-0.4	3.2	-2.6	0.3	0.4	0.4	0.5	-0.8	-0.1
3-Me, 4-OH	**C34-11**	-1.4	-0.1	-1.9	0.8	0.3	0.6	0.0	-1.2	-0.5
3-COOR, 4-OH	**C34-14**	-3.1	1.2	1.1	-1.1	0.5	0.8	0.6	-0.7	-1.1
3-Br, 6-Br	**C36-1**	0.4	-0.1	1.3	0.9	0.6	0.2	0.3	0.2	-0.4
4-OMe, 5-Me	**C45-2**	-0.1	1.9	5.8	6.1	2.5	-0.5	0.3	0.9	0.0
4-Me, 6-OH	**C46-8**	-0.3	-0.4	1.2	0.5	-1.2	0.1	-0.3	-0.1	-0.2
4-OH, 7-OMe	**C47-1**	-0.9	1.1	0.4	0.4	0.5	0.2	0.3	0.2	-0.4
4-OMe, 7-OMe	**C47-2**	-0.3	1.0	0.3	0.2	0.2	-0.4	-0.6	-0.3	-0.5
4-Me, 7-OH	**C47-6**	-0.4	0.2	0.2	0.1	-0.2	-0.3	-0.6	-0.3	-0.5
4-Me, 7-Me	**C47-13**	0.4	0.1	0.6	0.4	0.2	0.2	0.0	0.1	0.1
5-Me, 6-Me	**C56-1**	0.0	0.0	0.7	-1.8	-2.6	1.1	-0.5	1.9	-[b]
5-Me, 7-OMe	**C57-6**	-0.5	-0.4	-0.3	-0.2	0.0	-0.7	-0.5	1.0	-0.1
5-Me, 8-Me	**C58-4**	- 0.4	- 0.7	-0.8	-1.0	- 0.9	-1.0	-1.8	0.3	-1.0
6-OH, 7-OH	**C67-1**	1.0	0.8	0.4	-1.0	0.6	1.1	0.2	0.5	-0.4
6-OMe, 7-OMe	**C67-5**	0.2	0.1	0.5	-2.4	2.6	3.0	-2.0	-0.1	-1.4
6-Me, 7-Me	**C67-61**	0.2	0.2	0.4	0.9	-1.9	-1.9	0.6	0.3	0.6
6-Me, 8-Me	**C68-1**	-1.6	-1.4	-0.8	-0.7	-1.1	-0.9	-1.8	-1.1	-1.0
7-OH, 8-OH	**C78-4**	0.8	0.5	0.2	-0.5	-0.3	1.8	1.8	0.0	0.3
7-OMe, 8-OMe	**C78-6**	-0.1	0.3	0.4	2.8	-3.3	11.0	4.9	1.6	0.9
3-Cl, 4-OH, 7-OMe	**D347-1**	0.3	4.4	-2.1	0.9	0.6	0.0	0.6	-0.7	-0.5
3-Me, 4-OH, 7-OMe	**D347-3**	-1.2	0.8	-0.9	1.3	0.4	0.5	0.0	-1.2	0.9
4-OMe, 5-Me, 7-OMe	**D457-2**	-0.4	1.6	6.6	6.6	2.7	-1.2	-0.4	0.8	-0.3
4-OMe, 5-Me, 8-OMe	**D458-1**	0.1	0.2	6.8	5.6	1.9	-0.3	-0.1	-0.2	0.0
4-Me, 6-OH, 7-OH	**D467-2**	0.3	0.7	-0.2	-0.8	0.4	0.8	-0.6	-0.2	-1.1
4-Me, 6-Me, 7-Me	**D467-12**	0.0	0.0	0.7	1.2	-2.0	-2.1	0.3	0.1	0.4
4-Me, 7-OH, 8-OH	**D478-1**	0.3	0.6	2.0	-0.7	-0.5	1.5	1.2	0.1	-0.3
4-Me, 7-OH, 8-Me	**D478-4**	-0.5	0.0	-0.1	-1.1	-0.9	-3.8	-2.9	-0.7	-0.3

a δ_{exp}, experimental chemical shift; δ_{calc}, chemical shift calculated assuming additivity of individual SCS.

b Experimental value not reported.

Non-additivity (NA) effects occur only when functional groups within the molecule interact electronically, sterically, by hydrogen bridging or by other mechanisms. One case has already been discussed in the previous section - the effects of substituents in the 3-position are altered by the influence of the neighbouring lactone group. On the whole, one has to allow for NA effects if the substituents are in close proximity.

4.1 Substituents at vicinal carbon atoms

The C-3 signals of 3-bromo- and 3-chloro-4-hydroxycoumarins (**C34-1**, **C34-2** and **D347-1**) appear at higher, and those of C-4 at lower frequencies than expected by assuming additivity. In methylhydroxy derivatives **C34-11**, **D347-3** and **D478-1** only the hydroxylated carbons are affected; and only slight deviations from additivity, if at all, are observed for dimethyl (**C56-1**, **C67-61** and **D467-12**) and dihydroxy derivatives (**C67-1**, **C78-4**, **D467-2** and **D478-1**). Apparently, these interaction effects are mainly of electronic rather than steric origin. In dimethoxy compounds **C67-5** and **C78-6**, however, clear NA effects are observed at the substituted and the neighbouring unsubstituted carbons. The finding that the methine signals in the α position to methoxylated carbons (C-5/C-8 in **C67-5** and C-6 in **C78-6**) feature negative NA effects, suggests that the conformational behaviour of the methoxy groups is sterically perturbed. The methyl groups are forced outwards, increasing their diamagnetic γ_{syn} effects (see Fig. 10).

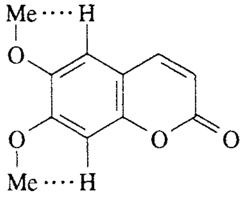


Fig. 10. Steric perturbation of methoxyl groups in **C67-5**.

Such NA effects increasingly lead to problems in signal assignments with the number of substituents becoming higher, for example in 6,7,8-trioxygenated coumarins (80). Carbon atoms of the substituents themselves are affected as well (section 5)

4.2 Substituents in *peri* position

This molecular arrangement is present in coumarins with substituents simultaneously in the 4-and 5-positions. For example, non-additivity effects can be evaluated for two derivatives (**D457-2** and **D458-1**) bearing 4-methoxy and 5-methyl groups. They are distinctly positive at the substituted carbons' signals (+5.6 to +6.8 ppm), and the neighbouring atoms C-3 and C-6 are also affected, whereas the individual SCS are additive for the quaternary carbons C-9 and C-10. The magnitudes and signs of NA effects at these six atoms, however, seem to be strongly dependent on the nature of the substituents. This can be guessed by inspecting dimethyl- (81, 82), diamino- (71b) and dihalonaphthalene (71c). The origin is apparently severe steric substituent interaction and molecular distortion (83).

4.3 Highly substituted coumarins

It stands to reason that with an increase in the number of substituents attached to the basic coumarin molecule there is an increase in the NA effects, and these become increasingly confusing. For example, the individual SCS of a given group in, for example, a furanocoumarin may be quite different from that in coumarin itself or in benzene. Thus, spectral interpretations which are based solely upon such SCS comparisons should be regarded with caution, and a rigorous signal assignment by modern multipulse NMR techniques is mandatory. Indeed, misassignments by neglecting this fact have appeared in the literature, and it is mentioned in section 6 that it was not possible to correct all of them from the tables 7-13. Fig. 11 demonstrates such different 8-methoxy SCS values (54).

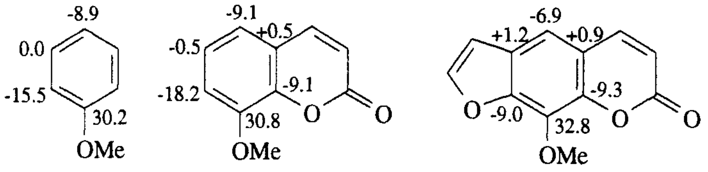


Fig. 11. Methoxy SCS on the benzenoic carbon atoms in benzene, coumarin (**A-1**) and psoralen (**F-1**).

This is even more drastic for bromo substituents (54); see Fig. 12. Comparing the ^{13}C chemical shifts of imperatorin and its tribromo derivative, one obtains 5-bromo SCS which, in part, differ enormously from those of bromobenzene; the α effect, for example, is 20 ppm larger.

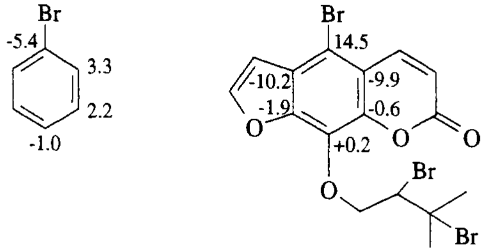


Figure 12. Bromo SCS on the benzenoic carbon atoms in bromobenzene and the tribromofuranocoumarin derivative **F58-1**.

5. ^{13}C CHEMICAL SHIFTS OF METHYL, METHOXYL AND SOME OTHER CARBON ATOMS

As expected, ^{13}C chemical shifts within substituents are quite uniform unless the carbon atoms are close to the coumarin system. In particular, carbon atoms directly attached to the ring system (α) display some dependence on their relative position. To some extent, this can be observed for β-positioned carbon atoms as well. These effects are demonstrated for methyl and methoxyl substituents (Table 3 and Table 4, respectively) as representative examples, as well as for some other atoms which provide valuable hints concerning the stereochemistry of ring-annulated coumarins.

5.1 Methyl substituents

In general, resonances of methyl carbons appear at $\delta \approx 17$, if they are attached to C-3, C-4 or C-5. At position 6 or 7, however, the values are larger (δ = 19-21) because, in contrast to those at C-3 through C-5, there is no *syn-periplanar* atom with respect to these methyl carbons which experiences a shielding γ-syn effect (60, 84). On the other hand, methyl groups at C-8 show an even stronger shielding (δ = 14-16) than those at C-3 to C-5. Apparently, the endocyclic oxygen atom is more effective in this mechanism than a methine group.

These chemical shifts, however, may be changed significantly if further substituents are close-by. Especially, substituents on neighbouring carbons atoms of the coumarin system may strongly shield the methyl carbons. Here again, methyl carbon at 3 or 8 position are particularly sensitive. On the other hand, substituents in *peri* position deshield a methyl carbon due to a δ-*syn* effect (60, 85), an influence which is exceptionally strong (4-5 ppm). Substituents further away do not have effects larger that a few tenths of a ppm.

Some typical examples for the abovementioned effects are shown in Fig. 13.

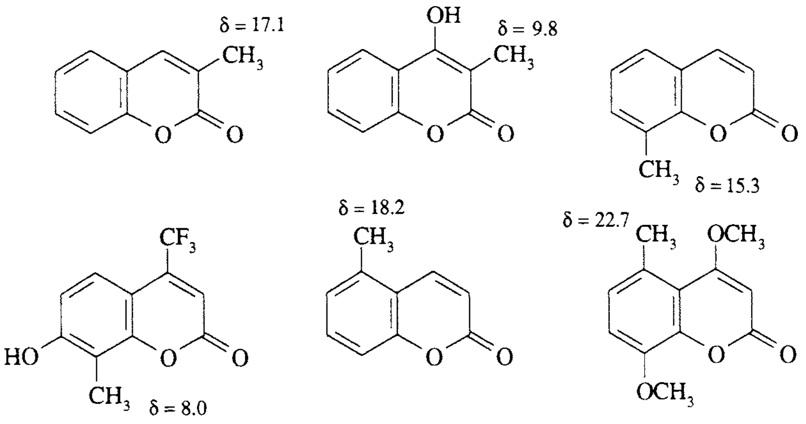


Fig. 13. Methyl chemical shifts depending on neighbouring substituents

Table 3. Methyl resonances in coumarins (selection of representative examples)

	C-3	C-4	C-5	C-6	C-7	C-8	Other substituents
B3-14	17.1						-
B4-12		18.5					-
B5-2			18.2				-
B6-8				20.7			-
B7-39					21.7		-
B8-3						15.3	-
C34-11	9.8						4-OH
C38-2	18.8					22.4	dithiocoumarin
C46-3				21.1			4-OEt
C46-7		18.4					6-Cl
C47-6		18.0					7-OH
C47-13		18.6			21.6		-
C57-6			18.4				7-OMe
C58-4		17.0				14.3	-
C67-61				19.2	20.3		-
C68-1				19.6		14.1	-
C68-2						15.6	6-Et
D347-3	9.5						4-OH, 7-OMe
D347-4		14.9					3-CH_2CH_2COOEt, 7-OH
D378-2						8.0	4-CF_3, 7-OH
D457-2			23.4				4,7-$[OMe]_2$
D457-3		23.3					5,7-$[OH]_2$
D457-8		21.8		20.7			4-CF_3
D458-1			22.7				4,8-$[OMe]_2$
D467-2		18.1					6,7-$[OH]_2$
D467-8				16.3			4-Pr^i, 7-OH
D467-11		18.3		16.9			7-NEt
D467-12		18.6		19.4	20.1		-
D478-1		18.3					7,8-$[OH]_2$
D478-4		18.4				8.0	7-OH
E3457-1	10.5		22.1				4,7-$[OMe]_2$
E3457-2		19.4					3-CH_2COOEt, 5,7-$[OH]_2$
E3458-1			22.6				3,4,8-$[OMe]_3$
E3467-1				16.4			4-Pr^i, 3,7-$[OMe]_2$
E3467-2		15.1					3-CH_2COOEt, 6,7-$[OH]_2$
E4567-1			16.0				4-SMe, 6-OMe, 7-OH
E4678-1		20.5				9.5	6-$CH_2CH{=}CH_2$, 7-OAc
E-34578-1	10.4		22.0				4,7,8-$[OMe]_3$

It is interesting to see that the δ-values of the methyl resonances in 3,8-dimethyl-dithiocoumarin (**C38-2**) are clearly larger [CH_3-(C-3): $\delta = 18.8$ and CH_3-(C-8): $\delta = 22.4$] than those expected for the corresponding coumarin itself.

The γ and δ effects discussed above are essentially additive as shown in Fig. 14:

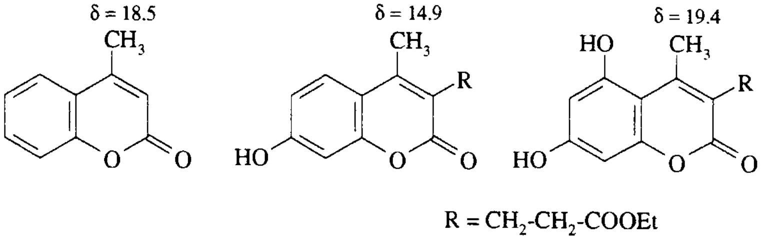


Fig. 14. ^{13}C chemical shifts of methyl carbons experiencing γ and δ effects from neighbouring substituents

Methyl resonances of a number of methylated furano-annulated coumarins have been reported (26, 27). The chemical shifts of methyl groups attached to the coumarinic rings correspond to the values in Table 3. Those, however, at C-2′ are δ ≈ 14 (δ ≈ 11.5 if there is another methyl group at C-3′). Chemical shifts of methyl carbons at C-3′ are δ ≈ 9.5 (δ ≈ 8 if there is another methyl group at C-2′).

5.2 Methoxyl substituents

Since the methyl carbon atoms of methoxyl groups are in β position with respect to the coumarin system, their ^{13}C chemical shifts are very uniform being between δ = 55 and 56.5 irregardless of their position. Only steric crowding affords larger δ-values (δ = 60-62); i.e. , if the methoxyl group is flanked by two *ortho* and/or *peri* oriented groups. This rule holds also if one or both *ortho*-neighbours is/are part of annulated rings, as for example in furano- or pyranocoumarins.

Some typical instances are collected in Fig. 15.

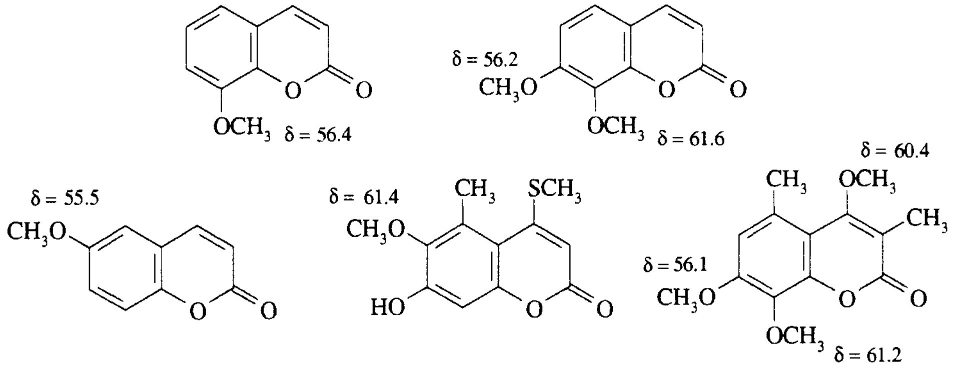


Fig. 15. Methoxyl chemical shifts depending on neighbouring substituents

Table 4. Methoxyl resonances in coumarins (selection of representative examples); values marked by "*" may be interchanged.

	C-4	C-5	C-6	C-7	C-8	Other substituents
B4-3	56.3					-
B5-1		56.1				-
B6-4			55.5			-
B7-4				55.6		-
B8-2					56.4	-
C34-22	61.9					3-CH(Ph)-CH$_2$Ac
C37-3				55.7		3-Ph
C38-1					55.6	3-NMe$_2$
C47-1				55.8		4-OH
C47-2	56.1			55.6		-
C47-7				55.5		4-Me
C57-4		56.1		55.9		-
C57-6				55.4		5-Me
C58-1		55.8			56.8	-
C58-3					56.8	5-CH$_2$CH=C(Me)$_2$
C67-2				56.3		6-OH
C67-4			55.2			7-OH
C67-5			56.2	56.2		-
C67-6			56.1			7-OCH$_2$CH=C(Me)$_2$
C67-28				56.3		6-CH=CH-C(Me)$_2$OMe
C78-5					60.6	7-OH
C78-6				56.2	61.6	-
C78-8				56.3		8-OCH$_2$CH=C(Me)$_2$
C78-9					61.3	7-OCH$_2$CH=C(Me)$_2$
C78-16				55.9		8-CH$_2$-CH$_2$-Pr^i
D347-3				55.8		3-Me, 4-OH
D357-1		56.7				3-Ar, 7-OH
D367-1			56.3	56.4		3-C(Me$_2$)-CH=CH$_2$
D378-3				56.2	61.0	3-C(Me)$_2$-CH=CH$_2$
D457-2	55.8			55.4		5-Me
D457-6		55.9				4,7-Me$_2$
D457-10		55.4				4-Ph, 7-OH
D457-11				55.6		4-Ph, 5-OH
D457-12		55.9*		55.6*		4-Ph
D458-1	55.9*				56.3*	5-Me
D467-3				55.8		4-Me, 6-OH
D467-4			56.3*	56.4*		4-Me
D567-7			60.9	56.3		5-CH=CH-Ac
D578-1		56.0		56.1		8-OAc
D678-4			56.3		61.7	7-OCH$_2$-CH=CMe$_2$
E3457-1	60.5			55.1		3,5-Me$_2$
E3457-3		55.8		55.7		3-CH$_2$COOEt, 4-Me
E3467-3			56.5	56.5		3-CH$_2$COOEt, 4-Me
E3478-2				56.1	61.3	3-CH$_2$COOEt, 4-Me
E4568-1			61.4			4-SMe, 5-Me, 7-OH
E5678-1			60.3			5-CHCH=CMe$_2$, 7,8-[OH]$_2$
E-34578-1	60.4			56.1	61.2	3,5-Me$_2$

5.3 Regio- and stereochemistry of pyranocoumarins

A simple diagnostic method has been proposed to distinguish regioisomers of natural benzodioxane lignoids (Fig. 16) with different aryl (Ar) and alkyl (R) substituents (**O7′8′-1** to **O7′8′-13**), based on small, but systematic differences in ^{13}C chemical shifts of C-7 and C-8 of the coumarin moiety, provided that both isomers are available (86).

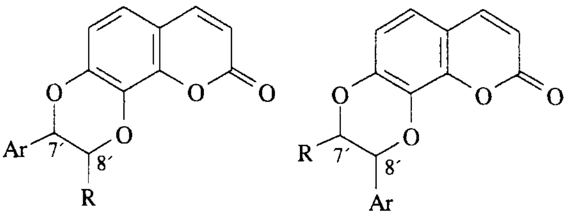
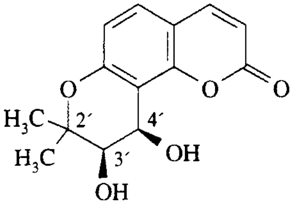
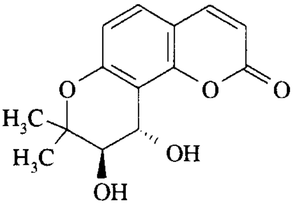


Fig. 16. Benzodioxane lignoids **O7′8′-1** to **O7′8′-13**

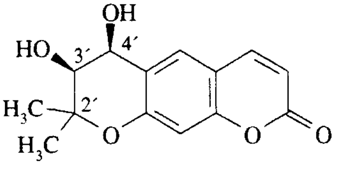
The two geminal methyl groups attached to C-2′ in dihydropyranocoumarins allow stereochemical assignments. In the angular 3′,4′-diols (**N3′4′-1** and **N3′4′-26**) the difference of the ^{13}C chemical shifts of these methyl groups is larger than 3 ppm in the *cis*- and smaller than 2 ppm in the *trans*-isomer. This seems to be a rule which holds also for 3′,4′-dialkoxy substituents (87).



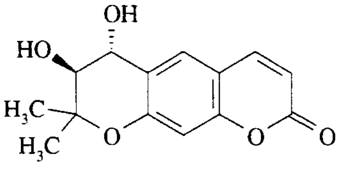
N3′4′-1



N3′4′-26



L3′4′-1



L3′4′-2

Fig. 17. Angular and linear 3′,4′-disubstituted dihydropyranocoumarins

In the case of linear dihydropyranocoumarins, however, these trends are opposite, i.e. the difference is up to 7 ppm in *trans*- but negligible in *cis*-isomers as shown for the pair **L3′4′-1** and **L3′4′-2** (Fig. 17). Apparently, effects of conformational preference and mobility are responsible for these observations.

It should be noted that a secure differentiation of the C2′-methyl signals from those of other methyl groups which might exist in the molecule, is a prerequisite for an application of this rule.

Acknowledgements

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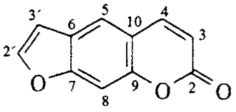
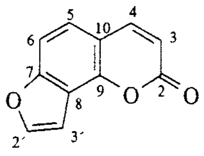
6. TABLES OF ^{13}C CHEMICAL SHIFTS OF COUMARIN AND ITS DERIVATIVES

Tables 5-13 contain ^{13}C chemical shifts of the coumarin moiety and some other atoms in the molecular backbones of 876 coumarin derivatives. They are arranged according to the substitution patterns and basic molecular systems compiled in Fig. 18 below. Therefore, compound chiffres have been composed in such a way that the basic system (initial letter) and the substitution pattern (numbers after the letter) can be read directly; the number after the hyphen indicates the hierarchical order which is given by the nature of that atom in a substituent which is directly connected to the coumarin moiety; sequencing according to the Cahn-Ingold-Prelog rule. For example, **D348-1** is a trisubstituted coumarin (**D**) carrying substituents at C-3, C-4 and C-8 (**348**; 3-Br, 4-OH, 8-Me). Since bromine has the top position of all substituents at C-3 in all 3,4,8-trisubstituted coumarins listed, the compounds is the first entry (**-1**). The only exception from this rule appears in di- and tricoumarins where the numbers after the letter indicate the positions at which the two (three) coumarin systems are connected.

A: Coumarin, deuterated species and chalcogen analogues
B: Monosubstituted coumarins
C: Disubstituted coumarins
D: Trisubstituted coumarins
E: Tetra- and pentasubstituted coumarins



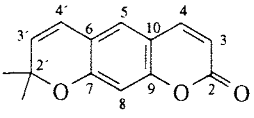
F: Linear furanocoumarins
G: 2,3′-Dihydro derivatives of **F**



H: Angular furanocoumarins
I: 2,3′-Dihydro derivatives of **H**

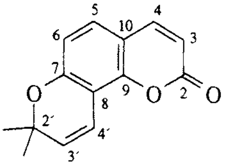
J: Coumarins with other annulated five-membered rings

Fig. 18. Molecular systems in Tables 5-13



K: Linear pyranocoumarins

L: 3′,4′-Dihydro derivatives of **K**

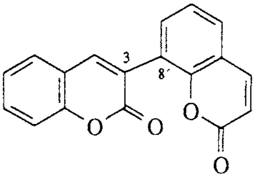


M: Angular pyranocoumarins

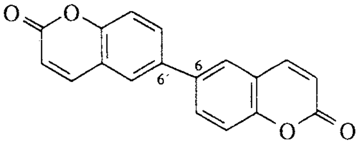
N: 3′,4′-Dihydro derivatives of **M**

O: Coumarins with other annulated six-membered rings

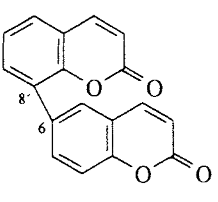
P: Dicoumarins directly connected by one bond



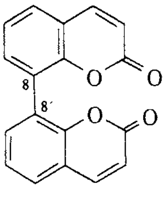
P38′-i



P66′-i



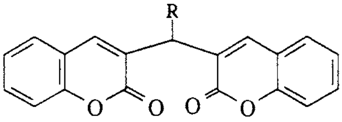
P68′-i

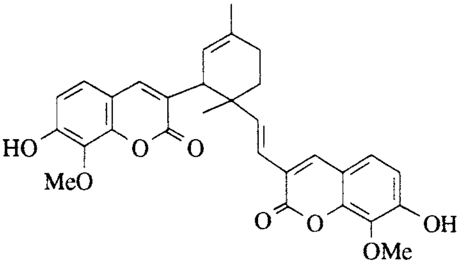


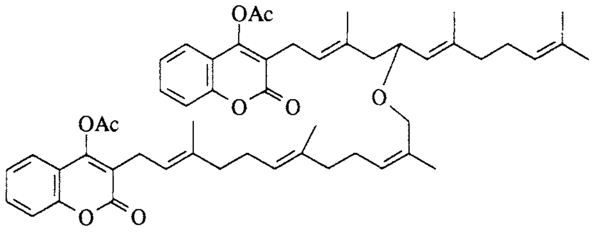
P88′-i

Continuation of Fig. 18.

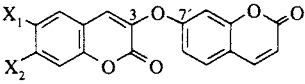
Q: Dicoumarins connected by more than one bond



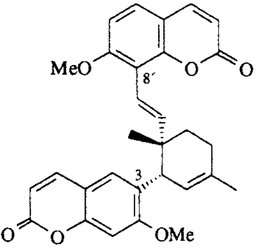




Q33´-i



Q37´-i



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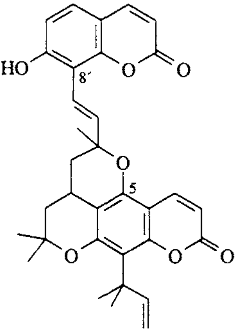
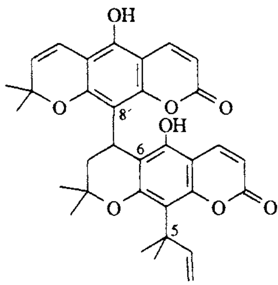
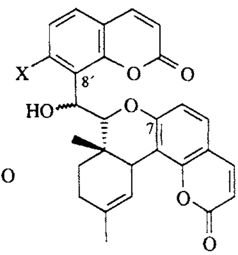


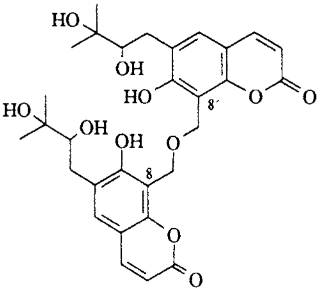
Q58´-i



Q68´-i

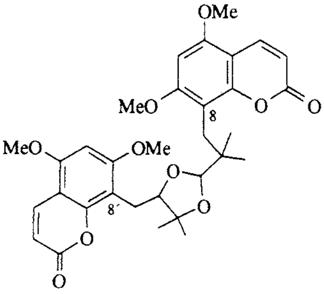


Q78´-i

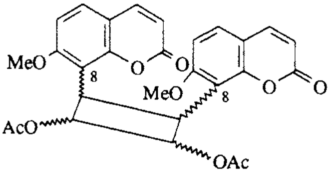


Q88´-i

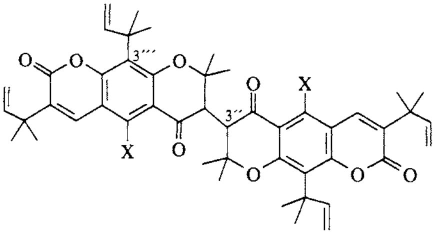
Continuation of Fig. 18.



Q88´-i

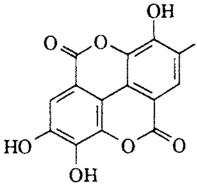


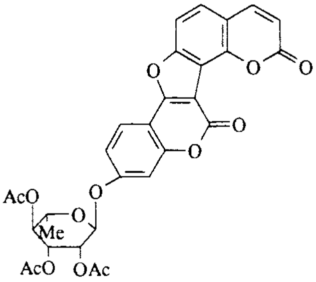
Q88´-i

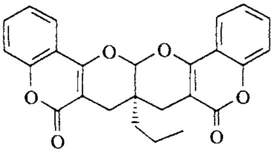


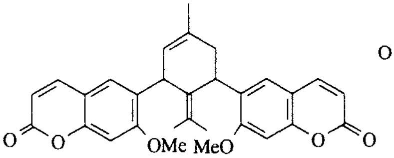
Q3´´3´´´-i

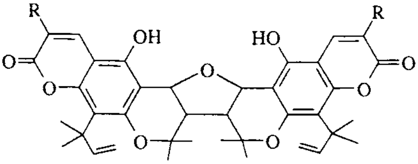
R: Dicoumarins connected by rings



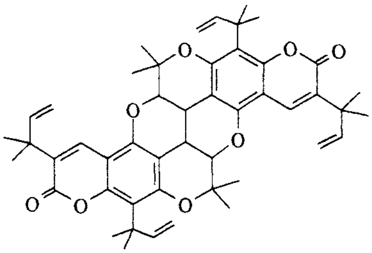




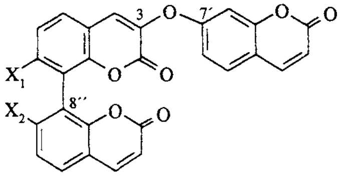




Continuation of Fig. 18.



S: Tricoumarins



Continuation of Fig. 18.

The following abbreviations have been used for substituents: Me ≡ methyl; Et ≡ ethyl; Pr ≡ propyl; Bu ≡ butyl; Pent ≡ pentyl; Hex ≡ hexyl; Oct ≡ octyl; Ph ≡ phenyl; Ac ≡ acetyl; apio*f* ≡ apiofuranoside; gal*p* ≡ galacto-pyranoside; glcp ≡ gluco-pyranoside; rham*p*≡ rhamno-pyranosyl, xyl*p* ≡ xylo-pyranosyl.

Abbreviations for solvents are: A ≡ acetone; B ≡ benzene; C ≡ chloroform; CCl ≡ carbon tetrachloride; D ≡ dimethyl sulphoxide; DX ≡ dioxane; M ≡ methanol; P ≡ pyridine; TFA ≡ trifluoro acetic acid; ? ≡ solvent unknown. Most solvents have been used in deuterated form.

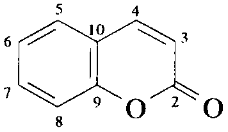
All ^{13}C chemical shifts are given in ppm relative to tetramethylsilane ($\delta = 0$). Open entries mean that chemical shifts have not been reported in the original papers. Values which might be interchanged are marked by "*", "$^{+}$" or "§", but only if their chemical shift difference in larger than 1 ppm.

If spectra exist in the literature which were recorded in different solvents, the data set obtained in deuteriochloroform has been chosen for the tables.

Many papers reporting chiral coumarin derivatives do not give clear information about the chirality and the enantiomeric purity. Therefore, it is stressed that in all cases the stereochemical notation of the structures in Tables 6-13 indicate only relative, not absolute configurations.

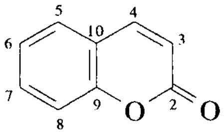
CAVEAT: It is strongly advisable to take data of highly substituted compounds with great caution. The data sets may contain inconsistencies in the signal positions and sequences indicating misassignments. This occurs particularly in tri- and tetrasubstituted coumarins where assigning merely based on analogy with similar structures and/or derivatives with fewer substituents is very dangerous. Unfortunately, however, it was not possible to correct all these mistakes because of missing experimental evidences. In such cases the authors decided to report the original data sequences. In a few instances where two divergent data sets have been published in different papers both data sets are listed.

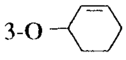
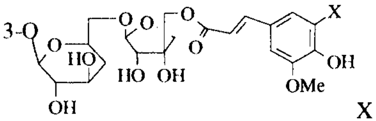
Table 5. ^{13}C chemical shifts of coumarin, deuteriated species and chalcogen analogues

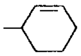


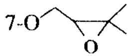
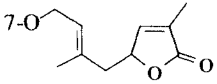
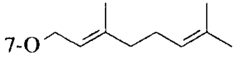
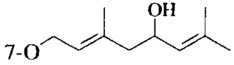
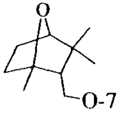
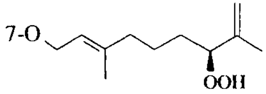
	Substituents	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Solv.	Reference
A-1	- (coumarin)	160.4	116.4	143.6	128.1	124.4	131.8	116.4	153.9	118.8	C	1-19
A-2	3-^{2}H	158.6		142.2	127.6	123.8	131.2	116.4	154.0	118.7	CCl	11
A-3	4-^{2}H	158.5	166.3	142.5	127.7	123.9	131.2	116.4	153.9	118.9	CCl	11
A-4	1-thio	185.4	126.0	143.7	130.0	124.2	131.6	126.5	137.7	126.2	C	12,19
A-5	2-thiono	198.0	129.7	134.5	127.8	125.5	132.2	116.8	156.7	120.5	C	10,12,13
A-6	1-thio-2-thiono	209.0	136.0	131.4	130.3	123.4	134.4	127.7	140.3	128.0	C	10,13
A-7	1-seleno	188.4	122.8	144.2	133.0	126.0	129.4	128.2	137.0	126.9	?	19
A-8	1-telluro	193.5	125.0	145.4	135.0	127.0	129.7	135.7	125.0	130.8	?	19

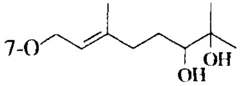
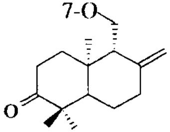
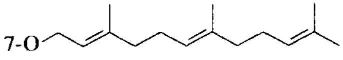
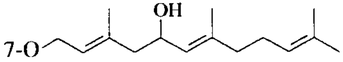
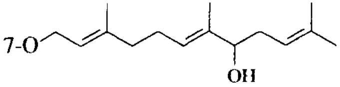
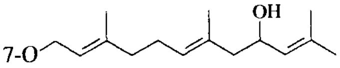
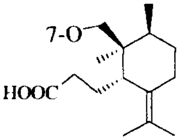
Table 6. ^{13}C chemical shifts of monosubstituted coumarins

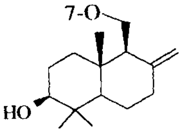
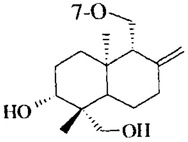
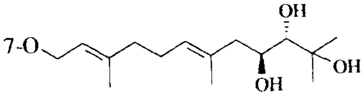
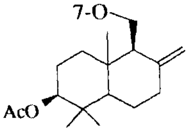
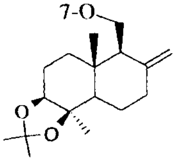
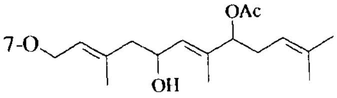


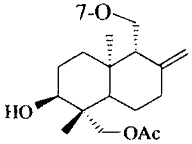
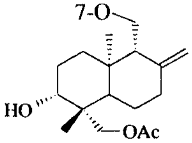
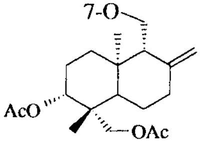
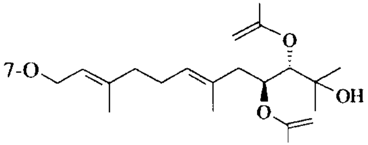
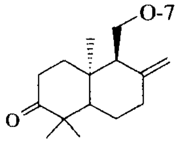
	Substituents	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**	**C-7**	**C-8**	**C-9**	**C-10**	**Solv.**	**Reference**
B3-1	3-Br	156.3	111.0	144.0	126.9	124.5	131.6	116.0	152.6	118.8	C	4
B3-2	3-Cl	156.5	120.8	140.7	127.9	124.9	131.8	116.1	152.2	118.8	C/D	20
B3-3	3-OH	158.5	141.8	115.0	126.3	124.5	127.5	115.6	149.2	120.7	D	21
B3-4	3-OCH$_2$-CH=CH$_2$	156.6	142.4	115.1	126.0	123.9	127.7	113.7	148.7	118.9	C	22
B3-5	3-OCH$_2$-C(Me)=CH$_2$	157.2	143.2	115.8	126.3	124.4	128.2	113.7	149.3	119.4	C	22
B3-6	3-OCH$_2$-CH=CMe$_2$	157.4	143.5	116.0	126.2	124.4	128.1	113.5	149.4	119.6	C	22
B3-7		157.5	142.1	115.6	126.1	124.2	127.9	115.3	149.1	119.4	C	22
B3-8	3-OCH$_2$-CH=CH-Ph (*trans*)	157.3	143.3	116.1	126.4	124.5	128.1	114.4	149.5	119.5	C	22
B3-9	 X = H	159.8	142.9	120.8	128.6	126.2	130.5	117.0	151.3	120.9	M	36
B3-10	X = OMe	159.9	143.1	120.9	128.8	126.4	130.7	117.2	151.5	121.0	M	36
B3-11	3-NH$_2$	158.8	133.3	125.4	108.0(?)	124.5	124.8	115.5	148.0	121.9	D	23
B3-12	3-NMe$_2$	158.0	137.3	116.5	125.4	123.7	126.6	114.9	149.2	120.3	C	24
B3-13	3-COOH	157.2	118.2	148.5	130.3	124.9	134.4	116.2	154.6	118.1	D	6,25
B3-14	3-Me	162.1	125.7	139.2	127.0	124.3	130.4	116.3	153.2	119.6	C	5,26
B3-15	3-Et	165.6	130.9	137.3	127.0	124.1	130.3	116.3	152.4	119.5	C	37
B3-16	3-Pr^n	161.0	129.8	138.3	127.0	124.0	130.3	116.3	153.0	119.5	C	37

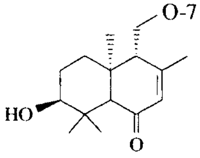
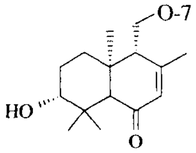
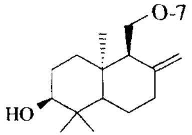
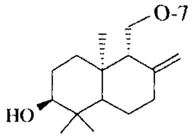
B3-17	3-Pr^{i}	165.4	135.8	138.3	127.2	123.8	130.3	116.3	152.4	119.5	C	37
B4-1	4-OH	162.9	91.3	160.0	123.3	123.5	132.1	116.1	153.7	116.1	C	3,7,21,27-29
B4-2	4-O^{-} (oxido)	166.6	87.1	177.2					161.6	104.7	D	30
B4-3	4-OMe	162.5	90.0	166.2	122.8	123.7	132.2	116.5	153.1	115.5	C	7,21,31,35
B4-4	4-OEt	162.5	90.3	165.8	122.8	123.7	132.2	116.7	153.3	115.8	C	32
B4-5	4-OCH$_2$-CH=CH$_2$	162.5	90.8	164.9	122.8	123.7	130.5	116.5	153.2	115.5	C	33,34
B4-6	4-OCH$_2$-C(Me)=CH$_2$	162.5	90.8	165.0	122.8	123.7	132.2	116.5	153.2	115.6	C	35
B4-7	4-OCH$_2$-CH=CMe$_2$	160.5	90.8	164.4	123.0	123.6	132.1	116.6	151.5	115.9	C	33
B4-8	4-OPent^{n}	162.5	90.3	165.6	122.8	123.7	132.2	116.7	153.3	115.8	C	32
B4-9	4-O 	162.8	90.4	164.3	123.0	123.5	132.0	116.3	153.2	115.9	C	35
B4-10	4-OHex^{n}	162.5	90.3	165.6	123.3	123.7	132.2	116.7	152.7	115.8	C	32
B4-11	4-OCH$_2$-CH=CH-Ph (*trans*)	162.5	90.7	165.0	123.0	123.6	132.1	116.5	153.2	115.5	C	35
B4-12	4-Me	160.5	115.1	152.3	124.6	124.2	131.7	116.9	153.5	120.0	C	5,26
B4-13	4-Pr^{n}	160.8	113.8	155.8	124.2	124.0	131.4	117.1	153.6	119.2	C	37
B4-14	4-Ph	160.5	115.0	155.5	126.8	124.0	131.7	117.1	154.0	118.8	C	37
B5-1	5-OMe	161.1	114.6	138.8	156.5	105.4	132.6	109.2	155.4	109.8	C	38
B5-2	5-Me	160.6	115.9	140.4	136.3	125.7	131.6	114.7	154.6	117.7	C	5,39
B6-1	6-Br	159.4	117.5	141.8	129.9	116.7	134.2	118.3	152.7	120.2	C	4
B6-2	6-Cl	159.6	117.6	141.9	126.8	129.4	131.4	118.0	152.1	119.6	C	3,9
B6-3	6-OH	160.1	116.1	143.8	112.4	153.7	119.7	116.9	146.8	119.1	D	9,21
B6-4	6-OMe	160.1	117.1*	142.6	109.8	155.9	119.0*	117.7*	148.4	119.1	C/CCl	2,9
B6-5	6-OAc	161.7	117.4	144.0	120.8	147.2	126.0	118.1	151.7	119.8	C/M	9
B6-6	6-NH$_2$	162.8	116.4	144.6	112.2	144.4	120.5	117.5	147.2	119.7	C/M	9
B6-7	6-NO$_2$	160.0	118.8	143.4	124.4	144.6	127.0	118.4	157.9	119.5	C/M	9
B6-8	6-Me	160.9	116.5	143.4	127.8	134.1	132.8	116.5	152.2	118.6	C	5,9,14,26
B6-9	6-C≡N	160.2	118.7	143.2	133.3	108.9	135.4	118.7	156.9	120.9	C/M	9
B6-10	6-CHO	160.7	117.9	144.0	131.0	133.4	132.7	118.3	158.1	119.7	C/M	9
B6-11	6-COOH	161.2	117.3	144.3	130.7	127.8	133.6	117.3	157.0	119.0	CM	9
B7-1	7-Br	159.4	116.6	142.4	128.6	127.6	125.5	119.8	154.1	117.6	C	4
B7-2	7-Cl	161.1	116.5	143.8	129.3	125.5	138.1	117.3	154.5	117.9	C/M	9

B7-3	7-OH	160.7	111.5	144.3	129.6	113.3	161.6	102.5	155.7	111.5	D	3,6,9,18,21
B7-4	7-OMe	160.8	112.7	143.3	128.7	112.1	162.6	100.6	155.6	112.3	C/Cl	2,8,9,11,14
B7-5	7-OAc	161.7	116.0	144.2	129.3	119.1	153.8	110.7	154.9	117.2	C/M	9
B7-6	7-OEt	162.7	112.7	144.8	129.4	113.6	162.8	101.6	156.1	112.9	C/M	9
B7-7	7-OCH_2-CH=CH_2	160.4	112.4	142.9	128.4	112.5	161.2	101.2	155.2	112.1	C	16
B7-8	7-OC(Me_2)-C≡CH	158.8	113.7	143.3	128.2	117.1	161.0	107.0	155.0	113.5	C	40
B7-9	7-OCH_2-CH=CMe_2	160.1	111.9	142.7	128.1	112.1	161.2	100.6	154.9	111.6	C	6
B7-10	7-OC(Me_2)-CH=CH_2	160.0	113.2	143.3	128.0	117.2	161.4	106.8	155.2	113.5	C	41
B7-11		160.8	112.7	143.2	128.9	113.1	161.7	101.7	155.7	112.9	C	42
B7-12	7-O-β-D-glc*p*	160.3	113.2	144.2	129.5	113.8	160.3	103.4	155.1	113.4	D	21
B7-13	7-OCO-CH_2Ph	160.2	116.7	142.8	128.6	118.3	154.7	110.3	153.3	116.1	C	17
B7-14		161.8	113.0	143.4	122.9	113.1	161.2	101.5	155.8	112.6	C	43
B7-15		160.7	112.5	143.0	128.3	112.7	161.7	101.3	155.4	112.1	C	16,44,45
B7-16		162.1	113.1	143.5	127.4	113.2	161.3	101.7	155.9	112.7	C	46
B7-17		172.6	117.5	135.2	120.0	104.4	151.5	135.9	151.7	118.2	C	47
B7-18		162.5	113.3	143.7	128.9	113.5	161.5	101.8	156.0	112.7	C	48

B7-19		160.1	112.2	144.0	129.2	112.7	161.5	101.3	155.2	112.2	D	16
B7-20		161.8	113.0	143.2	128.6	112.9	160.9	101.2	155.8	112.5	C	49
B7-21		161.2	112.8	143.3	128.5	113.1	162.0	101.4	155.8	112.3	C	40,50
B7-22		161.3	112.9	143.4	128.6	113.1	162.0	101.4	155.8	112.4	C	50
B7-23		161.2	112.9	143.4	128.6	113.2	162.0	101.5	155.8	112.4	C	50
B7-24		161.3	112.9	143.4	128.7	113.2	162.1	101.6	155.9	112.4	C	50
B7-25		161.3	113.1	143.5	128.6	112.8	162.8	101.1	155.9	112.2	C	50

B7-26		161.0	112.6	143.3	128.6	112.6	162.0	101.2	155.6	112.3	C	1
B7-27		161.8	112.5	143.2	128.5	112.5	160.8	101.0	155.4	112.1	C	49
B7-28		162.0	112.7	143.5	128.7	113.2	161.3	101.4	155.6	112.3	C	51
B7-29		160.7	112.6	143.0	128.4	112.7	161.7	101.0	155.5	112.1	C	1
B7-30		162.2	113.1	143.4	128.7	113.1	161.2	101.4	155.9	112.5	C	49
B7-31		161.2	112.9	143.3	128.7	113.0	161.9	101.5	155.7	112.4	C	50

B7-32		162.2	113.1	143.4	128.7	113.0	161.2	101.4	155.9	112.4	C	49
B7-33		162.0	112.9	143.3	128.7	112.9	161.1	101.3	155.8	112.5	C	49
B7-34		162.0	113.1	143.3	128.8	113.0	161.1	101.4	155.9	112.6	C	49
B7-35		161.9	112.8	143.3	128.5	113.0	161.1	101.4	155.7	112.3	C	51
B7-36		161.2	113.0	143.4	128.8	113.2	161.8	101.7	155.9	112.7	C	54

B7-37		161.0	113.5	143.3	128.9	113.0	161.4	101.4	155.9	112.9	C	54
B7-38		161.0	113.5	143.3	129.0	112.9	161.2	101.4	155.9	113.0	C	54
B7-39		161.3	112.9	143.5	128.8	113.2	162.3	101.8	155.9	112.4	C	54
B7-40		161.4	112.9	143.4	128.7	113.2	162.4	101.4	156.2	112.4	C	54
B7-41	7-NH_2	163.6	109.6	145.2	129.5	112.6	152.5	100.5	156.6	110.3	C/M	9
B7-42	7-NEt_2	162.0	108.8	143.6	128.7	108.5	150.5	97.2	156.5	108.1	C	67
B7-43	7-NO_2	160.1	120.1	142.7	129.5	119.5	148.2	112.7	154.1	124.1	C/M	9
B7-44	7-Me	160.9	115.4	143.4	127.6	125.6	143.1	116.9	154.2	116.5	C	5,9,26,39
B7-45	7-COOH	161.6	118.0	143.8	128.6	126.0	134.6	118.5	154.0	122.6	C/M	9

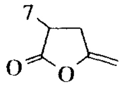
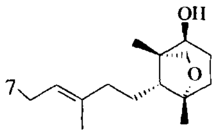
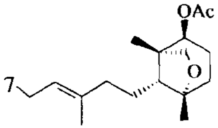
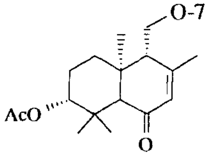
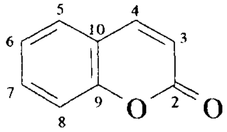
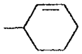
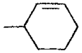
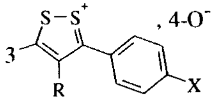
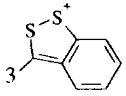
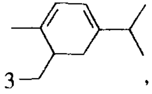
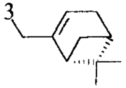
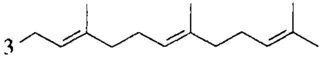
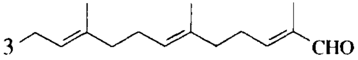
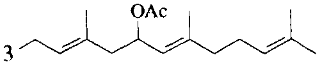
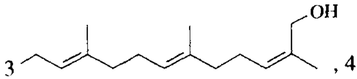
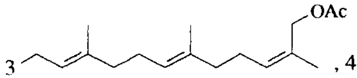
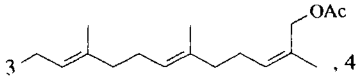
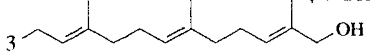
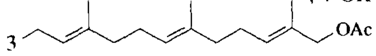
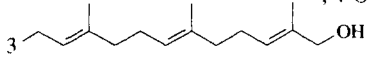
B7-46		160.5	113.6	143.9	129.6	112.7	144.3	106.9	151.6	113.6	C	53
B7-47		161.3	113.0	143.4	128.7	113.3	162.0	101.5	155.8	112.5	C	54
B7-48		161.2	113.0	143.5	128.8	113.2	162.0	101.6	155.9	112.5	C	54
B7-49		161.0	113.6	143.3	129.0	112.9	161.2	101.4	155.9	113.0	C	54
B8-1	8-OH	160.0	116.1	144.5	118.4	124.4	118.4	144.7	142.4	119.7	D	21
B8-2	8-OMe	159.4	116.9	143.0	119.0	123.9	113.6	147.2	144.8	119.3	C/Cl	2,38
B8-3	8-Me	160.9	116.3	143.8	125.6	124.0	133.2	126.3	152.4	118.6	C	5,26

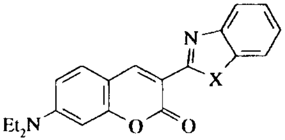
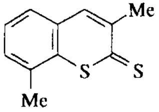
Table 7. ^{13}C chemical shifts of disubstituted coumarins

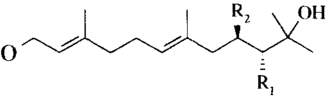


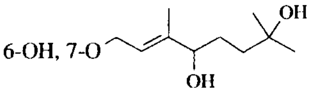
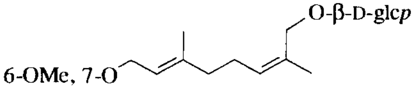
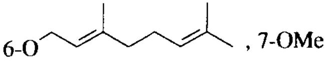
	Substituents	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Solv.	Reference
C34-1	3-Br, 4-OH	158.5	89.4	162.3	123.4	124.2	132.7	116.3	151.7	116.3	D	7,27
C34-2	3-Cl, 4-OH	158.6	98.9	160.5	123.4	124.4	132.5	116.3	151.2	116.0	D	27
C34-3	3-OPh, 4-OH	158.4	119.9	155.4	123.5	124.3	131.7	116.2	150.9	116.5	D	27
C34-4	3-OH, 4-CH_2-C(Cl)=CH_2	159.8	133.5	121.8	125.1	124.0	128.6	116.8	148.8	120.3	C	55
C34-5	3-OH, 4-CH_2-CH=CH_2	158.5	138.4	125.0	124.7	124.1	127.9	116.2	148.8	120.7	D	22
C34-6	3-OH, 4- CH_2-C(Me)=CH_2	159.9	137.7	122.9	124.7	124.2	128.1	116.5	148.7	120.9	C	22
C34-7	3-OH, 4- C(Me_2)-CH=CH_2	161.3	137.9	129.1	127.3	123.4	128.4	116.8	148.3	120.3	C	22
C34-8	3-OH, 4 	160.0	137.1	129.6	125.0	124.3	127.9	116.8	148.8	120.3	C	22
C34-9	3-OH, 4-CH(Ph)-CH=CH_2	158.3	138.7	125.9	124.8	124.0	127.4	116.2	148.6	119.5	D	22
C34-10	3-NO_2, 4-OH	156.1	121.2	163.9	124.3	125.6	134.2	116.6	152.4	117.8	D	27
C34-11	3-Me, 4-OH	163.2	100.5	159.7	123.0	123.7	131.3	116.0	151.8	116.4	D	27,28
C34-12	3-Ac, 4-OH	159.9	101.4	177.8	124.7	125.1	136.6	116.8	154.1	114.7	D	27
C34-13	3-CH_2-CH=CH_2, 4-OH	161.5	102.5	164.6	123.1	123.9	131.7	116.6	152.2	115.9	C	35
C34-14	3-COOEt, 4-OH	156.5	94.3	172.0	124.4	124.5	135.5	116.5	153.7	114.3	D	27
C34-15	3-CH_2-C(Me)=CH_2, 4-OH	161.6	101.8	163.9	122.9	123.8	131.8	116.3	152.3	115.6	C	35
C34-16	3-Ph, 4-OH	161.9	106.2	160.3	123.8	123.8	132.1	116.1	152.3	116.5	D	27,28
C34-17	3 , 4-OH	160.8	107.2	163.0	122.7	123.6	131.5	116.1	152.3	115.9	C	35
C34-18	3-CH_2Ph, 4-OH	162.9	104.4	160.6	123.3	123.7	131.6	116.1	152.1	116.3	D	27,28

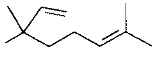
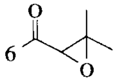
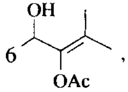
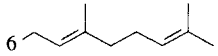
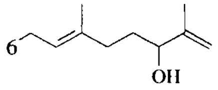
C34-19	3-CH(Ph)-CH=CH$_2$, 4-OAc	155.4	121.3	161.1	122.8	124.1	131.8	116.6	152.2	116.0	C	35
C34-20	3-CH(Ph)-Et, 4-OH	161.6	107.9	160.7	123.4	123.7	131.7	116.3	152.2	116.1	D	7,56
C34-21	3-CH(Ph)-CH$_2$Ac, 4-O$^-$ Na$^+$	167.9	103.4	175.7	126.6	123.9	131.6	116.7	153.5	122.3	DX	7,56
C34-22	3-CH(Ph)-CH$_2$Ac, 4-OMe	162.3	119.8	164.2	126.7	123.5	131.4	116.6	153.0	116.8	C	7
C34-23	 , 4-O$^-$ R = X = H	159.8	106.8	177.0					154.1	118.3	D	30
C34-24	R = H, X = F	159.9	107.2	177.1					154.1	118.2	D	30
C34-25	R = H, X = OMe	160.2	107.3	177.1					154.3	118.6	D	30
C34-26	R = Me, X = H	158.3	106.9	176.9					154.0	118.6	D	30
C34-27	R = X = Ph	156.8	107.8	176.8					154.1	118.4	D	30
C34-28	 , 4-O$^-$	159.4	109.2	177.1					153.2	118.3	D	30
C34-29	 , 4-OH	160.7	104.0	163.6	123.2	124.0	131.9	116.6	152.6	115.0	C	57
C34-30	 , 4-OH	159.8	105.0	164.2	123.0	123.8	131.4	116.5	152.2	115.9	C	57
C34-31	 , 4-OH	160.9	103.4	163.8	122.7	123.0	131.4	116.2	152.2	115.9	C	58
C34-32	 , 4-OH	160.7	103.0	163.8	122.6*	123.8*	131.6	116.4	152.4	115.8	C	59

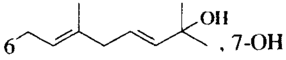
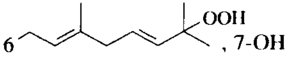
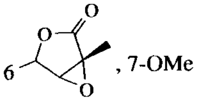
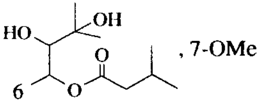
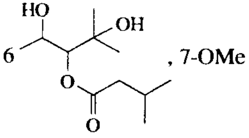
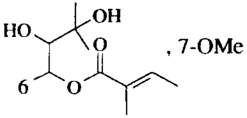
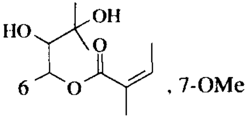
C34-33	, 4-OH	162.0	119.3	154.5	122.3	124.3	131.6	116.8	152.1	116.2	C	60
C34-34	, 4-OH	160.7	103.8	163.8	122.7*	123.7*	131.4	116.3	152.3	116.0	C	59
C34-35	, 4-OH	160.6	103.5	163.7	122.6*	123.7*	131.4	116.3	152.3	116.0	C	59
C34-36	, 4-OAc	161.9	119.4	154.3	122.7*	124.3*	131.3	116.5	151.9	116.2	C	59
C34-37	, 4-OH 	160.8	103.2	163.6	122.7*	123.6*	131.5	116.3	152.4	116.0	C	59
C34-38	, 4-OH 	161.0	102.9	163.1	122.7*	123.8*	131.6	116.4	152.0	116.0	C	59
C34-39	, 4-OAc 	161.8	119.4	154.4	122.2*	124.1*	131.3	116.4	151.9	116.1	C	59
C36-1	3,6-Br_2	155.7	112.0	143.5	129.6	120.9	134.2	118.2	151.6	116.3	D	4
C36-2	3-NMe_2, 6-NO_2	157.2	138.7	113.5	121.1	144.4	121.6	116.6	152.9	121.6	C	24
C37-1	3-NMe_2, 7-Br	157.9	138.3	114.4	127.7	129.4	122.7	117.2	148.4	116.8	C	24
C37-2	3-NMe_2, 7-OMe	159.1	136.1	119.0	126.7	112.3	159.7	100.3	151.4	114.1	C	24
C37-3	3-Ph, 7-OMe	160.5	124.7	139.8	128.7	112.6	162.5	100.3	155.2	113.2	C	61
C37-4	3-CH=CH-C(Me_2)OH (*trans*), 7-OMe	161.0	116.1	138.1	128.8	113.1	162.2	100.8	154.0		C	62
C37-5	3-C(Me_2)-CH=CH_2, 7-OH	159.2	131.2	138.6	129.0	113.4	161.1	102.6	154.7	112.8	C	41
C37-6	3-C(Me_2) C≡CH, 7-O-C(Me_2)CH=CH_2	158.1	132.7	137.6	128.0	117.1	158.1	106.6	154.3	114.3	C	41
C37-7	3-C(Me_2)-CH=CH_2 ,7-O-C(Me_2)CH=CH_2	159.8	132.0	137.7	127.9	117.3	158.7	106.5	154.0	113.8	C	41

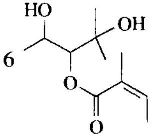
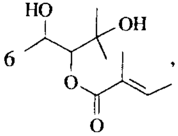
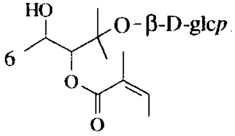
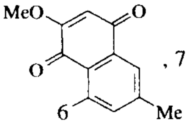
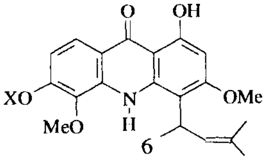
C37-8	3-C(Me$_2$)-CH=CH$_2$, 7-OMe		159.9	131.7	137.6	128.5	112.2	162.0	100.0	154.9	112.9	C	45,41
C37-9		X = NH	161.9	108.2	142.5	130.5	110.0	151.9	97.0	156.8	108.9	C/CCl	64
C37-10		X = NMe	159.8	111.4	146.0	130.0	109.4	151.8	97.4	157.7	108.8	C/CCl	64
C37-11		X = S	160.7	113.1	141.8	130.7	109.9	152.0	97.3	157.1	108.9	C/CCl	64
C38-1	3-NMe$_2$, 8-OMe		157.6	137.6	116.7	117.2	123.7	109.1	146.1	138.8	121.1	C	24
C38-2			208.7	141.0	130.5	129.0	126.9	135.0	131.3	140.8	129.3	C	12
C45-1	4-OH, 5-Me		161.8	91.4	168.8	137.2	127.1	131.6	114.8	155.1	114.4	D	65
C45-2	4-OMe, 5-Me		162.6	90.0	169.4	137.1	127.5	131.5	115.1	154.7	114.4	C	65
C45-3	4-O-β-D-glc*p*, 5-Me		161.3	93.0	166.6	137.1	127.8	132.0	114.8	154.4	113.8	D	65
C46-1	4-OH, 6-Me		162.1	91.1	165.6	122.8	133.0	133.4	116.1	151.7	115.5	?	65
C46-2	4-OMe, 6-Me		163.0	90.0	166.4	122.7	133.6	133.4	116.4	151.5	115.3	C	65
C46-3	4-OEt, 6-Me		162.5	90.3	165.6	122.8	123.7	133.8	116.6	152.9	115.8	C	32
C46-4	4-OPent^n, 6-Me		162.2	90.3	165.6	122.8	123.7	133.8	116.6	152.9	115.8	C	32
C46-5	4-OOct^n, 6-Me		162.5	90.3	165.6	122.8	123.7	133.9	116.6	152.9	115.8	C	32
C46-6	4-Me, 6-Br		163.3	115.0	154.3	127.4	121.5	135.2	118.9	151.6	118.0	C/TFA	66
C46-7	4-Me, 6-Cl		159.9	116.0	151.1	124.1	129.6	131.5	118.4	151.9	121.1	C	66
C46-8	4-Me, 6-OH		159.9	114.4	153.7	109.4	152.3	119.7	117.1	146.3	120.1	D	18
C47-1	4-OH, 7-OMe		162.4	88.7	166.1	124.4	111.7	163.1	100.6	155.6	109.2	D	27
C47-2	4,7-[OMe]$_2$		162.6	87.3	166.2	123.6	111.6	162.6	100.1	154.5	108.5	C	14
C47-3	4,7-[NEt$_2$]$_2$		163.7	90.3	160.0	126.0	107.5	149.8	98.0	156.6	104.9	C	67
C47-4	4-NHex^{cycl}, 7-NEt$_2$		164.4	80.1	152.7	121.3	107.8	150.4	98.2	155.9	102.5	C	67
C47-5	4-morpholino, 7-NEt$_2$		163.2	92.3	161.7	125.5	107.8	150.0	97.7	156.4	104.0		67
C47-6	4-Me, 7-OH		158.6	108.4	152.9	124.3	111.1	159.3	100.4	151.3	110.1	C	3,21
C47-7	4-Me, 7-OMe		161.1	111.6	152.6	125.4	112.0	162.4	100.7	155.1	113.3	C	38,66,68

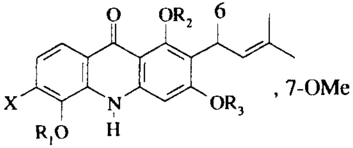
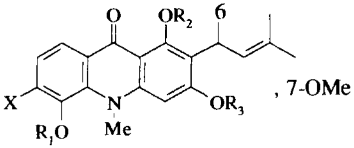
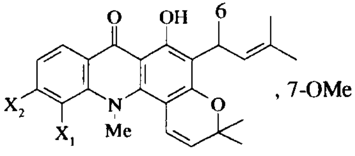
C47-8	4-Me, 7-OAc	160.4	118.1	151.9	125.4	117.8	154.2	110.4	153.1	114.5	C	68
C47-9	4-Me, 7-O-α-D-glc*p*	160.0	111.7	153.3	126.3	113.9	160.0	103.8	154.4		D	21
C47-10	4-Me, 7-O-β-D-glc*p*	160.3	111.9	153.4	126.4	113.6	160.3	103.5	154.5	114.3	D	21
C47-11	4-Me, 7-NH_2	160.4	108.1	152.2	124.9	110.6	151.4	99.1	155.1	110.1	C/CCl	64
C47-12	4-Me, 7-NEt_2	161.6	108.0	152.5	125.0	108.0	150.1	97.1	155.5	108.4	C	3,69
C47-13	4,7-Me_2	161.4	114.2	152.7	124.5	125.6	143.2	117.4	153.9	117.8	C	39
C47-14	4-CF_3, 7-OH	160.5	111.1	142.3	126.7	114.4	162.3	103.6	156.5	106.3	C/M	70
C47-15	4-CF_3, 7-NH_2	159.6	108.6	141.5	126.3	109.3	150.9	98.4	157.3	103.0	C/CCl	64
C47-16	4-CF_3, 7-NEt_2	159.7	108.2	141.5	126.1	109.2	151.1	98.0	157.2	102.6	C/CCl	64
C47-17	4-Ph, 7-OH	160.3	110.4	155.8	127.9	113.1	161.6	102.9	155.4	110.8	C/D	61,71
C47-18	4-Ph, 7-OMe	160.9	111.7	155.8	127.8	112.1	162.6	101.0	155.6	112.4	C	61
C47-19	4-Ph, 7-OAc	160.1	110.5	156.0	127.7	117.9	153.0	114.3	154.6	116.6	C	61
C48-1	4-OH, 8-Me	162.2	91.0	166.0	120.9	123.1	133.4	125.1	152.0	115.5	C	65
C48-2	4-OMe, 8-Me	162.9	89.8	166.8	120.6	123.4	133.6	126.2	151.7	115.4	C	65
C56-1	5,6-Me_2	161.1	116.0	140.9	134.2	132.8	133.7	114.3	153.4		C	39
C57-1	5-OX, 7-O  X = H, R^1 = OH, R^2 = H	162.5	110.4	139.1	154.5	97.7	162.0	98.4	156.7	103.3	C	51
C57-2	X = H, R^1 = OH, R^2 = OH	162.7	110.1	139.7	154.9	93.7	162.5	98.9	156.6	103.6	C	51
C57-3	X = Ac, R^1 = OAc, R^2 = OAc	161.9	113.0	137.4	147.7	106.7	160.6	99.5	156.0	106.3	C	51
C57-4	5,7-$[OMe]_2$	161.81	111.0	139.0	157.3	94.9	164.1	93.1	157.1	104.2	C	2,18,38
C57-5	5-CH_2-CH=C(Me)-CH_2-CH_2-CH=CMe_2, 7-OMe	161.3	110.4	138.7	156.0	95.5	163.5	92.5	156.5	104.0	C	6
C57-6	5-Me, 7-OMe	160.5	111.8	139.8	136.7	113.4	161.7	98.4	155.9	111.1	C	14
C58-1	5,8-$[OMe]_2$	159.4	114.7	138.2	149.5	103.7	114.9	141.3	144.7	110.2	CCl/C	2
C58-2	5-OMe, 8-OCH_2-CH=CMe_2	160.2	114.7	138.7	149.8	104.1	117.5	140.2	145.3	110.4	C	72
C58-3	5-CH_2-CH=CMe_2, 8-OMe	160.2	114.7	139.0	148.9	105.4	114.7	141.1	144.6	110.7	C	72
C58-4	5,8-Me_2	159.7	114.5	139.8	132.8	124.4	132.0	122.8	152.0	116.5	C	26
C67-1	6,7-$[OH]_2$	161.4	112.0	144.5	112.9	143.2	150.6	103.2	149.1	111.4	D	6,18,21
C67-2	6-OH, 7-OMe	160.6	112.5	144.1	111.8	143.3	151.6	99.9	148.2	111.5	D	73,74

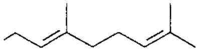
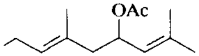
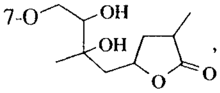
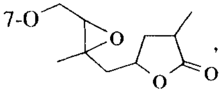
C67-3	6-OH, 7-O-β-D-glc*p*-(6←1)-β-D-apio*f*	160.6	112.7	144.0	113.4	143.4	148.6	103.2	147.7	113.0	D	75
C67-4	6-OMe, 7-OH	160.2	112.5	142.3	107.0	143.2	149.2	102.5	149.8	110.5	C	73,74,76
C67-5	6,7-[OMe]$_2$	160.7	113.5	142.8	108.0	146.2	152.8	99.9	150.0	111.2	C	2,18
C67-6	6-OMe, 7-OCH$_2$-CH=CMe$_2$	161.3	113.0	143.3	107.8	146.4	151.9	100.8	149.8	111.1	C	77
C67-7	6-OMe, 7-OCH$_2$-CHOH-C(Me$_2$)OH	162.1	114.2	144.1	108.1	146.9	152.2	101.7	150.2	112.4	C	78,79
C67-8		161.0	112.9	143.1	107.8	116.2	151.6	100.9	149.3	111.1	D	73
C67-9	6-OMe, 7-O-α-D-glc*p*	160.6	112.3	144.2	109.7	146.0	149.8	103.1	148.9	113.3	D	76,80
C67-10	6-OMe, 7-(2′-OAc)-O-α-D-glc*p*	160.8	114.6	143.5	111.0	147.5	151.3	105.9	149.8	113.9	P	80
C67-11	6-OMe, 7-(6′-OAc)-O-α-D-glc*p*	160.8	114.2	143.4	110.1	147.9	151.3	104.6	150.1	113.1	P	80
C67-12	6-OMe, 7-[2′,6′-(OAc)$_2$- O-α-D-glc*p*]	161.8	114.8	143.3	110.4	147.6	150.4	106.1	149.4	114.1	P	80
C67-13	6-OMe, 7-[3′,6′-(OAc)$_2$- O-α-D-glc*p*]	160.8	114.4	143.5	110.3	147.1	151.3	104.7	150.1	113.4	P	83
C67-14		160.5	112.5	144.3	109.0	146.1	151.6	101.1	149.3	111.1	D	81
C67-15	6-OMe, 7-O-β-D-glc*p*-(6←1)-β-D-apio*f*	160.6	112.4	144.2	109.8	146.0	149.8	103.2	149.0	113.4	D	76,82
C67-16	6-OMe, 7-O-β-D-glc*p*-(6←1)-β-D-apio*f* pentaacetate	160.7	115.1	142.8	109.8	147.3	149.1	107.1	149.5	114.0	C	76
C67-17	6-OMe, 7-O-β-D-glc*p*-(6←1)-β-D-apio*f* hexaacetate	160.6	115.0	142.7	109.7	147.3	148.9	105.8	149.2	114.1	C	76
C67-18	6-O-β- D-glc*p*, 7-OH	160.5	112.1	144.4	115.0	142.6	151.4	103.1	150.5	110.8	D	1,18,21,83
C67-19	6-O-β- D-glc*p*, 7-OMe	160.5	112.8	144.4	113.1	143.3	152.8	100.3	150.0	111.3	D	74
C67-20	6-O-β-D-glc*p*-(6←1)-β-D-apio*f*, 7-OMe	164.1	112.0	146.4	116.4	153.0	145.1	104.7	153.0	112.0	M	83
C67-21		160.1	113.1	143.1	108.0	146.5	149.6	101.0	151.7	111.1	C	84
C67-22	6-CH$_2$CH$_2$C(Me$_2$)OH, 7-OMe	161.9	113.3	143.9	128.2	128.9	161.3	99.0	155.0	112.4	C	85

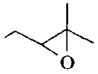
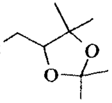
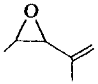
C67-23	6-CH_2-CH=CMe_2, 7-OH	162.0	112.7	143.7	128.4	129.0	158.5	103.3	153.5	112.8	C	86
C67-24	6-O  , 7-OH	161.6	113.1	143.9	126.9	132.1	158.7	105.3	154.6	112.4	C	87
C67-25	6-CO-CH=CMe_2, 7-OMe	157.4	113.9	143.3	130.3	128.2	160.8	99.6	156.7	112.1	C	77,88
C67-26	 , 7-OMe	159.9	114.6	143.1	131.3	123.3	162.0	99.8	158.7	112.7	C	77
C67-27	 , 7-OMe	160.5	113.9	143.3	130.4	122.3	160.7	99.6	157.3	112.2	C	88
C67-28	6-CH=CH-C(Me_2)OMe (*trans*), 7-OMe	162.5	113.8	143.8	125.0	124.2	160.4	99.0	155.7	112.6	C	85
C67-29	6-CH=CH-C(Me_2)OEt (*trans*), 7-OMe	162.5	113.4	144.2	125.6	124.0	160.3	99.3	155.5	112.6	C	85
C67-30	6-CH_2CHOH-C(Me_2)OH, 7-OMe	161.2	112.5	143.2	129.4	125.2	160.6	98.4	154.4	111.7	C	89
C67-31	6-CH_2CHOH-C(Me_2)OH, 7-O-β-D-glc*p*	163.5	114.1	145.8	131.3	128.9	160.1	103.9	155.5	114.8	M	90
C67-32	6-CH_2CHOAc-C(Me_2)OH, 7-O-β-D-glc*p* tetraacetate	160.7	114.5	142.8	130.4	124.1	157.0	96.8	154.4	113.4	C	90
C67-33	6-CH_2-CHOH-C(Me_2)OH, 7-O-β-D-glc*p*-(6←1)-β-D-apio*f*	163.8	114.1	146.0	131.2	128.9	160.2	104.2	155.5	114.8	M	90
C67-34	6-CH_2-CHOAc-C(Me_2)OH, 7-O-β-D-glc*p*-(6←1)-β-D-apio*f* hexaacetate	160.7	113.4	142.6	130.3	124.1	157.0	96.5	154.4	114.6	C	90
C67-35	 , 7-OH	162.9	111.2	144.6	127.8	126.4	158.9	102.7	153.8	111.8	C	44
C67-36	 , 7-OH	162.2	112.3	144.1	128.4	125.6	158.5	103.1	154.1	112.2	C	91

C67-37	 , 7-OH	162.2	112.2	144.1	128.3	125.6	158.5	103.1	154.1	112.2	C	91
C67-38	 , 7-OH	162.4	112.2	144.2	128.2	125.6	158.4	103.1	154.1	112.2	C	91
C67-39	 , 7-OMe	159.7	113.2	143.8	129.5	119.7	160.5	100.1	156.2	112.0	C	92
C67-40	 , 7-OMe	161.0	113.0	143.5	128.3	124.6	160.2	98.9	155.2	112.0	C	93
C67-41	 , 7-OMe	160.9	113.6	143.3	126.0	128.2	160.4	99.1	155.5	112.1	C	93
C67-42	 , 7-OMe	161.0	113.0	143.6	126.2	128.3	158.7	98.8	155.1	111.9	C	93
C67-43	 , 7-OMe	160.9	112.3	143.5	128.2	126.8	160.2	98.5	154.8	111.5	C	93

C67-44	, 7-OMe	161.3	112.9	143.6	126.5	127.2	159.1	98.5	155.2	111.8	C	93
C67-45	, 7-OMe	161.3	112.8	143.6	126.5	127.8	159.0	98.4	155.0	111.8	C	93
C67-46	, 7-OMe	160.2	112.4	143.9	126.6	128.0	159.3	98.2	155.2	111.6	A	94
C67-47	6-COOH, 7-CO-Pr^i	161.4	114.2	143.7	124.9	134.3	159.7	100.6	159.7	117.7	C/M	40
C67-48	6-COOEt, 7-OH	164.4	114.0	143.0	130.6	110.3	160.0	104.8	158.9	111.9	C	40
C67-49	, 7-OMe	163.3	113.2	143.4	127.3	127.1	161.3	98.9	155.9	112.2	C	95
C67-50	, 7-OMe X = H	161.5	113.1	143.8	127.3	129.1	160.7	99.2	154.7	112.1	C	96
C67-51	X = Me	161.2	113.1	143.6	127.3	129.1	160.8	99.2	154.8	112.0	C	97

C67-52	 , 7-OMe X = OH, R_1 = R_3 = Me, R_2 = H	161.8	113.6	145.6	131.5	111.6	147.3	99.7	155.8	112.9	C	97
C67-53	X = OMe, R_1 = R_3 = Me, R_2 = H		112.2	144.4	128.4	130.5	160.9	98.4	152.0	111.5	C	97
C67-54	 , 7-OMe X = H, R_1 = R_2 = R_3 = H	161.8	113.5	145.6	130.0	111.7	162.3	99.6	155.8	112.8	A	98
C67-55	X = OH, R_1 = Me, R_2 = R_3 = H	161.9	112.2	144.4	128.3	130.8	160.9	98.4	154.4	112.2	C	96
C67-56	X = OH, R_1 = R_3 = Me, R_2 = H	161.3	113.0	143.9	128.6	129.4	159.8	99.0	154.4	112.3	C	96
C67-57	X = OMe, R_1 = Me, R_2 = R_3 = H	161.3	113.8	144.6	129.2	130.5	160.3	98.9	154.9	112.2	C	97
C67-58	X = OMe, R_1 = R_3 = Me, R_2 = H	161.8	112.3	144.3	128.4	130.3	160.9	98.4	154.3	111.8	C	99
C67-59	 , 7-OMe X_1 = OH, X_2 = H	161.9	112.4	144.2	128.6	130.6	160.9	98.4	154.3	111.5	A	98
C67-60	X_1 = OMe, X_2 = OH	161.3	113.2	145.0	129.7	131.0	159.4	99.2	155.4	113.3	A	98
C67-61	6,7-Me_2	161.6	115.7	143.6	128.2	133.4	142.2	117.6	152.8	116.9	C	39
C68-1	6,8-Me_2	159.8	115.0	142.8	124.6	132.6	133.3	124.6	149.6	117.4	C	26
C68-2	6-Et, 8-Me	161.3	116.2	143.9	124.2	140.0	133.3	126.0	150.7	118.5	C	5
C78-1	7-OH, 8-I	162.7	112.8	145.8	112.9	130.4	163.1	74.2	156.8	113.8	M	40
C78-2	7-OCH_2Ph, 8-I	160.4	114.0	143.0	129.0	109.0	160.7	76.8	155.1	113.8	C	100

C78-3	7-OC(Me$_2$)-C≡CH, 8-I	159.3	114.5	143.0	114.5	128.0	160.4	81.3	155.0	114.5	C	40
C78-4	7,8-[OH]$_2$	161.1	111.7	145.4	119.4	113.0	150.0	132.6	144.2	112.7	D	21
C78-5	7-OH, 8-OMe	160.0	111.4	144.7	123.6	113.4	153.9	134.2	148.1	112.2	D	74
C78-6	7,8-[OMe]$_2$	159.7	113.5*	143.1	122.4	108.3*	155.4	136.3	148.1	113.7	C/CCl	2
C78-7	7-OH, 8-O-β-D-glc*p*	160.1	113.5	144.8	124.2	111.7	153.4	131.4	144.8	112.3	D	18
C78-8	7-OMe, 8-OCH$_2$-CH=CMe$_2$	160.5	113.3	143.6	122.7	108.3	156.0	134.9	148.4	113.6	C	72
C78-9	7-OCH$_2$-CH=CMe$_2$, 8-OMe	160.6	113.3	143.6	122.6	110.0	154.9	136.5	148.6	113.6	C	72
C78-10	7-OCH$_2$-CH=CMe$_2$, 8-CH$_2$CO-Pr^i	160.0	113.4	143.9	127.2	114.9	159.5	108.4	153.3	112.7	C	46
C78-11	7  , 8-OMe	159.7	112.6	144.4	123.3	110.4	154.3	135.4	147.3	112.6	?	101
C78-12	7  , 8-OMe	160.3	113.3	143.3	122.2	109.8	154.6	137.1	147.9	113.5	?	101
C78-13	 , 8-OMe	160.3	113.5	144.5	123.8	110.6	155.9	136.7	148.6	114.3	A	43
C78-14	 , 8-OMe	160.3	113.4	143.5	122.7	110.1	154.2	136.3	147.9	114.0	C	43
C78-15	7-O-β-D-glc*p*, 8-OH	160.1	113.4	144.7	118.3	114.5	148.2	134.0	144.7	112.3	D	18
C78-16	7-OMe, 8-CH$_2$-CH$_2$-Pr^i	161.3	112.8	143.7	125.9	107.1	160.3	119.3	152.8	112.8	C	89
C78-17	7-OMe, 8-CH$_2$-CH$_2$-C(Me$_2$)OH	161.3	112.6	143.7	126.1	107.2	160.1	118.6	152.7	112.7	C	89
C78-18	7-OMe, 8-CH$_2$-C(Me$_2$)-CH$_2$-CHO	160.7	112.9	143.6	127.3	107.2	160.3	114.7		113.9	C	89
C78-19	7-OH, 8-CH$_2$-CH=CMe$_2$	162.1	112.1	144.5	126.5	113.2	158.5	115.0	153.1	112.6	C	40
C78-20	7-OMe, 8-CH$_2$-CH=CMe$_2$	160.9	112.4	143.5	126.0	107.1	159.9	117.4	152.4	112.6	C	1,6,41,44
C78-21	7-OAc, 8-CH$_2$-CH=CMe$_2$	160.4	119.0	143.3	125.7	115.8	161.8	116.8	151.4	111.8	C	41
C78-22	7-OC(Me$_2$)-C≡CH, 8-CH$_2$-CH=CMe$_2$	160.3	115.3	143.2	126.0	113.2	161.2	116.0	152.5	112.2	C	41
C78-23	7-OH, 8-CH$_2$-CH=C(Me)CH$_2$OH (*E*)	160.6	111.0	144.9	126.8	112.3	158.8	114.5	153.1	111.4	D	103
C78-24	7-OH, 8-CH$_2$-CH=C(Me)-O-β-D-glc*p* (*E*)	163.8	111.8	146.4	127.8	113.5	160.4	116.0	154.6	113.2	M/C	103

C78-25	7-O-β-D-glc*p*, 8-CH_2-CH=C(Me)CH_2OH (*E*)	163.2	113.0	146.0	128.0	115.4	159.7	119.5	153.9	114.0	M	103
C78-26	7-OMe, 8-CH_2-CHOH-C(Me)=CH_2	161.1	113.1	143.8	127.0	107.3	160.6	115.0	153.5	112.2	C	40
C78-27	7-OMe, 8-CH_2-CHOAc-C(Me)=CH_2	160.9	113.1	143.7	127.2	107.2	159.0	114.4	153.7	112.8	C	40,240
C78-28	7-OH, 8-CH_2-CHOH-C(Me_2)OH	163.8	111.9	146.5	128.2	114.2	161.3	115.5	155.1	113.4	M	104
C78-29	7-OMe, 8-CH_2-CHOH-C(Me_2)OH	163.8	112.7	143.9	126.8	107.4	160.5	115.8	153.3	113.0	C	40,89,104
C78-30	7-OMe, 8-CH_2-CHOAc-C(Me_2)OH	160.6	112.2	143.6	126.8	106.8	160.2	114.1	152.8	112.2	C	89
C78-31	7-OAc, 8-CH_2-CHOAc-C(Me_2)OH	161.3	113.5	144.2	127.4	112.2	158.8	125.7	153.7	112.3	C	40,104
C78-32	7-OAc, 8-CH_2-CHOAc-C(Me_2)OAc	161.0	113.4	144.0	127.4	112.3	158.8	126.7	153.5	115.8	C	40
C78-33	7-OMe, 8 	160.7	112.7	143.5	127.0	107.2	160.5	113.9	153.1	112.6	C	89
C78-34	7-OMe, 8 	160.7	113.2	143.7	127.0	107.5	161.0	115.0	153.4	112.4	C	40
C78-35	7-OH, 8-CH_2-CHOH-C(Me_2)-O-β-D-glc*p*	163.9	111.9	146.5	128.3	114.3	155.1	115.5	161.1	113.5	M	104
C78-36	7-OAc, 8-CH_2-CHOAc-C(Me_2)-O-β-D-glc*p* tetraacetate	159.9	115.5	143.2	126.3	118.8	152.1*	119.3	153.5*	116.3	C	104
C78-37	7-OMe, 8-CH_2-CO-Pr^i	161.0	113.0	143.8	127.5	107.2	160.4	113.0	153.2	112.0	C	40,105
C78-38	7-OCH_2-CHOH- C(Me_2)Cl, 8-CH_2-CO-Pr^i	160.8	113.4	143.8	127.8	108.6	159.6	113.4	153.2	112.0	C	105
C78-39	7-OMe, 8-CHOH-CHOH-C(Me)=CH_2 (*threo*)	160.3	113.4	143.8	128.4	108.0	160.6	116.6	153.4	113.3	C	106
C78-40	7-OMe, 8 	161.6	113.0	143.2	128.8	107.4	160.0	112.2	153.6	112.5	C	89,106

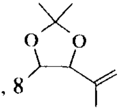
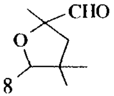
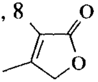
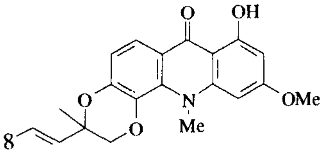
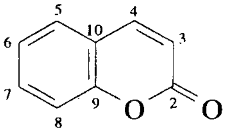
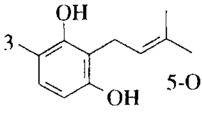
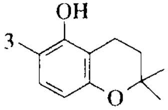
C78-41	7-OMe, 8 	160.5	113.2	143.2	129.1	108.2	160.8	109.6	154.4	112.4	C	106
C78-42	7-OH, 8-CHOH-CHOH-C(Me_2)OH	163.3	111.9	145.3	129.0	111.7	160.8	117.8	153.0	117.0	A	100
C78-43	7-OCH_2Ph, 8-CHOH-CHOH-C(Me_2)OH	160.1	113.5	143.8	129.0	109.5	159.5	117.4	152.9	113.6	C	100
C78-44	7-OMe, 8 	160.1	113.3	143.5	129.2	108.2	160.9	113.1	153.5	112.2	C	106
C78-45	7-OMe, 8-CHO	159.7	114.1	143.0	134.1	108.2	163.3	114.1	156.9	113.3	C	106
C78-46	7-OCH_2Ph, 8-CH=CH-C(Me_2)OH (*trans*)	160.9	113.3	144.9	127.2	109.2	159.3	71.6(?)	152.7	113.2	C	100
C78-47	7-OMe, 8-CH(CHO)=CMe_2	160.9	112.9	143.6	128.5	107.5	159.4	113.1	153.0	113.0	C	106,107
C78-48	7-OMe, 8 	160.4	113.2	143.6	129.8	108.0	160.7	107.0	152.9	113.0	C	92
C78-49	7-OH, 8 	160.0	113.0	144.9	128.3	113.4	160.0	109.7	152.8	111.0	D	99

Table 8. ^{13}C chemical shifts of trisubstituted coumarins

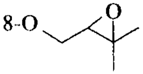


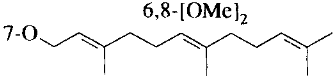
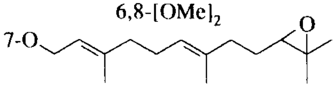
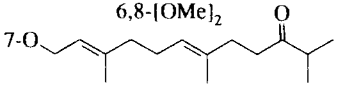
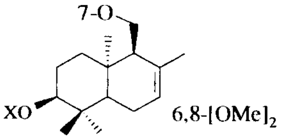
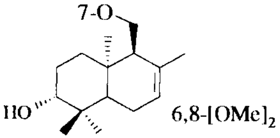
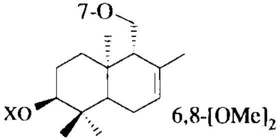
	Substituents	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Solv.	Reference
D345-1	3-Br, 4-OH, 5-Me	158.1	89.3	164.5	137.1	127.8	131.7	114.7	153.1	114.4	D	65
D345-2	3-OC(Me)=CH_2, 4-OH, 5-Me	158.8	101.0	181.7	140.6	127.5	135.3	114.7	155.4	113.6	D	65
D345-3	3-NO_2, 4-OH, 5-Me	156.8	121.8	169.6	139.9	126.9	131.7	114.8	154.0	119.0	D	65
D345-4	3-CH_2Ph, 4,5-[OH]$_2$	162.5	102.4	162.6	154.6	110.2	132.1	107.9	153.1	103.8	D	7
D346-1	3-Br, 4-OH, 6-Me	158.5	89.3	162.0	122.8	133.4	133.6	116.0	149.7	115.3	D	65
D346-2	3-OC(Me)=CH_2, 4-OH, 6-Me	158.5	101.0	177.6	124.1	133.9	137.2	116.2	152.2	114.1	D	65
D346-3	3-NO_2, 4-OH, 6-Me	157.0	121.3	165.2	125.3	133.3	134.3	116.4	150.7	119.2	D	65
D347-1	3-Cl, 4-OH, 7-OMe	158.9	96.4	160.7	124.6	112.3	162.9	100.6	153.0	109.1	D	27
D347-2	3-OPh, 4-OH, 7-OMe	159.0	118.3	156.2	124.8	112.4	162.5	100.7	152.9	109.6	D	27
D347-3	3-Me, 4-OH, 7-OMe	163.8	97.7	160.4	124.1	111.5	162.0	100.2	153.5	109.7	D	27
D347-4	3-CH_2CH_2COOEt, 4-Me, 7-OH	160.6	115.1	149.5	126.8	112.6	160.6	101.9	153.4	112.1	C or D	68
D347-5	3-CH_2CH_2COOEt, 4-Me, 7-OMe	161.7	121.4	147.4	125.7	112.2	161.9	100.6	153.8	114.0	C	68
D347-6	3-CH_2CH_2COOEt, 4-Me, 7-OAc	160.2	122.1	146.7	125.4	117.9	161.1	110.0	152.6	124.1	C	68
D347-7	3-CH_2COOEt, 4-Me, 7-OH	160.9	115.0	145.6	126.8	113.0	160.7	102.0	153.4	112.1	C or D	68
D347-8	3-CH_2COOEt, 4-Me, 7-OMe	160.7	115.8	139.3	126.5	112.1	161.8	100.4	153.2	112.1	C	68
D347-9	3-CH_2COOEt, 4-Me, 7-OAc	161.1	126.0	148.4	125.6	119.3	153.0	110.2	152.7	118.1	C	68
D347-10	3-CH_2Ph, 4-OH, 7-OMe	163.3	101.8	160.9	124.5	111.6	162.3	100.5	153.9	109.5	D	27
D347-11	3-Ph, 4-OH, 7-OMe	162.2	103.7	160.6	124.9	111.7	162.7	100.4	154.2	109.6	D	27
D348-1	3-Br, 4-OH, 8-Me	158.4	89.0	162.4	121.1	123.8	133.7	125.7	150.0	115.6	D	65
D348-2	3-OAc, 4-OH, 8-Me	158.5	100.7	177.6	122.3	123.7	137.0	125.5	152.1	114.1	D	65
D348-3	3-NO_2, 4-OH, 8-Me	156.5	121.3	164.5	123.4	123.9	135.1	125.7	150.9	118.3	D	65

D357-1	 5-OCH$_3$, 7-OH	163.6	121.9	138.6	158.6	96.4	163.0	95.5	156.8	104.8	C	108
D357-2	 5-OCH$_3$, 7-OH	163.5	121.3	139.0	158.9	96.6	163.5	95.8	157.1	104.9	C	108
D367-1	3-C(Me$_2$)-CH=CH$_2$,, 6,7-[OMe]$_2$	160.1	132.2	137.3	108.3	146.3	149.2	99.5	152.2	111.8	C	45
D367-2	3-C(Me$_2$)-CH=CH$_2$, 6-CH$_2$CHO, 7-OMe	160.0	132.5	137.4	129.6	130.0	159.8	98.5	154.8	112.6	C	109
D367-3	3-C(Me$_2$)-CH=CH$_2$, 6-CH$_2$-CH=CMe$_2$, 7-OMe	160.2	131.5	137.9	127.3	127.1	159.9	97.8	153.6	112.3	D	45
D367-4	3-C(Me$_2$)-CHO, 6-CHO, 7-OH	164.2	130.0	134.4	138.3	136.0	164.2	104.8	164.2	118.4	C	86
D367-5	3-CH=CH-Pr^i (*trans*), 6-CH$_2$-CH=CMe$_2$, 7-OH	161.1	131.0	138.6	128.1	125.4	157.5	102.5	153.2	112.6	C	86
D368-1	3,6,8-Br$_3$	154.9	112.8	143.1	129.2	121.6	136.2	116.4	148.4	109.9	D	4
D368-2	3-NMe$_2$, 6,8-Cl$_2$	157.0	138.7	113.3	123.2	129.3	126.6	121.4	143.8	123.3	C	27
D378-1	3-C(Me$_2$)-CH=CH$_2$,, 7,8-[OMe]$_2$	158.8	131.6	137.6	122.6	108.4	146.6	135.1	154.2	113.7	C	110
D378-2	3-C(Me$_2$)-CH=CH$_2$,, 7-OH, 8-CH$_2$-CH=CMe$_2$	160.1	132.6	138.4	126.4	112.9	157.4	114.7	153.6	112.9	C	41
D378-3	3-C(Me$_2$)-CH=CH$_2$, 7-OMe, 8-CH$_2$-CH=CMe$_2$	160.3	132.9	137.9	125.8	107.1	157.2	117.1	152.5	113.2	C	41
D378-4	3-C(Me$_2$)-CH=CH$_2$, 7-OAc, 8-CH$_2$-CH=CMe$_2$	160.2	133.1	137.5	125.5	118.6	159.4	117.2	150.4	112.3	C	41
D378-5	3-C(Me$_2$)-CH=CH$_2$, 7-OC(Me$_2$)-C≡CH, 8-CH$_2$-CH=CMe$_2$	160.2	132.0	137.9	124.9	114.6	159.3	114.3	155.7	112.1	C	41
D456-1	4-OH, 5-Me, 6-Cl	160.5	92.1	167.5	133.8	129.6	131.9	115.7	153.5	114.9	D	65
D457-1	4,7-[OH]$_2$, 5-Me	162.2	88.2	169.1	138.6	115.6	160.3	100.5	157.1	106.6	D	65
D457-2	4,7-[OMe]$_2$, 5-Me	162.7	87.4	169.3	138.2	115.4	161.6	98.6	156.3	107.6	C	14
D457-3	4-Me, 5,7-[OH]$_2$	161.0	108.8	156.4	160.0	99.0	157.8	94.4	154.9	102.0	D	68
D457-4	4-Me, 5,7-[OMe]$_2$	160.3	111.4	154.7	159.5	95.5	163.1	93.6	154.3	105.1	C	38,68

D457-5	4-Me, 5,7-[OEt]$_2$	161.5	111.4	154.9	158.7	96.4	162.5	94.0	157.3	104.9	C	38
D457-6	4-Me, 5,7-[OAc]$_2$	160.3	112.2	151.6	159.2	108.2	155.5	100.7	148.6	112.2	C	68
D457-7	4,7-Me$_2$, 5-OMe	161.3	113.6	154.5	158.2	107.5	143.4	110.4	155.6	108.5	C	38
D457-8	4-CF$_3$, 5,7-[OH]$_2$	161.3	109.9	141.8	155.9	98.9	162.2	95.6	157.2	97.7	C/M	70
D457-9	4-CF$_3$, 5,7-Me$_2$	158.4	116.4	140.5	135.4	130.8	143.4	116.1	155.7	110.6	C/M	70
D457-10	4-Ph, 5,7-[OH]$_2$	159.8	110.1	155.9	157.0	99.1	161.6	94.8	156.7	100.5	D	111,112
D457-11	4-Ph, 5-OMe, 7-OH	159.6	110.8	155.4	158.3	96.4	162.1	95.7	156.5	101.3	D	112
D457-12	4-Ph, 5-OH, 7-OMe	159.7	111.2	155.7	156.9	98.0	162.8	92.9	156.7	101.7	D	112
D457-13	4-Ph, 5,7-[OMe]$_2$	159.4	111.8	155.1	158.0	95.0	163.2	93.9	156.5	102.5	D	112
D457-14	4-(*p*-OH-Ph), 5,7-[OH]$_2$	159.8	109.5	156.0	156.9	99.1	161.2	94.5	156.6	100.5	D	112
D457-15	4-(*p*-OMe-Ph), 5,7-[OH]$_2$	159.7	109.7	155.5	156.9	99.1	161.3	94.5	156.5	100.5	D	112
D457-16	4-(*p*-OH-Ph), 5,7-[OMe]$_2$	159.4	111.2	155.1	157.9	95.7	162.8	93.6	156.4	102.6	D	112
D457-17	4-(*p*-OMe-Ph), 5,7-[OMe]$_2$	159.4	111.5	154.9	157.9	95.8	163.0	93.7	156.4	103.3	D	112
D457-18	4-(*o*,*m*′-[OH]$_2$-Ph), 5-OH, 7-OMe	162.6	110.6	157.0	156.8	92.9	159.8	98.2	156.1	102.1	C/D	113
D457-19	4-(*m*,*p*-[OH]$_2$-Ph), 5,7-[OMe]$_2$	159.7	111.3	155.5	158.2	95.8	163.0	93.7	156.7	103.0	D	112
D457-20	4-(*m*-OMe, 4′-OH-Ph), 5,7-[OH]$_2$	159.8	109.7	155.8	156.9	99.3	161.2	94.6	156.7	100.8	D	112
D457-21	4-(*m*-O-CH$_2$-O-4′-Ph), 5,7-[OH]$_2$	159.8	109.8	155.3	156.7	99.0	161.3	94.5	156.5	100.5	D	112
D457-22	4-(*m*-OMe, 4′-OH-Ph), 5,7-[OMe]$_2$	159.6	111.1	155.2	158.1	95.4	163.0	93.3	156.5	102.3	D	112
D457-23	4-(*m*-OH, 4′-OMe-Ph), 5,7-[OMe]$_2$	159.6	111.2	155.1	158.1	95.9	163.0	93.8	156.5	102.8	D	112
D457-24	4-(*m*,*p*-[OMe]$_2$-Ph), 5,7-[OMe]$_2$	159.6	110.7	155.1	158.1	95.9	163.2	93.8	156.6	102.7	D	112
D457-25	4-(*m*-O-CH$_2$-O-4′-Ph), 5,7-[OMe]$_2$	159.2	111.6	154.4	157.9	95.9	163.0	93.8	156.3	102.8	D	112
D457-26	4-(*m*,*p*-[OH]$_2$-Ph), 5-O-β-D-glc*p*, 7-OH	163.6	112.3	158.3	158.1	98.1	163.2	101.1	157.3	104.5	M	114
D457-27	4-(*m*,*p*-[OH]$_2$-Ph), 5-O-β-D-glc*p*, 7-OMe	163.0	113.2	158.0	158.0	96.7	165.0	100.0	157.2	105.5	M	114
D457-28	4-(*m*,*p*-[OH]$_2$-Ph), 5-O-β-D-gal*p*, 7-OMe	159.5	112.2	156.3	155.4	98.5	162.7	95.2	156.0	103.3	D	115
D457-29	4-(*m*,*p*-[OH]$_2$-Ph), 5-O-β-D-glc*p*-(6←1)-β-D-xylo*p*, 7-OMe	162.9	113.3	158.1	158.1	96.6	165.0	100.6	157.1	105.8	M	114
D457-30	4-(*m*,*p*-[OH]$_2$-Ph), 5-O-β-D-glc*p*-(6←1)-apio*f*, 7-OH	163.5	112.3	158.3	158.1	98.7	163.3	101.1	157.3	105.1	M	114
D458-1	4,8-[OMe]$_2$, 5-Me	161.8	90.2	169.2	127.5	126.4	113.5	145.7	144.5	114.9	C	31
D467-1	4-OH, 6-Cl, 7-Me	161.4	91.0	164.3	122.3	128.3	140.3	118.3	151.8	114.9	D	65

D467-2	4-Me, 6,7-[OH]$_2$	160.8	110.6	153.0	109.6	142.8	150.2	102.9	148.0	111.9	D	21
D467-3	4-Me, 6-OH, 7-OMe	159.9	110.9	152.2	109.0	143.2	151.2	99.8	147.4	112.2	D	74
D467-4	4-Me, 6,7-[OMe]$_2$	161.4	112.2	152.4	105.3	146.2	152.7	100.0	149.4	112.1	C	74,68
D467-5	4-Me, 6,7-[OAc]$_2$	160.1	115.1	151.2	118.8	138.7	151.5	112.2	144.6	118.2	C	74
D467-6	4-CF$_3$, 6,7-[OH]$_2$	161.0	111.1	142.5	109.0	143.2	151.1	103.5	149.9	105.9	C/M	70
D467-7	4-Ph, 6-OH, 7-OMe	160.3	111.3	135.5	111.3	148.3	143.6	111.3	110.5	151.9	D	111
D467-8	4-Pr^i, 6-Me, 7-OH	161.7	107.3	160.5	126.1	122.9	162.5	102.6	154.7	111.1	P	116
D467-9	4-Pr^i, 6-Me, 7-OMe	160.6	107.9	153.2	124.9	123.5	162.2	98.8	151.8	111.6	C	116
D467-10	4-C(Me$_2$)-CH=CH$_2$, 6-CH$_2$CH$_2$OH, 7-OMe	160.1	131.7	137.8	124.1	127.0	159.6	98.1	153.9	112.4	C	109
D467-11	4,6-Me$_2$, 7-NEt	161.9	109.1	152.6	125.0	118.4	149.6	96.1	154.8	109.5	C/CCl	64
D467-12	4,6,7-Me$_3$	161.6	114.2	152.6	125.0	133.1	141.9	117.8	152.2	117.9	C	39
D478-1	4-Me, 7,8-[OH]$_2$	160.7	110.5	154.1	115.7	112.6	149.6	132.5	143.6	113.3	C	21
D478-2	4-Me, 7,8-[OMe]$_2$	160.6	112.4	147.8	119.5	108.1	155.4	136.3	152.6	114.6	C or D	68
D478-3	4-Me, 7,8-[OAc]$_2$	159.2	114.8	145.3	121.7	118.6	151.9	130.5	146.8	114.9	C	68
D478-4	4,8-Me$_2$, 7-OH	160.8	110.1	153.1	122.5	111.8	159.1	111.1	153.1	112.0	C	117
D478-5	4-CF$_3$, 7,8-[OH]$_2$	160.3	110.7	142.7	116.5	113.2	150.3	132.5	143.7	106.6	C/M	70
D478-6	4-CF$_3$, 7-OH, 8-Me	160.0	110.9	140.7	123.3	112.9	160.6	113.1	154.3	106.5	C/M	70
D567-1	5-OH, 6-OMe, 7-OCH$_2$-CHOH-C(Me$_2$)OH	161.3	111.6	138.8	146.1	131.8	154.7	93.0	151.6	103.2	C	79
D567-2	5,6-[OMe]$_2$, 7-OCH$_2$-CHOH-C(Me$_2$)OH	168.2	114.1	137.4	160.4	138.3	155.4	99.1	150.9	107.3	C	79
D567-3	5-OAc, 6-OMe, 7-OCH$_2$-CHOAc-C(Me$_2$)OH	161.1	112.9	138.6	146.9	136.6	155.9	96.8	151.4	107.8	C	79
D567-4	5,7-[OMe]$_2$,6-O-β-D-gal*p*	164.8	109.4	142.3	146.2	139.2	158.0	98.2	151.9	112.5	M	120
D567-5	5,7-[OMe]$_2$, 6-CH=CH-Ac (*trans*)		111.4	138.5							C	121
D567-6	5,7-[OH]$_2$, 6-β-D-glc*p*	160.4	109.2	139.4	153.7	102.2	154.9	94.6	159.9	108.6	D	118
		154.0	107.9	139.0	159.9	108.2	159.9	93.8	154.4	104.2	D	119
D567-7	5-CH=CH-Ac (*trans*), 6,7-[OMe]$_2$		113.9	140.2				101.4			C	121

D578-1	5,7-[OMe]$_2$, 8-OAc	163.5	113.9	138.5	156.4	100.5	164.3	139.2	155.7	110.5	C	40
D578-2	5-OH, 7-OMe. 8-O-α-D-glc*p*	160.1	109.8	139.5	150.1	95.3	155.5	124.4	147.8	102.3	D	122
D578-3	5,7-[OMe]$_2$, 8-CH$_2$CH$_2$-Pr^i	161.4	110.9	138.6	155.5	90.6	161.3	109.8	154.3	104.3	C	106
D578-4	5,7-[OMe]$_2$, 8-CH=CH-Pr^i	161.0	110.9	138.8	155.2	90.5	161.4	107.6	153.5	103.8	C	106
D578-5	5,7-[OMe]$_2$, 8-CH=CHAc	161.2	110.8	138.9	155.0	90.6	161.3	108.5	154.8	104.2	C	106,121
D578-6	5-OMe, 7-OH, 8-CH$_2$-CHOH-C(Me)=CH$_2$	161.4	110.8	138.8	147.3	90.3	155.7	113.2	154.2	107.0	C	40
D578-7	5,7-[OMe]$_2$, 8-CH$_2$-CHOH-C(Me)=CH$_2$	161.2	110.9	138.8	155.8	90.3	161.4	107.3	147.3	113.2	C	40
D578-8	 5,7-[OMe]$_2$	161.1	110.5	138.6	155.7	90.2	161.2	106.0	153.9	103.5	C	6,106
D578-9	5,7-[OMe]$_2$, 8-CH$_2$-CHOH-C(Me$_2$)OH	161.2	111.0	138.8	155.8	90.4	161.2	107.5	154.0	104.2	C	106
D578-10	5,7-[OMe]$_2$, 8-CH$_2$-CHOAc-C(Me$_2$)OEt	161.4	110.7	138.7	156.8	90.3	159.3	107.4	151.2	104.0	C	40
D578-11	5,7-OMe, 8-CH$_2$CO-Pr^i	161.8	110.9	138.8	156.5	90.4	161.7	103.8	156.2	104.1	C	40,106
D578-12	5,7-[OH]$_2$, 8-CH$_2$-CH=C(Me)-CH$_2$CH$_2$CH=CMe$_2$	160.1	110.1	140.0	152.5	108.3	155.4	98.9	155.1	103.3	A	124
D578-13	5-CH=CH-Ac (*trans*), 7,8-[OMe]$_2$		114.4	139.0		106.4					C	121
D678-1	6,7,8-[OH]$_3$	161.4	112.0	144.5	103.5	143.5	137.5	132.0	139.1	112.0	?	125
D678-2	6-OMe, 7,8-[OH]$_2$	159.8	111.4	144.9	100.0	144.7	138.8	132.3	138.3	110.0	D	78
D678-3	6-OMe, 7-OCH$_2$-CH=CMe$_2$, 8-OH	160.2	114.4	144.7	100.2	150.1	139.0	137.4	138.8	114.3	D	78
D678-4	6,8-[OMe]$_2$, 7-OCH$_2$-CH=CMe$_2$	160.6	115.1	143.5	103.6	144.9	150.7	143.0	141.8	114.4	C	77
D678-5	6-OMe,	159.3	113.8	143.8	99.8	149.2	137.9*	137.9	140.4*	113.8	D	78
	7-OCH$_2$-CH=CMe-CH$_2$OH (*E*), 8-OH	159.3	113.8	143.8	99.8	143.8	140.4*	137.9	137.9*	113.8	D	128
D678-6	6-OMe, 7-O-β-D-glc*p*, 8-OH	160.0	115.0	144.4	100.9	149.4	138.2	137.2	138.4	115.0	D	78

D678-7			160.4	115.1	143.3	103.8	150.7	145.8	141.9	143.1	114.4	C	123
D678-8			160.5	115.3	143.5	103.8	150.7	145.1	141.9	143.2	114.5	C	123
D678-9			160.5	115.2	143.5	103.9	150.7	145.3	141.9	143.1	114.5	C	123
D678-10		X = H	160.4	115.2	143.5	104.1	150.6	145.3	141.8	143.2	114.6	C	123
D678-11		X = Ac	160.4	115.3	143.4	104.2	150.6	145.4	141.7	143.4	114.6	C	123
D678-12			160.4	115.2	143.3	104.1	150.5	145.4	141.7	143.2	114.5	C	123
D678-13		X = H	160.4	114.9	143.4	104.1	150.5	145.5	141.6	143.2	114.3	C	123
D678-14		X = Ac	160.3	115.3	143.4	104.2	150.6	145.6	141.7	143.4	114.5	C	123

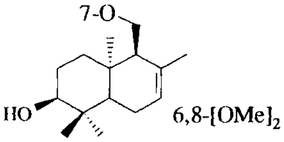
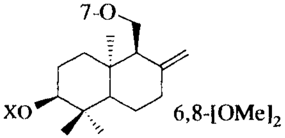
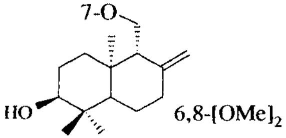
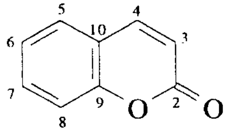
D678-15			160.4	115.4	143.3	104.3	150.6	145.4	141.7	143.4	114.6	C	126
D678-16		X = H	160.5	115.3	143.3	104.1	150.7	145.6	141.7	143.4	114.5	C	123
D678-17		X = Ac	160.4	115.3	143.3	104.2	150.6	146.0	141.6	143.3	114.5	C	123,126
D678-18			160.3	115.0	143.4	104.0	150.5	145.6	141.5	143.0	114.4	C	123,126

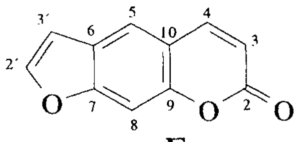
Table 9. ^{13}C chemical shifts of tetra- and pentasubstituted coumarins



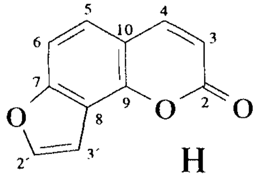
	Substituents	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	Solv.	Reference
E3457-1	3,5-Me_2, 4,7-$[OMe]_2$	164.3	109.9	166.8	137.1	115.8	161.2	98.8	155.4	115.8	C	127
E3457-2	3-CH_2COOEt, 4-Me, 5,7-$[OH]_2$	160.7	113.0	151.2	160.4	99.4	157.7	94.2	154.8	102.2	D	68
E3457-3	3-CH_2COOEt, 4-Me, 5,7-$[OMe]_2$	158.9	115.4	151.1	162.0	95.8	161.4	93.2	155.2	105.3	C	68
E3457-4	3-CH_2COOEt, 4-Me, 5,7-$[OAc]_2$	160.1	120.5	147.2	153.6	113.8	151.6	108.2	147.9	111.9	C	68
E3457-5	3-CH_2CH_2COOEt, 4-Me, 5,7-$[OH]_2$	160.5	117.4	149.7	159.9	99.3	157.4	94.1	154.7	102.3	D	68
E3457-6	3-CH_2CH_2COOEt, 4-Me, 5,7-$[OMe]_2$	159.9	120.2	149.5	161.9	95.7	161.4	93.1	155.3	105.4	C	68
E3457-7	3-CH_2CH_2COOEt, 4-Me, 5,7-$[OAc]_2$	159.3	124.7	145.5	152.6	114.4	151.1	108.0	147.7	111.8	C	68
E3458-1	3,4,8-$[OMe]_3$, 5-Me	159.4	130.5	157.6	127.3	126.9	112.0	145.5	141.0	116.9	C	31
E3467-1	3-$[OMe]_2$, 4-Pr^i, 6-Me, 7-OH	158.8	139.1	151.5	126.4	123.0	158.9	102.6	146.2	111.5	P	116
E3467-2	3-CH_2COOEt, 4-Me, 6,7-$[OH]_2$	161.2	115.1	146.3	109.8	142.3	149.6	102.4	149.1	111.7	D	68
E3467-3	3-CH_2COOEt, 4-Me, 6,7-$[OMe]_2$	161.9	116.9	148.8	105.7	146.8	152.4	100.0	148.2	112.9	C	68
E3467-4	3-CH_2COOEt, 4-Me, 6,7-$[OAc]_2$	150.8	119.5	150.1	119.1	138.8	150.1	112.1	147.7	118.6	C	68
E3467-5	3-CH_2CH_2COOEt, 4-Me, 6,7-$[OH]_2$	161.0	119.5	146.1	109.1	142.7	149.2	102.3	147.6	111.8	D	68
E3467-6	3-CH_2CH_2COOEt, 4-Me, 6,7-$[OMe]_2$	161.8	121.9	147.2	105.7	146.1	152.0	99.9	147.9	113.0	C	68
E3467-7	3-CH_2CH_2COOEt, 4-Me, 6,7-$[OAc]_2$	160.0	124.9	146.4	118.7	138.7	149.8	111.7	143.9	119.1	C	68
E3478-1	3-CH_2COOEt, 4-Me, 7,8-$[OH]_2$	160.8	112.8	142.0	115.6	112.2	149.9	131.9	148.9	114.9	D	68
E3478-2	3-CH_2COOEt, 4-Me, 7,8-$[OMe]_2$	161.0	116.5	146.4	119.6	108.0	154.7	135.8	149.0	114.8	C	68
E3478-3	3-CH_2COOEt, 4-Me, 7,8-$[OAc]_2$	159.2	119.2	145.6	121.9	118.6	148.4	130.3	144.8	119.7	C	68
E3478-4	3-CH_2CH_2COOEt, 4-Me, 7,8-$[OH]_2$	160.6	119.3	141.9	115.4	112.0	148.3	137.9	148.3	113.1	D	68
E3478-5	3-CH_2CH_2COOEt, 4-Me, 7,8-$[OMe]_2$	161.4	121.7	147.1	119.7	108.1	154.6	136.0	146.5	115.3	C	68
E3478-6	3-CH_2CH_2COOEt, 4-Me, 7,8-$[OAc]_2$	159.7	121.7	145.0	121.7	118.3	146.7	130.0	144.2	119.3	C	68
E3678-1	3-$C(Me_2)$-$CH=CH_2$, 6,7,8-$[OH]_3$	158.5	129.2	145.0	99.9	144.7	141.4*	131.8	138.4*	110.0	D	128

E4567-1	4-SMe, 5-Me, 6-OMe, 7-OH	159.3	104.3	160.1	129.6	143.1	151.9	102.2	151.5	111.9	C	129
E4568-1	4-Pr^n, 5-OH, 6-CH_2-CH=CMe_2, 8-$COCH_2Pr^i$	159.4	110.1	159.0	158.8	102.3	156.3	104.5	165.4	109.9	C	130,131
E4568-2	4-Pr^n, 5-OH, 6-CH_2-CH=CMe_2, 8-COCH(Me)Et	159.4	110.1	159.0	158.8	102.3	156.1	104.2	165.4	109.9	C	130,132
E4578-1	4-(*p*-OMe-Ph), 5,7,8-$[OMe]_3$	160.4	112.8	156.8	156.0	94.0	154.5*	132.8	149.9*	103.9	A	133
E4578-2	4-(*p*-OMe-Ph), 5,7-$[OMe]_2$, 8-OEt	160.4	112.8	157.4	156.8	94.1	154.6	132.4	150.7	103.0	C	133
E4578-3	4-(*m,p*-$[OMe]_2$-Ph), 5,7-$[OMe]_2$,	161.6	111.1	144.8	157.1	93.4	150.8	127.6	150.2	103.4	D	134
	8-OH	162.8	112.6	158.7	152.9	95.9	152.5	129.6	145.2	105.4	D	135
E4578-4	4-(*m*-OH, *p*-OMe-Ph), 5,7-$[OMe]_2$,	160.6	111.4	145.6	156.3	94.5	151.9	128.1	150.8	103.3	D	134
	8-OH	162.8	112.5	158.4	152.9	94.7	152.2	129.5	145.2	104.2	D	136
E4578-5	4-(*m*-OH, *p*-OMe-Ph), 5,7,8-$[OMe]_3$	159.3	111.2	155.3	153.6	94.0	155.3	129.8	144.6	102.8	D	134
E4578-6	4-(*m*-OCH_2O-*p*-Ph), 5,7,8-$[OMe]_3$	160.2		153.8	155.1	92.7	155.8	129.7	145.9	102.3	C	134
E4678-1	4,8-Me_2, 6-CH_2CH=CH_2, 7-OAc	160.6	114.3	152.3	122.8	119.7	150.4	117.9	151.1	128.5	C	137
E5678-1	5-CH_2-CH=CMe_2, 6-OMe, 7,8-$[OH]_2$	159.3	111.0	142.7	121.9	142.4	141.4	130.8	140.7	108.6	D	128
E5678-2	5-CH_2-CH=CMe-CH_2OH (*E*), 6-OMe, 7,8-$[OH]_2$	159.3	111.0	142.7	121.7	142.4	141.4	130.9	140.5	108.6	D	128
E34578-1	3,5-Me_2, 4,7,8-$[OMe]_3$	163.6	110.2	166.5	130.7	112.1	153.6	134.4	147.5	110.6	C	127
E45678-1	4-Ph, 5,7-$[OH]_2$, 6-$COCH_2Pr^i$, 8-CH_2-CH=CMe_2	159.4	112.7	154.5	156.7	100.9	163.2	107.3	159.2	108.1	C	130,138
E45678-2	4-Ph, 5,7-$[OH]_2$, 6-COCH(Me)Et, 8-CH_2-CH=CMe_2	159.4	112.7	163.2*	154.5*	100.9	156.9*	109.3	159.2	103.1	?	139

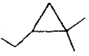
Table 10. ${}^{13}C$ chemical shifts of linear (**F**) and angular furanocoumarins (**H**), their 2′,3′-dihydro derivatives (**G** and **I**) and of coumarins with other annulated five-membered rings (**J**)

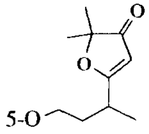
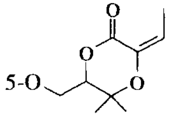
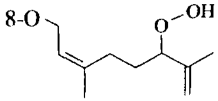
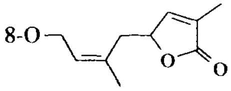


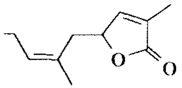
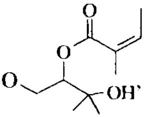
F



H

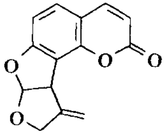
	Substituents	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-2′	C-3′	Solv.	Reference
F-1	- (linear furanocoumarin)	161.1	114.7	144.2	120.0	125.0	156.6	99.9	152.2	115.6	147.0	106.6	C	8,10,44
F-2	2-thiono	197.4	127.0	136.6	120.4	125.7	156.0	99.1	153.2	116.8	148.6	106.7	D	10
F-3	1′-thio	159.8	114.9	142.8	121.3	135.4	142.2	108.8	149.7	115.7	126.5	122.4	C	140
F-4	1′-seleno	160.6	115.7	143.7	123.5	138.8	144.8	113.0	150.4	116.6	129.4	126.7	C	140
F3-1	3-C(Me$_2$)-CH=CH$_2$	159.2	132.4	144.9	119.1	124.0	155.2	98.2	150.2	115.3	146.0	105.9	C	44,84, 110,141
F3-2	3 	162.9	126.6	138.0	118.7	124.5	155.5	99.2	150.7	117.7	146.4	106.2	C	110
F5-1	5-OH	160.1	110.8	139.5	147.7	112.4	156.8	90.9	152.6	103.7	144.7	104.6	D	142
F5-2	5-OMe	160.3	112.8	139.4	149.6	113.0	158.5	94.0	152.7	106.7	145.0	105.3	C	8,10,44 45,141,143
F5-3	2-thiono, 5-OMe	197.2	125.3	131.2	149.4	113.1	157.9	92.7	154.2	107.4	146.4	105.6	D	8,10
F5-4	5-OCH$_2$-CH=CMe$_2$	160.7	112.0	139.0	148.4	113.7	157.6	93.7	152.1	106.9	144.4	104.7	C	77,142
F5-5	5-O 	160.3	112.3	138.5	147.8	113.5	157.4	93.8	151.9	106.6	144.8	104.1	C	1
F5-6	5-OCH$_2$-CHOH-C(Me)=CH$_2$	161.1	112.9	139.2	148.4	114.2	158.0	94.7	152.6	107.3	145.2	104.7	C	143
F5-7	5-OCH$_2$-CHOH-C(Me$_2$)Cl	161.2	112.5	139.0	148.8	113.8	158.8	94.3	152.7	107.5	145.4	104.4	C	143
F5-8	5-OCH$_2$-CHOAc-C(Me$_2$)Cl	161.0	113.1	138.9	148.2	113.7	150.1	94.5	152.6	106.8	145.2	104.7	C	143

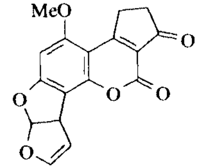
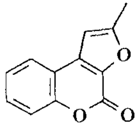
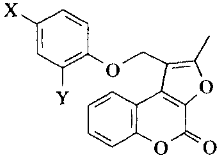
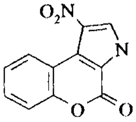
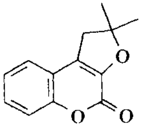
F5-9	5-OCH$_2$-CHOH-C(Me$_2$)OH	160.4	111.8	139.9	149.1	113.2	157.6	93.0	152.1	106.4	145.4	105.5	C	44
F5-10	5-OCH$_2$-CHOH-C(Me$_2$)OMe	161.2	112.7	139.4	148.8	113.4	158.1	94.4	152.5	107.2	145.0	104.9	C	143
F5-11	5-OCH$_2$-CHOAc-C(Me$_2$)OAc	160.8	113.2	139.0	148.8	113.2	158.1	94.5	152.3	106.9	145.2	104.7	C	143
F5-12	5-OCH$_2$-COPr^i	160.5	112.7	138.9	147.5	113.2	157.5	94.5	152.1	107.0	145.1	103.8	C	1
F5-13		161.0	113.0	139.0	148.5	113.5	158.2	99.4	152.7	106.9	145.1	104.7	C	144
F5-14		161.3	112.4	139.5	148.4	112.8	158.1	93.9	152.4	106.4	145.0	104.9	C	145
F8-1	8-OH	160.0	113.7	145.3	110.1	125.2	145.3	130.1	139.8	116.2	147.2	106.9	D	1,8,10
F8-2	8-OMe	160.4	114.5	144.4	113.1	126.2	147.6	132.7	142.9	116.5	146.6	106.8	C	1,8,10,143
F8-3	2-thiono, 8-OMe	196.6	127.1	136.8	113.4	127.1	147.0	131.6	144.8	117.9	148.5	107.0	D	10
F8-4	8-OCH$_2$-CH=CMe$_2$	160.2	114.2	144.3	113.2	125.7	148.3	131.2	143.5	116.2	146.4	106.5	C	1,8
F8-5	8-OCH$_2$-CHOH-C(Me)=CH$_2$	161.2	114.4	144.9	115.6	126.8	148.7	132.4	143.1	116.9	147.4	107.4	C	143
F8-6	8-OCH$_2$-CHOH-C(Me$_2$)OH	160.1	113.5	144.2	116.4	126.0	146.7	131.5	143.2	114.6	147.6	106.7	C	146
F8-7	8-OCH$_2$-CHOAc-C(Me$_2$)OH	160.1	114.8	144.2	113.7	125.9	147.9	131.3	143.2	116.5	146.7	106.8	C	103
F8-8	8-OCH$_2$-CHOH-C(Me$_2$)-O-β-D-glc*p*	160.0	114.2	145.4	113.8	125.9	147.2	131.6	142.7	116.5	147.9	107.1	D	147
F8-9	8-OCH$_2$-COPr^i	160.0	113.3	144.3	114.8	126.0	146.6	131.2	142.7	116.5	146.6	106.8	C	143
F8-10		160.8	115.0	144.6	113.2	126.1	148.9	131.6	143.7*	116.7	146.9*	107.0	C	48
F8-11		159.3	114.8	145.2	113.6	125.0	148.4	129.2	144.4*	116.6	146.8*	106.9	C	147,148

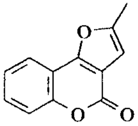
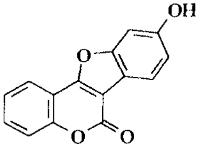
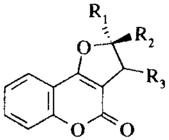
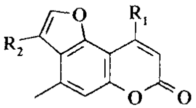
F2′-1	2′-Pr^i	161.1	114.1	144.2	118.8	126.5	156.3	99.1	151.5	115.0	167.3	99.5	C	8,10
F2′-2	2-thiono, 2′-Pr^i	197.2	126.7	136.7	119.2	127.0	155.7	98.6	153.6	116.5	167.4	99.9	C	10
F58-1	5-Br, 8-OCH_2-CHBr-C(Me_2)Br	159.0	115.8	142.1	127.7	115.5	146.4	130.6	143.7	106.3	147.1	107.3	C	150
F58-2	5-OMe, 8-OH	159.7	112.2	139.6	141.0	114.7	146.9	125.3	139.6	107.1	146.0	105.1	C	44,141
F58-3	5,8-$(OMe)_2$	160.5	112.8	139.5	144.4	114.9	149.9	128.3	143.7	107.7	145.3	105.3	C	8,10,44, 45,110
F58-4	5-OMe, 8-OAc	159.7	112.6	139.1	146.7	113.6	149.9	118.1	143.8	106.9	145.1	105.3	C	44,141
F58-5	5-OMe, 8-OCH_2-CHOH-C(Me_2)Cl	161.1	113.8	140.3									C	105
F58-6	5-OMe, 8-OCH_2-CH(O-β-D-glc*p*)-C(Me_2)OH	159.4	112.5	139.6	144.1	114.4	149.2	126.4	142.9	106.8	146.2	105.6	D	149
F58-7	5-OMe, 8-OCH_2-CHOH-C(Me_2)-O-β-D-glc*p*	159.5	112.5	139.6	144.1	114.5	149.6	126.8	143.2	106.9	146.2	105.4	D	149
F58-8	5-OCH_2-CHOH-C(Me)=CH_2 ,8-OMe	162.1	112.5	140.3	143.1	114.3	148.9	127.4	146.5	107.1	145.4	105.0	C	151
F58-9	5-OCH_2-CHOH-C(Me_2)-O-β-D-glc*p*, 8-OMe	159.6	112.4	140.2	143.8	115.8	149.0	127.5	142.8	107.9	146.3	105.5	D	149
F58-10	5-OMe, 8-O 	160.4	114.8	144.3	131.0	126.0	148.3	131.5	148.6	116.6	146.7	106.8	C	152
F58-11	5-O  , 8-OMe	160.3	113.1	139.5	143.6	115.3	149.8	128.6	143.1	108.1	145.3	105.0	C	145
F58-12	5-OH, 8-C(Me_2)-CH=CH_2	162.3	109.9	140.5	146.0	113.5	156.1	111.4	150.2	104.6	143.4	103.2	C/M	143
F58-13	5-OMe, 8-C(Me_2)-CH=CH_2	160.7	112.3	139.4	142.6	115.0	156.7	114.2	150.8	107.8	144.2	104.0	C	143
F2′3′-1	2′-Pr^i, 3′-OMe	160.9	114.3	144.0	116.5	121.6	153.5	99.8	151.5	114.7	152.5	136.3	C	1
F582′-1	5-OH, 8-C(Me_2)-CH=CH_2, 2′-C(Me)=CH_2	159.9	110.1	139.9	150.7	114.2	155.0	112.8	154.6	104.4	146.1	100.6	C	84
F482′-1	4,8,2′-Me_3	161.6	112.9	155.7	112.3	125.6	153.4	116.2	149.1	109.3	157.6	102.9	C	8

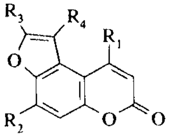
G3-1	3-C(Me$_2$)Et	162.6	130.7	138.6	123.1	124.1	160.2	97.0	154.5	113.0	89.1	28.6	C	86
G5-1	5-OMe	161.5	110.5	139.2	152.7	105.9	165.5	92.9	156.6	110.4	72.4	28.3	C	8
G2´-1	2´-C(Me)=CH$_2$	162.0	111.8	143.6	123.4	125.5	162.0	97.5	155.3	111.6	87.8	33.4	C	143
G2´-2	2´-C(Me$_2$)OH	162.2	111.6	144.3	123.6	125.6	163.7	97.7	155.6	112.7	91.3	29.5	C	1,8,153-155
G2´-3	2´-C(Me$_2$)OCOC(Me)=CHMe (*Z*)	161.1	112.0	143.8	123.4	124.5	163.4	97.6	155.7	112.6		29.6	C	153
G2´-4	2´-C(Me)OCO-CH=CMe$_2$	161.0	111.8	143.5	123.1	124.4	163.1	97.6	155.4	112.5	88.7	29.3	C	1
G2´-5	2´-C(Me$_2$)O-β-D-glc*p*	160.4	111.2	144.6	123.8	125.6	163.0	96.7	155.0	112.1	90.0	27.8	D	154
G2´-6	2´-CH$_2$-CH=CMe$_2$	161.3	112.2	143.7	123.4	124.6	163.5	98.0	156.1	112.8	87.6	33.6	C	150
G2´-7	2´-C(Me$_2$)-O-β-D-glc*p*-(1←6)-apio*f*	160.3	111.9	144.4	123.8	125.4	162.9	96.7	154.9	112.2	89.7	29.0	D	156
G32´-1	3-C(Me$_2$)-CH=CH$_2$, 2´-C(Me$_2$)OH	160.0	130.5	137.9	123.1	124.5	162.1	96.8	154.4	112.9	90.8	29.5	C	84
G32´-2	3-C(Me$_2$)-CH=CH$_2$, 2´-C(Me$_2$)OAc	159.6	130.4	137.7	122.8	123.7	161.9	96.7	154.2	112.8	88.2	29.7	C	110
G52´-1	5-OH, 2´-C(Me)=CH$_2$	161.3	110.2	139.8	151.2	109.0	165.2	90.6	157.8	104.4	88.1	32.0	A	143,157
G82´-1	8-OMe, 2´-C(Me)=CH$_2$	161.1	107.3	137.3^+	115.9*	113.6	160.5	126.9*	146.4^+	113.3	87.1	31.5	C	103
G82´-2	8-OH, 2´-C(Me$_2$)OH	160.2	110.8	144.9^+	113.9*	125.2	151.3	128.0*	143.6^+	112.7	90.5	29.4	D	154,158
G82´-3	8-OH, 2´-C(Me$_2$)$OSO_3^-K^+$	160.3	110.9	145.1^+	114.0*	125.2	151.2	128.1*	143.8^+	113.0	89.4	29.8	D	158
G82´-4	8-O-β-D-glc*p*, 2´-C(Me$_2$)OH	160.1	112.9	147.8^+	117.3*	127.0	152.7	126.6*	145.9^+	111.4	91.3	28.9	D	45,154
G82´-5	8-OH, 2´-C(Me$_2$)O-β-D-glc*p*	160.3	111.0	143.7^+	114.0*	125.5	151.1	128.1*	145.1^+	112.9	89.8	29.6	D	154
G82´-6	8-OH, 2´-C(Me$_2$)O-(6´´OMe)-β-D-glc*p*	161.3	111.0	143.7	114.0	125.2	151.0	128.1	145.0	113.0	89.5	29.6	D	154
G2´3´-1	(*cis*)-2´-C(Me$_2$)OH, 3´-OH	160.4	111.9	144.8	125.7	128.5	162.8	97.8	156.2	112.8	91.9	71.0	D	159
G2´3´-2	(*cis*)-2´-C(Me$_2$)OH, 3´-OAc	160.6	114.2	143.9	127.4	124.4	163.9	96.9	158.1	114.3	91.8	73.2	D	159
G2´3´-3	(*trans*)-2´-C(Me$_2$)O-β-D-glc*p*, 3´-OH	160.1	111.5	144.5	125.2	127.9	163.0	97.0	155.9	112.6	97.0	70.0	D	156
G2´3´-4	(*cis*)-2´-C(Me$_2$)O-β-D-glc*p*, 3´-OH	160.6	111.8	144.9	125.7	128.6	162.4	97.7	156.1	112.9	91.9	77.5	D	160
G352´-1	3-C(Me$_2$)-CHOH-CH$_2$OH, 5-OMe, 2´-C(Me$_2$)OH	162.3	129.4	139.2	123.7	125.0	159.8	95.8	153.8	112.5	90.7	28.8	D	109
G352´-2	3-C(Me$_2$)-CHOAc-CH$_2$OAc, 5-OMe, 2´-C(Me$_2$)OH	162.7	127.8	139.3	123.4	124.9	160.0	97.1	154.7	112.7	91.0	29.5	C	109

H-1	- (angular furanocoumarin)	160.2	114.5	144.5	123.9	108.8	157.3	116.9	148.5	113.5	145.9	104.0	C	161
H3-1	3-Me	162.2	123.1	140.2	123.0	108.5	156.6	116.6	147.3	114.1	145.6	103.9	C	162
H3-2	1´-thiono, 3-COOMe	155.5	113.2	119.1	149.7	124.7	145.7	115.6	150.0	127.4	129.7	119.7	D	163
H3-3	1´-thiono, 3-COOEt	155.7	113.0	119.1	149.5	124.7	145.5	115.6	150.1	127.3	129.7	119.7	D	163
H3-4	1´-thiono, 3-CONH$_2$	160.1	114.1	119.5	148.4	124.8	145.5	118.3	150.0	127.8	129.5	119.7	D	163
H3-5	1´-thiono, 3-CSNH$_2$	159.0	114.1	119.6	150.2	124.9	145.5	122.2	149.4	127.4	129.8	119.7	D	163
H3-6	1´-thiono, 3-C≡N	156.7	100.2	119.8	154.0	124.2	146.6	114.6	149.8	127.7	130.4	119.7	D	163
H4-1	4-Me	160.7	112.8	153.6	120.5	108.3	157.2	116.9	147.9	114.5	145.8	104.3	C	162
H5-1	5-OMe	160.8	112.0	139.7	154.1	90.4	157.8	109.9	148.6	105.7	144.2	103.8	C	149
H5-2	5-Me	160.6	113.5	141.3	132.2	109.6	157.3	115.1	149.1	112.7	145.0	104.0	C	162
H6-1	6-Me	161.1	114.0	144.5	123.7	119.1	156.7	116.3	146.9	113.6	145.6	104.4	C	162
H6-2	6-OMe	160.1	114.1	145.3	104.8	142.5	146.1	117.7	142.3	113.8	147.4	104.2	D	149
H2´-1	2´-Me	161.0	113.8	144.6	122.7	108.1	157.1	118.3	147.6	113.4	156.8	99.9	C	162
H2´-2	2-Pr^i	160.9	113.7	144.6	122.7	108.2	157.0	118.0	147.8	113.3	166.3	97.2	C	161
H2´-3	2´-C(Me$_2$)OH	160.9	113.8	144.5	123.4	108.6	157.0	117.7	147.9	113.4	164.7	98.0	C	161
H2´-4	2´-C(Me$_2$)Ph	160.7	113.8	144.5	123.0	108.0	157.2	117.8	148.0	113.4	167.1	98.9	C	161
H2´-5	2´-C(Me$_2$)(*p*-OMe-Ph)	160.7	113.8	144.6	122.9	108.1	157.2	117.8	147.9	113.2	167.4	98.6	C	161
H3´-1	3´-Me	160.4	113.7	144.4	123.7	108.7	157.9	117.4	149.8	113.4	142.3	115.9	C	162
H34-1	3,4-Me$_2$	161.8	119.7	147.0	120.3	108.0	156.3	116.5	147.0	114.9	145.4	104.1	C	162
H32´-1	3,2´-Me$_2$	162.3	122.7	140.4	121.8	107.9	156.3	117.9	146.6	114.0	156.4	99.8	C	162
H32´-2	1´-thio, 3-COOEt, 2´-Br	155.2	113.8	118.6	149.0	125.4	146.1	116.7		127.3	116.9	122.8	D	163
H32´-3	1´-thio, 3-COOEt, 2´-Me	155.6	113.2	118.7	149.0	124.0	145.2	115.8		127.7	145.2	117.5	D	163
H32´-4	1´-thio, 3-CONH$_2$, 2´-Me	160.0	114.0	119.0	148.5	124.1	144.9	117.7	149.2	127.8	143.5	117.4	D	163
H32´-5	1´-thio, 3-CSNH$_2$, 2´-Me	159.0	114.0	119.2	150.2	124.2	145.2	122.1		127.8	143.6	117.5	D	163
H32´-6	1´-thio, 3-C≡N, 2´-Me	156.6	100.0	119.4	153.9	123.6	146.3	114.5	149.8	128.1	144.1	117.4	D	163
H33´-1	3,3´-Me$_2$	162.1	122.8	140.3	122.9	108.5	157.1	117.2	148.7	114.0	142.0	115.8	C	162
H46-1	4,6-Me$_2$	161.1	112.7	153.5	120.4	118.6	156.2	116.3	146.4	114.6	145.5	104.6	C	162
H42´-1	4,2´-Me$_2$	160.8	112.7	153.5	119.3	107.7	157.1	118.5	147.2	114.5	156.7	100.2	C	162
H43´-1	4,3´-Me$_2$	160.4	112.5	153.3	120.3	108.2	157.9	117.4	149.4	114.3	142.2	116.2	C	162
H56-1	5,6-[OMe]$_2$	159.5	113.7	140.0	142.6	134.6	149.1	113.4	144.2	109.0	146.9	103.8	D	149
H56-2	5,6-Me$_2$	160.9	113.2	141.9	129.5	117.4	156.7	114.0	147.2	112.8	144.8	104.3	C	162
H52´-1	5,2´-Me$_2$	161.0	113.0	141.5	130.9	109.1	157.0	116.4	148.1	112.5	155.8	99.8	C	162
H62´-1	6,2´-Me$_2$	161.2	113.5	144.5	122.6	118.4	156.0	117.5	146.0	113.3	156.4	100.1	C	162

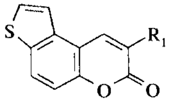
H63′-1	6,3′-Me$_2$	161.0	113.5	144.5	123.5	119.0	156.8	116.7	148.2	113.3	142.0	116.2	C	162
H2′3′-1	2′,3′-Me$_2$	160.9	113.3	144.6	122.4	108.0	156.2	118.4	148.8	113.3	151.7	109.8	C	162
H342′-1	3,4,2′-Me$_3$	162.1	119.4	147.2	119.0	107.4	156.1	118.0	145.2	114.9	156.3	100.0	C	162
H343′-1	3,4,3′-Me$_2$	161.6	119.4	146.9	120.1	108.0	156.9	116.9	147.4	114.8	141.9	116.0	C	162
H462′-1	4,6,2′-Me$_2$	161.3	112.4	153.6	119.3	118.0	156.0	117.7	145.6	114.4	156.3	100.4	C	162
H463′-1	4,6,3′-Me$_2$	161.1	112.5	153.5	120.3	118.5	156.8	116.8	147.7	114.4	141.9	116.5	C	162
H562′-1	5,6,2′-Me$_2$	161.1	112.7	141.9	128.3	116.7	156.3	115.2	146.2	112.5	155.4	100.0	C	162
H563′-1	5,6,3′-Me$_2$	160.8	112.7	141.8	129.2	117.2	157.1	114.4	148.5	112.5	141.2	116.1	C	162
I2′-1	2′-C(Me$_2$)OH	161.0	112.3	144.0	128.7	106.7	163.7	114.0	151.3	108.6	91.4	27.6	C	41
I2′-2	2′-C(Me$_2$)OCO-C(Me)=CHMe (*Z*)	161.0	112.1	144.0	128.9	106.7	164.0	113.0	151.2	113.5	89.3	27.6	C	143,145
I52′-1	5-OMe, 2′-C(Me$_2$)OH	161.8	108.5	141.5	154.7	93.3	145.6	131.7	151.5	102.5	65.9	27.1	C	166
I52′-2	5-OMe, 2′-C(Me$_2$)OCH$_2$-CH=CMe$_2$	161.6	111.3	138.7	154.8	93.2	115.7	131.6	151.5	102.4	65.9	26.1	C	166
I2′3′-1	2′-C(Me$_2$)OAc, 3′-OCOEt	159.7	113.3	143.4	131.3	107.6	163.6	81.0	151.9	113.4	88.2	68.6	C	167
I2′3′-2	2′-C(Me$_2$)OAc, 3′-OCOC(Me)Et	159.4	113.1	143.3	131.3	107.5	163.5	80.8	151.7	113.3	88.2	68.3	C	167
I2′3′-3	2′-C(Me$_2$)OCOCH$_2$Pr^i, 3′-OCO-C(Me)=CHMe (Z)	160.4	113.7	111.1	131.2	108.1	164.3	113.5	152.4	113.9	88.9	68.5	C	168
I2′3′-4	2′-C(Me$_2$)OCO-C(Me)=CHMe (*E*), 3′-OCO-CH(Me)Et	159.5	113.2	143.4	131.3	107.6	163.6	81.1	151.8	113.3	88.3	68.3	C	167
I2′3′-5	2′-C(Me$_2$)OCO-C(Me)=CHMe (*Z*), 3′-OCO-CH(Me)=CHMe (*Z*)	160.4	113.7	144.1	131.2	108.1	164.3	113.1	152.4	113.8	89.2	68.5	C	168
I2′3′-6		160.7	112.9	144.1	129.7	107.1	162.4	113.7	151.8	113.8	113.9	48.8	C	169

I2´3´-7		155.2	117.4	177.1	161.6	90.9	165.8	107.9	153.0	104.0	113.6	47.9	C	170,171
J23-1		152.4	136.4	134.7	123.9	124.4	129.5	117.3	152.3	116.2	162.2	102.7	C	55
J23-2	 X = H, Y = Cl	152.4	136.5	133.1	125.0	124.7	129.7	117.4	152.4	116.2	160.4	113.3	C	55
J23-3	X = Cl, Y = H	152.3	136.5	132.9	124.0	124.7	129.6	117.5	152.4	116.2	160.2	113.4	C	55
J23-4	X = Me, Y = H	152.4	136.5	133.1	124.8	124.6	129.5	117.4	152.4	116.4	160.0	113.9	C	55
J23-5	X = Y = Me	152.5	136.5	133.3	124.9	124.6	129.6	117.5	152.5	116.4	160.0	114.1	C	55
J23-6		153.3	117.5	114.7	126.1	124.3	129.6	117.0	151.2	120.3	131.6	132.5	D	173
J23-7		162.5	128.0	127.9	122.9	124.5	128.0	116.3	151.1	118.8	89.2	41.6	D	22

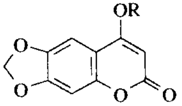
J23-8		158.2	111.6	156.6	120.4	124.3	130.0	117.2	152.3	112.8	155.6	104.0	C	55
J23-9		163.2	113.7	155.9	122.6	114.5	154.0	155.9	157.4	104.1	158.2	113.9	D	174
														
J23-10	R_1 = Me, R_2 = H, R_3 = H	160.5	101.5	166.1	122.4	123.5	131.9	116.6	154.7	112.4	83.9	33.7	C	35
J23-11	R_1 = R_2 = Me, = H	160.8	101.2	165.3	122.6	123.6	132.0	116.8	154.9	112.8	92.7	39.6	C	35
J23-12	R_1 = R_2 = R_3= Me	159.6	110.2	164.5	122.4	123.3	131.7	116.6	154.5	112.6	92.3	43.6	C	33
J23-13	R_1 = H, R_2 = Ph, R_3 = Me	160.1	107.4	165.3	122.7	123.8	132.3	116.8	154.9	116.8	90.9	39.0	C	35
														
J56-1	R_1 = Me, R_2 = H	160.9	113.5	151.6	150.2	123.9	135.2	112.9	152.0	105.3	144.9	105.3	C	176
J56-2	R_1 = H, R_2 = Me	160.8	114.7	136.8	150.5	123.0	136.4	112.5	151.2	103.6	141.9	116.9	C	176
J56-3	R_1 = R_2 = Me	161.0	113.2	151.6	149.5	125.4	134.0	112.2	151.0	104.7	155.5	101.1	C	176



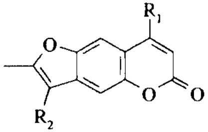
J56-4	$R_1 = R_2 = R_3 = R_4 = H$	161.0	116.2	140.1	124.5	151.0	114.9	113.4	151.0	111.5	147.5	104.6	C	176
J56-5	$R_1 = R_2 = Me, R_3 = R_4 = H$	161.3	114.0	153.1	122.6	150.8	126.7	114.5	151.2	111.3	146.5	107.5	C	176
J56-6	$R_1 = R_3 = Me, R_2 = R_4 = H$	161.0	114.5	153.1	125.1	151.1	114.1	112.3	150.7	112.4	158.0	103.5	C	176
J56-7	$R_1 = R_3 = H, R_2 = R_4 = Me$	161.1	114.6	139.5	123.4	150.9	126.7	113.8	151.3	110.4	143.9	116.3	C	176
J56-8	$R_1 = H, R_2 = R_3 = R_4 = Me$	161.3	114.1	139.7	124.8	149.0	125.7	112.5	151.2	110.0	153.5	110.7	C	176



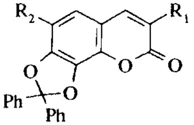
J56-9	$R_1 = COOMe$	155.9	112.0	145.3	116.6	137.2	113.2	128.8	153.6	135.4	132.4	121.6	D	163
J56-10	$R_1 = COOEt$	155.9	112.0	145.2	116.9	137.1	113.2	128.8	153.5	135.3	132.4	121.7	D	163
J56-11	$R_1 = CONH_2$	160.6	113.0	144.2	118.8	137.2	113.2	128.4	153.2	135.8	132.3	121.5	D	163
J56-12	$R_1 = CSNH_2$	158.8	112.7	144.7	123.3	137.0	113.0	128.3	152.5	135.6	132.5	121.1	D	163
J56-13	$R_1 = C{\equiv}N$		100.9	150.4	114.4	137.1	113.5	129.8	153.4	136.2	133.0	121.7	D	163



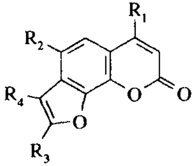
J67-1	$R = Me$	161.4	111.7	138.9	138.0	131.7	151.5	92.4	152.6	106.6	101.8		C	177
J67-2	$R = CH_2\text{-}CH{=}CMe_2$	161.2	111.6	139.0	137.3	132.4	151.6	92.4	152.6	107.4	101.9		C	178



J67-3	$R_1 = Me, R_2 = H$	161.0	113.3	152.5	106.7	151.1	132.6	104.9	149.5	115.7	159.8	102.8	C	176
J67-4	$R_1 = H, R_2 = Me$	161.5	114.6	144.1	108.0	150.3	134.5	105.6	150.3	114.8	155.4	110.6	C	176

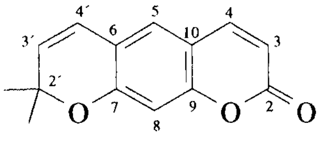


J78-1	$R_1 = R_2 = H$	159.8	113.5	143.9	121.8	105.7	150.9	133.5	143.7	115.1	119.7		C	100
J78-2	$R_1 = CH_2\text{-}CH{=}CMe_2$, $R_2 = H$	161.0	119.2	138.6	120.8	105.5	149.8	132.4	139.5	115.9	125.8		C	100
J78-3	$R_1 = H$, $R_2 = CH_2\text{-}CH{=}CMe_2$	160.1	113.2	144.0	121.5	119.3	149.0	132.8	139.6	114.8	126.4		C	100
J78-4	$R_1 = H$, $R_2 = CH_2\text{-}CHOH\text{-}C(Me_2)OH$	160.0	113.3		123.0	118.2	149.4	132.9	139.4	114.9	126.2		C	100

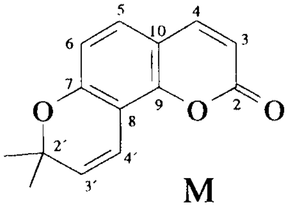


J78-5	$R_1 = R_2 = R_3 = R_4 = H$	159.7	114.5	144.4	122.2	116.9	131.8	141.1	140.3	115.0	147.6	107.4	C	176
J78-6	$R_1 = R_2 = R_4 = H$, $R_3 = Me$	159.8	113.6	144.5	121.9	115.9	133.5	140.4	139.5	114.1	158.8	103.5	C	176
J78-7	$R_1 = R_2 = Me$, $R_3 = R_4 = H$	160.0	113.4	153.5	118.4	126.5	131.6	141.2	138.5	116.0	147.3	106.1	C	176
J78-8	$R_2 = R_3 = Me$, $R_1 = R_4 = H$	159.8	113.1	144.2	120.9	125.5	133.0	139.5	137.6	113.7	158.0	102.0	C	176
J78-9	$R_1 = R_2 = H$ $R_3 = R_4 = Me$	160.1	113.8	144.7	121.6	114.6	134.9	139.8	139.7	114.4	154.4	111.0	C	176
J78-10	$R_1 = R_2 = R_3 = Me$, $R_4 = H$	160.1	112.6	153.6	118.0	125.5	133.3	140.5	137.8	115.1	158.4	102.3	C	176

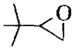
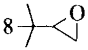
Table 11. ^{13}C chemical shifts of linear (**K**) and angular pyranocoumarins (**M**), their 3′,4′-dihydro derivatives (**L** and **N**) and of coumarins with other annulated six-membered rings (**O**)

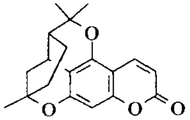


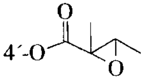
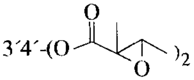
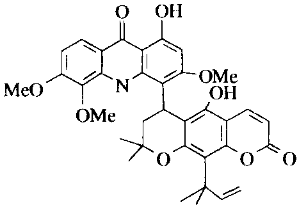
K

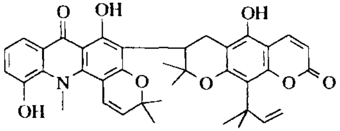
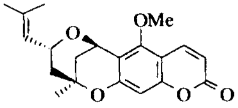
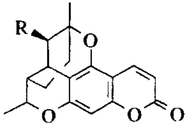
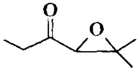


M

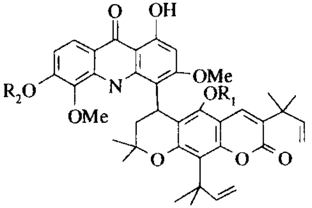
	Substituents	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-2′	C-3′	C-4′	Solv.	Reference
K-1	- (linear pyranocoumarins)	160.6	112.5	143.1	120.4	118.2	156.4	103.9	155.0	112.3	77.5	130.8	124.6	D	84
K3-1	3-C(Me_2)-CH=CH_2	160.0	131.0	137.6	120.1	118.0	154.9	103.3	154.5	112.8	77.5	129.2	124.0	C	179
K5-1	5-OMe	161.0	112.4	138.5	157.6	107.4	152.9	100.8	155.7	111.3	77.5	130.6	115.8	C	180
K8-1	8-OMe	160.3	112.8	143.4	120.8	118.9	148.9	135.1	147.9	114.3	77.5	130.9	118.9	C	44
K8-2	8-OCH_2-CH=CMe_2	160.6	112.9	143.5	121.0	118.7	149.6	134.1	148.7	112.9	76.9	130.9	119.0	C	157
K8-3	8-CH_2-CH=CMe_2	161.5	112.5	144.0	115.4	119.6	156.5	113.5	146.9	112.1	77.5	130.4	127.1	C	41
K38-1	3-C(Me_2)-CH=CH_2, 8-CH_2-CH=CMe_2	159.4	131.0	138.7	115.8	120.3	161.9	116.0	150.2	112.0	77.5	130.6	127.1	C	41
K58-1	5-OH, 8 	161.0	110.2	139.2	150.5	102.0	157.4	113.7	150.9	103.9	78.1	128.0	115.7	C	181
K358-1	3,8-[C(Me_2)-CH=CH_2]$_2$, 5-OH	160.8	128.5	134.2	147.0	106.4	155.1	115.2	153.2	104.2	79.0	129.3	115.8	C	181
K358-2	3-C(Me)$_2$-CH=CH_2, 5-OH 8 	159.6	129.1	133.0	150.1	103.8	156.5	112.9	150.2	104.0	77.8	127.8	115.9	C	181
K3458-1	3-(*p*-OH-Ph), 4,5-[OMe]$_2$, 8-$CH_2CH_2Pr^i$	161.3	111.9	164.1	151.5	112.2	153.6	113.3	150.5	104.5	77.1	130.6	115.6	?	182

K3458-2	3-(*p*-OH-Ph), 4,5-[OMe]$_2$, 8-CH$_2$-CH=CMe$_2$	161.3	111.9	164.1	151.5	112.2	153.6	113.3	150.5	104.5	77.1	130.6	115.6	?	182
L-1	-	161.5	112.8	143.3	128.2	118.4	157.7	104.6	154.0	112.2	75.8	32.4	21.9	C	103
L3′-1	3′-OH	160.5	112.3	144.2	129.4	118.1	156.6	103.2	153.6	112.3	78.4	67.6	30.4	C	44,142,184
L3′-2	3′-OCO-CH$_2$Pr^i	160.9	113.1	142.9	128.1	115.8	156.2	104.3	154.1	112.6	76.4	69.1	27.7	C	104
L3′-3	3′-OCO-CH=CMe$_2$	160.9	113.0	142.9	128.5	115.9	156.3	104.4	154.1	112.6	76.6	69.0	27.7	C	184
L3′-4	3′-OCO-C(Me)=CHMe (*Z*)	161.2	113.4	143.2	128.7	115.9	156.5	104.7	154.5	112.9	76.7	70.1	27.9	C	86
L33′-1	3-C(Me$_2$)-CH=CH$_2$, 3′-OH	160.0	132.0	137.4	128.7	116.0	155.5	103.9	153.3	113.4	77.9	69.3	30.8	C	86
L33′-2	3-C(Me$_2$)-CH=CH$_2$, 3′-O[(*p*-SO$_3$Me)-Ph]	160.0	132.3	137.3	128.3	114.7	154.8	104.0	153.4	113.6	77.9	76.1	28.7	C	185
L54′-1		162.1	110.9	138.4	153.7	112.5	160.0	97.1	154.7	105.2	86.6	46.4	28.1	C	185
L3′4′-1	(*cis*)-3′,4′-[OH]$_2$	160.8	112.8	143.7	129.2	122.5	157.3	103.7	155.4	112.8	80.2	71.7	65.0	P	155
L3′4′-2	(*trans*)-3′,4′-[OH]$_2$	161.4	113.1	144.4	129.0	123.8	156.5	103.6	154.9	112.7	81.0	75.4	68.5	P	155
L3′4′-3	(*trans*)-3′-OAc, 4′-OMe	160.7	113.6	143.1	129.5	117.8	156.1	104.8	155.2	113.3	77.4	75.0	71.2	C	187
L3′4′-4	(*trans*)-3′-OH, 4′-OCO-CH=CMe$_2$	160.0	113.4	143.3	128.3	117.9	156.4	104.6	155.1	113.0	79.9	73.4	70.3	C	155
L3′4′-5	(*trans*)-3′-OCO-CH=CMe$_2$, 4′-OH	159.8	113.5	143.3	128.1	121.1	155.4	104.4	155.0	113.2	78.4	75.7	67.4	C	155
L3′4′-6	(*trans*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OH	160.9	113.7	143.2	128.0	121.0	155.2	104.5	155.1	113.2	78.3	76.7	67.7	C	155
L3′4′-7	(*trans*)-3′-OAc, 4′-OCO-CH=CMe$_2$	160.7	113.8	143.1	129.0	117.1	156.1	104.8	155.3	113.3	77.8	72.7	66.3	C	187
L3′4′-8	(*trans*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OAc	160.5	113.8	142.9	128.8	116.7	156.0	104.8	155.3	113.2	77.9	72.0	67.5	C	155

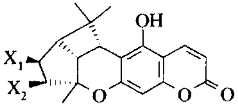
L3′4′-9	(*trans*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OCO-CH$_2$Pr^i	160.4	113.9	143.1	128.8	117.2	156.1	104.7	155.4	113.5	78.2	72.1	67.3	C	187
L3′4′-10	(*trans*)-3′,4′-[OCO-CH=CMe$_2$]$_2$	160.7	113.6	143.1	129.2	117.1	156.2	104.7	155.2	113.2	77.9	71.2	66.1	C	187,153
L3′4′-11	(*cis*)-3′,4′-[OCO-C(Me)= CHMe (*E*)]$_2$	160.4	113.3	142.2	127.2	116.0	156.1	104.1	154.9	112.7	77.9	68.7	64.3	C	1
L3′4′-12	(*cis*)-3′-OCO-C(Me)= CHMe (*E*), 	160.6	113.7	143.1	127.5	115.3	156.3	104.5	155.3	113.1	78.0	68.9	66.1	C	1
L3′4′-13	(*cis*)- 	160.3	113.7	143.0	126.8	114.6	155.9	104.5	155.2	113.1	77.7	69.9	65.9	C	1
L584′-1		159.5	109.3	139.7	152.1	106.8	157.2	114.7		103.6	76.5	37.6	25.2	D	99

L583′-2		161.5	110.5	140.6	151.5	107.5	159.3	115.9	153.9	104.7	77.6	38.8	23.5	A	189
L52′4′-1		161.5	110.9	138.9	151.4	104.1	160.2	96.1	156.3	103.1	74.1	34.9	62.3	C	188
L53′4′-1	 R = OH	162.0	110.4	138.2	154.2	110.2	158.5	97.2	154.7	105.9	86.5	47.4	36.2	C	185
L53′4′-2	R = CH_2-CO-CH=CMe_2	162.1	111.1	138.8	152.4	111.5	159.9	99.0	155.1	104.2	85.2	47.4	30.4	C	124
L53′4′-3	R = CH_2-CH=CH-C(Me_2)OH (*E*)	162.1	111.1	138.8	152.5	110.8	160.6	98.2	155.2	104.3	85.6	47.1	34.3	C	124
L53′4′-4	R = CH_2-CH=CH-C(Me_2)OOH (*E*)	162.0	111.1	138.8	152.4	110.8	160.7	99.0	155.3	104.3	85.6	47.1	34.2	C	124
L53′4′-5	R = CH_2-CH_2-CH(OOH)-CMe_2(OOH)-C(Me)=CH_2	162.1	111.1	138.7	152.5	110.4	161.0	98.9	155.2	104.2	86.1	47.1	26.0	C	124
L53′4′-6	R = CH_2-CHOH-CHOH- C(Me_2)OH	162.0	111.1	138.7	152.3	110.8	160.3	99.0	155.1	104.2	85.5	47.3	28.1	C	124
L53′4′-7	R = CH_2-CO-CHOH-Pr^i	161.9	111.2	138.6	152.4	112.0	159.5	98.9	154.9	104.2	84.6	48.1	36.5	C	124
L53′4′-8	R = 	161.7	111.6	138.3	151.8	111.1	159.8	99.4	155.1	104.2	85.2	46.9	29.5	C	124

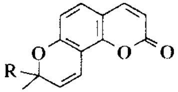
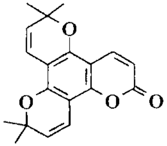
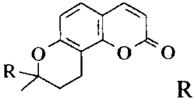
L3584´-1	3,8-[C(Me$_2$)-CH=CH$_2$]$_2$, 5-OH, 4´-keto	159.7	129.8	132.5	158.8	104.0	159.3	113.9	158.9	103.5	79.8	47.8	198.3	C	190



L3584´-2	R$_1$ = R$_2$ = H	158.3	127.5	133.7	151.7	106.8	156.3	114.0	151.9	103.1	76.3	37.6	25.1	D	191
L3584´-3	R$_1$ = H, R$_2$ = Me	159.2	130.8	133.0	154.5	104.4	156.3	119.9	152.8	105.7	77.5	38.1	25.4	C	191
L3584´-4	R$_1$ = R$_2$ = Me	159.6	129.3	133.0	150.6	103.2	155.9	115.9	152.9	103.5	77.5	37.9	25.1	C	191

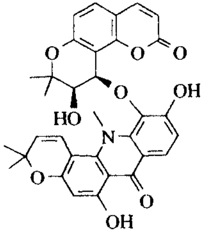


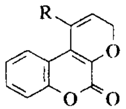
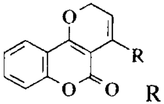
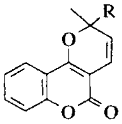
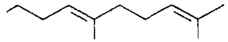
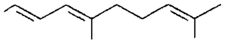
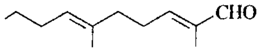
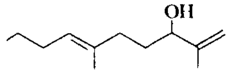
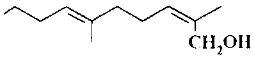
L53´4´5´-1	X$_1$ = X$_2$ = H	162.3	111.1	139.1	151.5	107.2	157.9	99.1	154.7	103.2	84.7	37.4	35.7	C	188
L53´4´5´-2	X$_1$ = OH, X$_2$ = H	161.4	110.8	139.9	154.6	110.6	158.4	98.4	155.3	104.8	85.3	38.3	36.2	P	188
L53´4´5´-3	X$_1$ = H, X$_2$ = OH	161.3	110.7	139.8	154.7	110.6	158.5	98.3	155.2	104.7	86.2	37.0	36.5	P	188

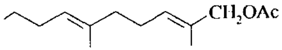
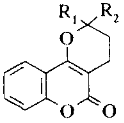
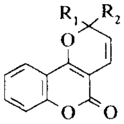
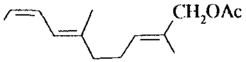
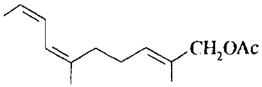
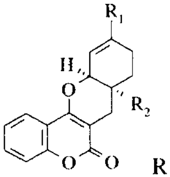
M-1	- (angular pyranocoumarin)	160.4	112.2	143.5	127.5	114.6	155.9	108.8	149.8	112.2	77.2	130.4	113.1	C	44
M3-1	3-C(Me$_2$)-CH=CH$_2$	159.7	131.5	138.1	127.6	115.3	155.5	108.9	149.4	113.0	77.2	130.6	113.2	C	41
															
M2′-1	R = CH$_2$-CH$_2$-CH=CMe$_2$	161.3	112.7	144.1	128.0	113.5	156.9	109.3	150.3	112.7	80.3	129.9	115.7	C	192
M2′-2	R = CH$_2$-CH=CH-C(Me$_2$)OOH (*E*)	161.2	112.9	144.1	128.2	113.4	156.7	109.5	150.3	112.8	79.8	129.4	116.1	C	192
M56-1		161.5	110.8	139.0	150.3	106.4	150.3	102.5	152.2	103.3	78.2	127.9	115.4	C	84,62
M456-1	4-Ph, 5-OH, 6-COCH$_2$Pr^i	159.3	112.5	154.6	158.0	101.3	164.3	102.0	156.2	107.0	79.8	126.1	115.3	C	194
M3456-1	3-(*p*-OMe-Ph), 4,5-[OMe]$_2$, 6-CH$_2$CH$_2$Pr^i	161.2	112.1	163.9	154.9	107.8	153.9	119.9	147.4	103.8	77.4	129.7	114.3	?	182
M3456-2	3-(*p*-OMe-Ph), 4,5-[OMe]$_2$, 6-CH$_2$CH=CMe$_2$	161.2	112.1	163.9	154.9	107.8	153.9	119.9	147.4	103.8	77.4	129.7	114.3	?	182
N-1	 R = Me	161.0	111.5	143.6	125.9	114.1	157.2	108.8	152.8	111.2	75.1	31.1	16.1	C	44
N-2	R = CH$_2$OH	161.4	112.4	143.9	126.1	114.4	157.0	109.6	153.1	112.0	78.0	26.4	15.8	C	103
N3′-1	3′-OH	161.3	112.5	143.9	126.7	114.2	156.4	107.4	153.6	112.2	78.1	68.5	24.6	C	183,41,158
N3′-2	3′-OSO$_3^-$K$^+$	160.4	111.8	144.8	126.9	113.7	156.2	107.5	153.2	111.7	77.3	71.3	23.5	D	158
N3′-3	3′-O-β-D-glc*p*	160.2	111.6	144.7	126.8	113.6	155.9	107.6	152.9	111.7	77.3	72.7	21.8	D	183
N4′-1	4′-OH	160.7	112.7	144.9	126.6	114.2	159.2	110.1	153.8	110.9	76.9	71.8	25.0	D	183
N4′-2	4′-O-β-D-glc*p*	160.6	112.4	144.9	127.0	113.1	159.2	111.1	153.9	111.6	85.0	71.6	24.8	D	183

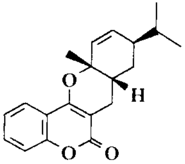
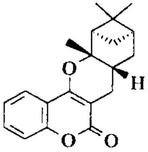
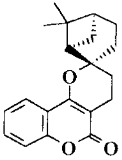
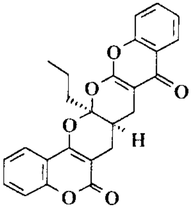
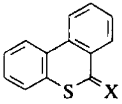
N36-1	3,6-Cl$_2$	154.2	118.4	138.7	125.0	119.3	152.4	110.5	149.7	111.1	76.5	31.0	16.8	C	44
N33´-1	3-C(Me$_2$)-CH=CH$_2$, 3´-OH	160.3	131.2	138.4	126.8	114.2	155.5	116.8	149.4	112.9	78.0	68.7	26.0	C	41
N3´4´-1	(*cis*)-3´,4´-[OH]$_2$,	160.2	111.7	144.5	128.8	113.8	155.7	111.2	153.8	111.7	78.8	71.1	60.1	C	151,183, 196,153
N3´4´-2	(*cis*)-3´-OH, 4´-OMe	160.6	112.6	143.7	128.9	114.6	159.7	109.6	156.7	112.3	78.8	71.0	70.6	C	195
N3´4´-3	(*cis*)-3´-OH, 4´-OEt	160.7	112.6	143.8	128.8	114.6	156.8	109.7	154.8	112.4	78.8	70.3	69.6	C	196
N3´4´-4	(*cis*)-3´-OSO$_3^-$K$^+$, 4´-OH,	159.9	111.8	144.5	128.9	113.8	155.4	111.2	153.8	111.8	77.6	76.5	58.8	D	158
N3´4´-5	(*cis*)-3´-OH, 4´-OCO-C(Me)=CHMe (*Z*)	159.9	114.5	143.3	129.3	113.0	157.0	107.3*	154.3	112.3*	78.6	71.6	63.3	C	198
N3´4´-6	(*cis*)-3´-OAc, 4´-OCO-C(Me)=CHMe (*Z*)	160.0	114.4	143.1	129.2	113.4	156.8	107.8*	154.4	112.6*	78.7	70.6	60.2	C	198
N3´4´-7	(*cis*)-3´-OH, 4´-OCO-CH=CMe$_2$	159.6	113.0	143.3	129.2	114.6	157.0	107.2*	154.4	112.4*	78.7	71.6	62.9	C	195,198,199
N3´4´-8	(*cis*)-3´-OAc, 4´-OCO-CH=CMe$_2$	159.8	113.2	143.2	129.1	114.3	156.6	107.4*	153.9	112.5*	71.3	70.6	59.4	C	195,198
N3´4´-9	(*cis*)-3´-OCO-CH=CMe$_2$, 4´-OH	160.6	112.5	143.9	128.7	114.5	156.1	110.7*	156.1	112.3*	77.8	71.6	60.2	C	195,198,151
N3´4´-10	(*cis*)-3´-OCO-CH=CMe$_2$, 4´-OAc	159.8	113.2	143.1	129.1	114.4	156.4	107.5*	154.0	112.5*	77.6	70.7	59.6	C	195,198
N3´4´-11	(*cis*)-3´-OCO-C(Me)=CHMe (*Z*), 4´-OEt	160.7	112.7	143.4	128.4	114.3	156.1	108.2*	154.8	112.3*	76.6	70.6	69.4	C	153,200
N3´4´-12	(*cis*)-3´-OCO-CH=CMe$_2$, 4´-OEt	160.8	112.4	143.6	128.5	114.6	156.2	108.6*	155.0	112.8*	79.7	69.9	69.5	C	196

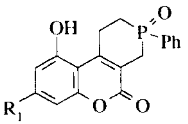
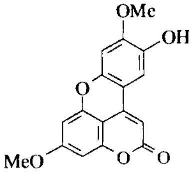
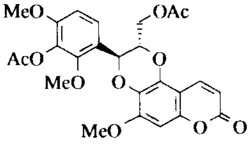
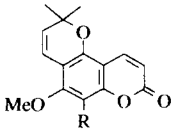
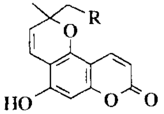
N3′4′-13	(*cis*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OAc,	160.4	113.4	143.8	129.8	115.0	154.6	107.7*	157.2	113.0*	77.6	70.8	60.5	C	153,200-202
N3′4′-14	(*cis*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OCOPr^i,	159.8	114.4	143.2	129.1	113.3	156.9	107.5*	154.5	112.5*	78.2	70.0	60.8	C	198
N3′4′-15	(*cis*)-3′,4′-[OCO-CH$_2$Pr^i]$_2$	159.7	113.2	143.2	129.3	114.4	156.6	107.3*	154.0	112.5*	72.2	70.2	60.4	C	165,195
N3′4′-16	(*cis*)-3′-OCO-CH$_2$Pr^i, 4′-OCO-C(Me)=CHMe (*Z*)	159.7	113.2	143.1	129.2	114.4	156.6	107.3*	154.0	112.5*	72.2	70.2	60.2	C	195
N3′4′-17	(*cis*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OCO-CH$_2$Pr^i,	159.7	113.2	143.1	129.2	114.4	156.6	107.4*	154.0	112.5*	77.4	70.5	60.4	C	153,195,200
N3′4′-18	(*cis*)-3′-OCO-CH=CMe$_2$, 4′-OCO-CH$_2$Pr^i	159.8	113.2	143.1	129.1	114.4	156.7	107.6*	154.1	112.6*	77.5	70.4	59.6	C	196
N3′4′-19	(*cis*)-3′,4′-[OCO-C(Me)=CHMe (*Z*)]$_2$	160.3	111.8	144.8	129.0	114.1	156.2	109.0*	150.8	111.9*	77.1	70.1	59.9	C	44,153,196 198,200
N3′4′-20	(*cis*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OCO-CH=CMe$_2$,	159.8	113.3	143.1	129.1	114.3	156.8	107.8*	154.1	112.5*	77.5	70.5	59.6	C	153
N3′4′-21	(*cis*)-3′,4′-[OCO-CH=CMe$_2$]$_2$	159.8	113.2	143.2	129.0	114.4	156.8	107.6*	154.1	112.5*	77.3	69.5	59.8	C	196
N3′4′-22	(*cis*)-3′-OCO-C(Me)=CHMe (*Z*), 4′-OCO-CH=CH(*trans*)-(4″-OH-Ph)	160.1	114.6	143.4	129.2	113.1	156.9	107.4*	154.1	112.6*	77.5	70.2	59.9	C	203
N3′4′-23	(*cis*)-3′-OCO-CH=CMe$_2$, 4′-OCO-CH=CH-(*trans*)-(*p*-OH-Ph),	160.1	114.5	143.2	129.1	113.2	156.9	107.9*	154.1	112.6*	77.8	70.4	60.0	C	203
N3′4′-24	(*cis*)-3′-O-β-D-glc*p*, 4′-OH	160.3	111.9	144.6	129.1	113.8	155.5	110.6*	154.0	112.0*	77.6	78.2	58.1	C	195

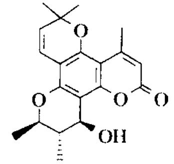
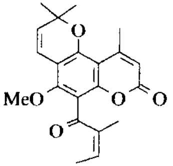
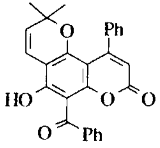
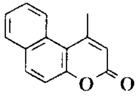
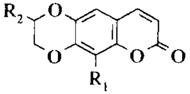
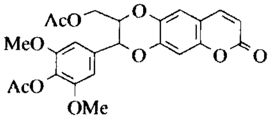
N3′4′-25		159.0	113.2	144.4	131.6	115.4	157.7	109.9*	155.4	114.0*	80.4	72.9	76.7	A	189
N3′4′-26	(*trans*)-3′,4′-$[\mathrm{OH}]_2$,	161.5	112.0	144.4	128.4	114.8	156.4	111.8*	154.3	112.5*	79.5	74.8	66.4	C	151,183, 196,197
N3′4′-27	(*trans*)-3′-OH, 4′-OMe,	160.8	112.8	143.6	128.6	114.6	156.1	108.9*	155.1	112.6*	78.4	74.1	70.7	C	44,195
N3′4′-28	(*trans*)-3′-OH, 4′-OEt,	160.9	112.8	143.6	128.5	114.6	156.3	109.3*	155.1	112.6*	78.4	72.7	71.4	C	196
N3′4′-29	(*trans*)-3′-OAc, 4′-OMe,	160.7	112.8	143.6	128.6	114.5	155.9	108.1*	154.8	112.4*	76.4	70.9	70.3	C	195
N3′4′-30	(*trans*)-3′,4′-$[\mathrm{OAc}]_2$,	159.9	113.2	143.3	129.2	114.5	156.5	106.8*	154.5	112.6*	77.4	72.0	63.9	C	195
N3′4′-31	(*trans*)-3′-OCO-$\mathrm{CH_2Pr^i}$, 4′-OH	160.6	112.6	143.9	128.5	114.8	156.0	110.8*	154.5	112.4*	77.3	73.9	63.2	C	151,195
N3′4′-32	(*trans*)-3′-OCO-C(Me)= CHMe (*E*), 4′-OAc,	160.5	113.8	143.8	129.6	114.9	154.9	107.1*	157.2	112.9*	77.6	71.6	63.7	C	202
N3′4′-33	(*cis*)-3′-OCO-$\mathrm{CH_2Pr^i}$, 4′-OCO-CH=$\mathrm{CMe_2}$,	159.9	113.2	143.2	129.1	114.4	156.6	107.5*	154.1	112.5*	77.6	70.2	59.6	C	165
N3′4′-34	(*cis*)-3′,4′-$(\mathrm{OCO\text{-}CH{=}CMe_2})_2$	160.0	113.2	143.2	129.0	114.4	156.8	107.6*	154.1	112.6*	77.7	69.4	59.8	C	165
N3′4′-35	(*trans*)-3′-O-β-D-glc*p*, 4′-OH	160.3	111.7	144.6	128.4	114.0	155.8	110.3*	154.3	111.8*	77.7	80.6	62.1	C	183
N3′4′-36	3′-(R)-OCO-C(Me)=CHMe (*Z*), 4′-keto	159.4	113.9	143.0	134.6	114.8	161.8	108.1*	153.5	112.7*	82.3	76.4	184.3	C	151,153 200,204

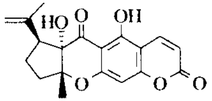
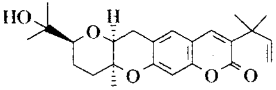
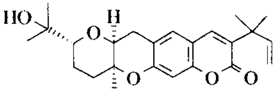
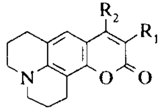
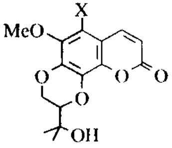
O34-1	 R = H	156.6	137.2	122.8	121.9	124.4	128.8	116.6	149.7	116.9	65.8	126.7	117.8	C	55
O34-2	R = CH$_2$O-Ph	156.7	139.9	125.3	125.0	124.7	128.8	117.3	149.5	117.0	64.9	125.9	130.3	C	55
O34-3	R = CH$_2$O-(*o*-Cl-Ph)	156.7	140.0	125.3	124.7	125.1	128.9	117.4	149.6	117.1	65.0	125.7	129.9	C	55
O34-4	R = CH$_2$O-(*p*-Cl-Ph)	156.6	140.0	125.1	124.7	124.9	128.9	117.4	149.6	117.0	64.9	126.7	130.1	C	55
O34-5	R = CH$_2$O-(*o*,*p*-Me$_2$-Ph)	156.7	139.9	125.4	125.1	124.6	128.7	117.2	149.5	117.2	64.9	125.3	130.7	C	55
O34-6	 R = H	160.6	101.5	160.1	122.6	124.0	132.2	116.7	153.2	114.9	67.3	117.0	119.1	C	55
O34-7	R = CH$_2$O-Ph	159.7	101.4	161.7	123.0	124.0	132.5	116.4	153.2	114.7	67.2	113.0	129.4	C	55
O34-8	R = CH$_2$O-(*o*-Cl-Ph)	159.9	101.2	161.7	123.1	124.1	132.6	116.5	153.2	114.7	67.4	112.9	128.7	C	55
O34-9	R = CH$_2$O-(*o*,*p*-Cl-Ph)	159.9	101.1	161.9	123.1	124.1	132.7	116.5	153.2	114.7	67.4	113.1	128.5	C	55
O34-10	R = CH$_2$O-(*o*-NO$_2$-Ph)	160.0	100.9	161.8	123.1	124.1	132.7	116.5	153.2	114.7	67.5	113.4	127.6	C	55
O34-11	 R = 	161.8	100.0	159.4	115.5	122.6	123.1	131.9	153.2	116.7	83.1	117.2	125.0	C	63
O34-12	R = 	163.1	100.4	158.9	122.2	123.7	131.2	116.5	152.3	115.9	79.8	31.4	17.4	C	102
O34-13	R = 	160.9	99.9	159.0	122.6	123.7	132.1	115.4	153.2	116.6	83.1	125.0	117.3	C	59
O34-14	R = 	160.5	99.4	158.9	122.6	123.9	132.1	116.8	153.2	117.3	83.2	125.0	117.3	C	59
O34-15	R = 	161.0	99.9	159.0	122.6	123.4	132.1	115.4	153.0	116.7	83.2	123.9	117.2	C	59

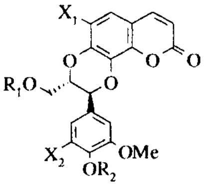
O34-16	R = 	160.7	100.0	159.0	122.6	123.6	132.1	115.5	153.2	116.8	83.2	125.1	117.3	C	59
															
O34-17	R_1 = Et, R_2 = H	163.2	99.8	159.1	122.3	123.6	131.2	116.5	152.3	115.9				C	57
O34-18	R_1 = Et, R_2 = Me	163.1	100.8	159.9	122.3	123.6	131.2	116.4	152.4	116.2				C	57
															
O34-19	R_1 = Me, R_2 = 	163.1	100.4	158.9	122.2	123.7	131.2	116.5	152.3	115.9				C	57
O34-20	R_1 = Me, R_2 = 	163.1	100.8	158.9	122.4	123.6	131.1	116.6	152.5	116.1				C	57
															
O34-21	R_1 = R_2 = H	163.5	99.2	158.0	122.4	123.7	131.2	116.4	152.0	116.0				C	57
O34-22	R_1 = Me, R_2 = Pr^i	163.7	99.9	158.2	122.6	123.7	131.2	116.4	152.3	115.9				C	57
O34-23	R_1 = Pr^i, R_2 = Me	163.7	99.4	157.8	122.6	123.7	131.2	116.5	152.3	115.9				C	57

O34-24			163.2	99.4	158.0	122.4	123.5	131.1	116.4	152.3	115.9	C	57
O34-25			163.6	99.0	160.7	122.2	123.6	131.6	116.5	152.6	115.7	C	57
O34-26			163.1	100.2	159.2	122.3	131.1	131.1	116.5	152.5	116.5	C	57
O34-27			162.0	100.0	156.0	122.3	124.1	132.0	116.7	152.6	114.6	C	57
O34-28		X = O	186.2	127.0	132.2					136.0	128.5	C	12
O34-29		X = S	212.5	134.5	130.2					135.0	127.9	C	12

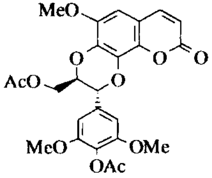
														
O34-30	R = Me	160.0	114.8	150.3	152.6	105.7	142.2	108.3	155.6	112.4				C	206
O34-31	R = $Pent^n$	161.0	113.0	149.5	152.5	106.2	147.4	107.4	155.8	112.0				C	206
O45-1		160.9	100.5	153.7	150.5	96.4	163.0	93.1	154.5	99.8				D	115
O56-1		161.2	112.3	137.6	139.5	128.9	152.3	93.3	149.6	103.3				C	207
O56-2															
	R = CH=CH-C(Me_2)OOH (*Z*)	161.1	116.5	138.5	149.4	110.5	155.4	112.5	152.2	106.4	71.6	129.4	113.2	C	62
O56-3	R = CH=CH-C(Me_2)OOH (*E*)	161.1	116.6	138.5	149.3	110.9	157.2	111.3	152.7	106.3	71.4	129.3	112.8	C	62
															
O56-4	R = CH=CH-C(Me_2)OH	162.8	110.2	139.6	151.3	106.3	156.4	95.7	155.4	103.2	80.0	126.0	117.2	C	209
O56-5	R = CH=CH-C(Me_2)OOH	161.6	111.5	138.6	150.6	106.6	158.5	91.8	156.2	103.6	79.9	126.2	117.2	C	209

O56-6		160.7	110.7	151.7	154.7	106.1	153.0	104.0	153.3	106.0				C	52
O56-7		159.7	113.3	151.9	154.4	111.9	153.6	114.1	152.6	108.0	77.6	116.1	130.9	C	52
O56-8		158.0	112.6	155.3	156.4	105.7	161.5	103.8	155.9	102.4				C	164
O56-9		160.3	116.7	154.3	130.4	131.5	133.8	117.9	154.9	114.6				C	172
															
O67-1	R_1 = OMe, R_2 = C(Me)=CH$_2$	160.5	114.5	143.4	108.9	141.1	140.3	142.5	139.2	112.7	75.6	67.6		C	175
O67-2	R_1 = H, R_2 = C(Me$_2$)OH	161.3	114.4	143.0	114.1	140.8	146.8		104.8	112.8	78.7	65.4		C	186
O67-3		160.9	114.4	142.7	114.3	139.9	146.7	105.0	149.3	113.2				C	193

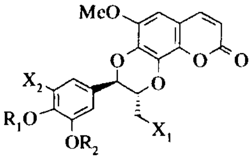
O67-4			160.2	112.1	138.1	160.5	101.5	161.3	97.4	162.1	103.5				C	188
O67-5			162.6	130.3	138.2	122.9	124.9	160.2	96.8	154.4	112.7	75.3	74.2	32.0	C	197
O67-6			162.4	130.3	137.9	123.0	124.3	159.8	96.7	154.4	112.7	84.0	87.2	30.5	C	197
																
O67-7	R_1 = H, R_2 = Me		162.2	107.8	150.8	121.4	117.6	145.4	106.4	152.7	108.6				C/CCl	64
O67-8	R_1 = COOEt, R_2 = H		157.5	108.5	148.7	126.8	118.7	148.1	107.7	153.5	105.9				C/CCl	64
O78-1		X = H	160.9	114.1	143.8	100.2	145.8	139.0	132.4	136.8	111.6	65.9	79.0		C	142,205,208
O78-2		X = OMe	160.6	113.2	138.9	128.8	138.0	141.2	142.4	139.7	107.1	65.8	78.9		C	210



O78-3	$R_1 = R_2 = H, X_1 = OMe, X_2 = H$	160.7	113.8	144.4	101.2	146.2	138.1	133.2	139.4	111.8	77.1*	80.2*	P	211
O78-4	$R_1 = R_2 = Ac, X_1 = OMe, X_2 = H$	160.4	114.3	143.5	100.8	145.7	136.3	132.1	140.7	111.8	76.0	75.6	C	211
O78-5	$R_1 = R_2 = H, X_1 = H, X_2 = OMe$	160.4	113.6	144.3	119.8	113.2	147.6	138.4	149.2	113.6	79.9*	77.8*	P	212
O78-6	$R_1 = R_2 = Ac, X_1 = H, X_2 = OMe$	160.2	113.9	143.8	119.9	113.9	146.5	133.3	150.6	113.7	77.2*	75.5*	C	212



O78-7		160.2	114.2	143.5	101.0	145.8	137.0	133.1	145.7	111.8	77.0*	75.0*	C	213



O78-8	$R_1 = X_1 = X_2 = H, R_2 = Me$	160.7	113.9	144.4	101.3	146.3	138.5	132.6	139.3	112.0	81.5*	74.5*	P	214
O78-9	$R_1 = X_1 = X_2 = H, R_2 = Ac$	160.6	114.2	143.6	100.6	146.0	137.7	132.4	140.9	111.9	81.1*	74.2*	C	214
O78-10	$R_1 = X_2 = H, R_2 = Me, X_1 = OH$	160.8	113.6	144.5	101.1	146.3	138.4	133.0	139.3	111.9	79.9*	77.5*	P	211
O78-11	$R_1 = X_2 = H, R_2 = Me, X_1 = OEt$	160.7	113.3	144.5	101.0	146.3	138.2	132.0	139.2	112.2	79.7*	77.3*	P	125
O78-12	$R_1 = X_1 = OAc, R_2 = Me, X_2 = H$	160.4	114.4	143.5	100.5	145.8	136.9	131.7	140.8	111.9	76.7*	75.1*	C	211
O78-13	$R_1 = X_1 = H, R_2 = Me, X_2 = OMe$	160.8	113.7	144.5	101.0	146.3	138.1	132.5	139.2	111.9			P	215

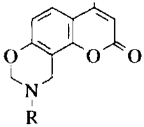
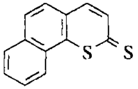
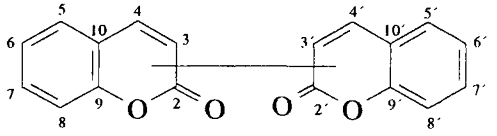
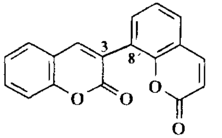
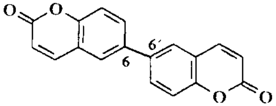
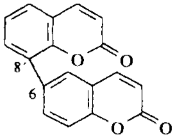
O78-14	 R = Ph	162.9	113.9	152.2	125.9	100.6	144.4	123.7	148.7	118.2	C	216
O78-15	R = *p*-Cl-Ph	162.8	114.1	152.1	125.5	100.4	143.8	120.9	147.9	118.5	C	216
O78-16	R = *o*-OMe-Ph	162.8	113.8	151.8	124.2	101.2	142.7	121.6	147.9	119.5	C	216
O78-17	R = *m*-Me-Ph	162.8	114.2	152.2	125.9	99.8	142.9	122.7	149.0	120.1	C	216
O78-18	R = CH_2-Ph	162.9	113.8	152.2	125.4	100.5	144.6	121.5	150.3	117.4	C	216
O78-19	R = CH_2-CH_2-Ph	161.8	113.9	151.8	124.8	100.2	143.6	120.8	148.5	117.1	C	216
O78-20		206.4	136.6	131.3					141.9	130.9	C	12

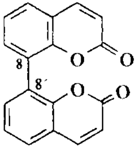
Table 12. ^{13}C chemical shifts of dicoumarins directly connected by one bond (**P**), over more than one bond (**Q**), by rings (**R**). In cases of unsymmetrical dicoumarins the second data row corresponds to the coumarin moiety with dashed atoms numbers



	Substituents	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**	**C-7**	**C-8**	**C-9**	**C-10**	**other carbons**	**Solv.**	**Reference**
	 O O O O 3 8'												
P38'-1	4,4',7'-[OMe]$_3$, 6,6'-Me$_2$, 7-OH	164.0	77.2	170.3	139.3	116.2	159.4	101.1	155.9	109.3		C	217
		162.3	87.7	168.2	138.5	111.5	160.3	109.3	153.9	108.4			
P38'-2	4,4',7,7'-[OMe]$_4$, 5-CH$_2$OH, 5'-Me	161.1	97.9	166.7	144.0	110.6	162.2	98.8	155.1	107.2			
		161.4	87.6	169.3	139.1	111.3	159.6	107.7	153.4	107.7		D	218
	 O O 6 6' O O												
P66'-1	4,4'-[OMe]$_2$, 5,5'-Me$_2$, 7,7'-[OH]$_2$	166.0	87.5	172.6	139.3	124.4	160.5	101.6	157.3	108.3		M	219
P66'-2	4,4',7'-[OMe]$_3$, 5,5'-Me$_2$, 7-OH	162.4	88.1	170.5	138.3	123.9	161.4	97.8	157.4	108.8		M	217,219
		162.4	87.7	170.5	138.3	123.2	159.1	101.0	156.8	108.2			
P66'-3	4,4',7,7'-[OMe]$_4$, 5,5'-Me$_2$	163.0	87.9	170.0	137.2	123.4	160.1	97.4	156.2	108.1		C	219

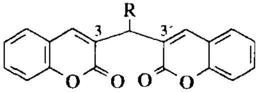


P68′-1	7-OMe, 7′-OH	160.2	112.5	144.1	128.6	118.2	160.6	99.4	155.3	111.4	D	220
		160.1	112.7	144.7	131.1	111.0	159.0	111.2	152.9	111.9		
P68′-2	7,7′-[OMe]$_2$	160.7	113.1	143.6	128.6	117.9	161.2	99.6	156.0	113.0		
		160.2	113.4	143.5	130.8	107.7	160.8	112.3	152.8	113.8	C	220
P68′-3	4,4′,7,7′-[OMe]$_4$, 5,5′-Me$_2$,	163.6	86.5	169.6	136.8	119.0	158.8	100.2	155.3	106.2	D	221
	7-[OH]$_2$	161.7	86.8	169.6	137.3	115.5	158.0	109.3	153.7	106.2		
P68′-4	4,4′,7′-[OMe]$_3$, 5,5′-Me$_2$,	161.4	87.3	169.4	137.1	118.6	158.6	100.3	155.3	106.2	D	221
	7-OH	161.6	86.9	169.3	137.7	110.7	158.9	111.3	152.7	107.6		
P68′-5	4,4′,7,7′-[OMe]$_4$, 5,5′-Me$_2$	161.5	87.4	169.3	136.7	119.4	160.0	97.6	155.9	107.4	D	221
		161.3	87.7	169.2	137.9	111.4	158.8	110.4	152.6	107.7		

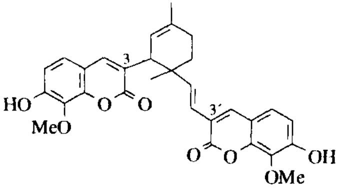
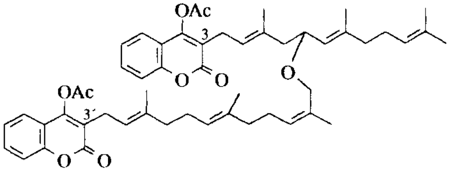
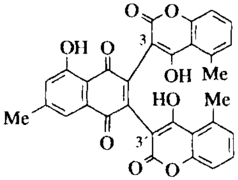


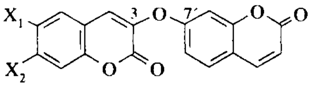
P88′-1	7,7′-[OH]$_2$	160.9	111.3	145.4	129.4	113.0	159.9	107.3	153.8	111.6	D	222
P88′-2	7,7′-[OMe]$_2$	161.0	113.0	143.1	130.4	107.3	159.5	99.2	153.0	112.7	C	223
P88′-3	7-OH, 7′-O-α-L-rham*p*	160.7	111.3	145.1	129.6	112.9	159.7	106.6	153.6	111.4	D	222
		160.5	113.2	145.4	129.6	111.6	157.4	110.2	153.0	113.7		
P88′-4	4,4′-[OMe]$_2$, 5,5′-Me$_2$,	169.4	86.3	153.7	136.8	115.3	158.3	105.9	161.4	105.5	D	224
	7,7′-[OH]$_2$	161.4	86.3	169.4	136.8	111.3	159.4	108.4	153.3	107.4	D	221
P88′-5	4,4′,7,7′-[OMe]$_4$, 5,5′-Me$_2$	169.6	87.7	153.3	138.3	111.3	159.4	108.4	162.8	107.4	C	224
		162.8	87.7	169.4	138.3	111.3	159.4	108.4	153.3	107.4	C	221

P88´-6	4,4´-[OMe]$_2$, 5,5´-Me$_2$, 7,7´-[OAc]$_2$	169.0	89.6	153.0	138.4	121.8	150.4	112.3	161.9	111.2	C	224

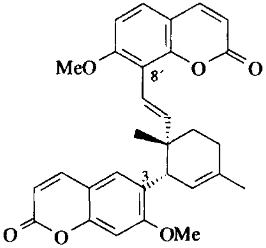


Q33´-1	R = H	166.1	102.7	169.8	124.6	124.9	132.4	116.8	153.3	120.2	D	28
Q33´-2	R = OCOEt	167.9	102.3	164.6	124.2	124.7	132.8	116.4	152.0	116.2	C	29
		167.8										
Q33´-3	R = Me	168.8	106.8	164.1	124.0	124.6	132.4	116.4	152.1	117.0	C	29
		167.3										
Q33´-4	R = CH$_2$OMe	168.2	104.0	164.7	124.0	124.7	132.6	116.4	152.1	116.6	C	29
Q33´-5	R = CH$_2$Ph	168.8	105.4	164.7	124.0	124.6	132.4	116.3	152.1	117.0	C	29
		167.5		164.2	123.9				151.9	116.1		
Q33´-6	R = Et	169.1	105.8	164.8	124.1	124.6	132.4	116.4	152.3	117.1	C	29
		167.3	105.5	164.1								
Q33´-7	R = CH$_2$CH$_2$-SMe	168.8	105.1	164.9	123.9	124.7	132.5	116.4	152.2	116.9	C	29
		167.5		164.2								
Q33´-8	R = Pr^n	169.0	105.9	164.5	124.0	124.6	132.3	116.3	152.2	117.1	C	29
		167.3	105.7	164.1	123.9							
Q33´-9	R = Bu^n	169.0	106.0	164.5	124.0	124.6	132.3	116.4	152.2	117.1	C	29
		167.2	105.8	164.0	123.9							
Q33´-10	R = COOEt	165.3	103.4	165.7	125.0	124.9	133.3	117.3	153.3	118.4	D	28
Q33´-11	R = Ph	169.1	105.5	165.3	124.3	124.8	132.8	116.5	152.3	116.5	C	29
		166.9	104.0	164.5								
Q33´-12	R = *o*-Cl-Ph	168.6	105.1	164.7	124.3	124.8	132.8	116.5	152.2	116.5	C	29
		168.2	104.8									

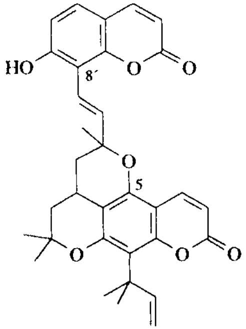
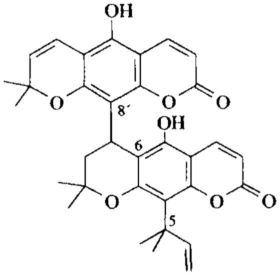
Q33′-13	R = *p*-Cl-Ph	169.1 105.2 165.9 124.4 124.9 132.7 116.6 152.3 116.6 166.7 103.7 164.5	C	29
Q33′-14	R = *p*-NO_2-Ph	168.9 104.7 166.2 123.8 124.4 133.3 116.7 152.4 116.7 167.0 103.3 164.7	C	29
 **Q33′-15**		163.2 126.9 142.4 124.3 115.0 155.2 135.7 148.7 113.9 161.1 121.9 138.1 124.2 114.9 155.7 135.6 148.4 114.2	P	225
 **Q33′-16**		162.0 119.5 154.4 122.4 124.2 131.5 116.7 152.1 116.4 162.0 119.5 154.1 122.4 124.2 131.5 116.7 152.1 116.4	C	60
 **Q33′-17**		159.2 97.6 165.7 137.7 127.6 131.6 114.6 153.9 114.9 159.2 98.1 165.6 137.7 127.6 131.6 114.6 153.9 114.5 (no assignment of the data sets to the individual coumarin moieties)	C	241

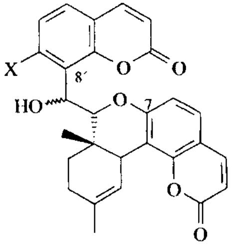
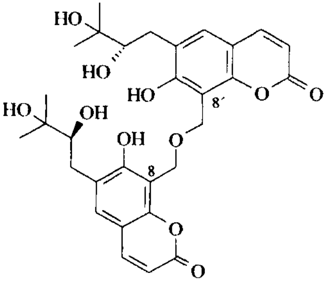


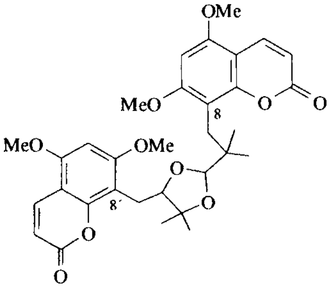
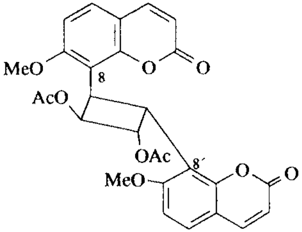
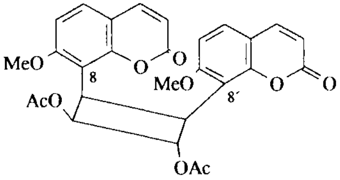
Q37′-1	X_1 = H, X_2 = OH	157.3	135.6	131.4	129.8	113.8	161.0	102.4	153.8	115.2	D	226
		160.4	114.1	144.4	130.2	113.6	160.1	104.1	155.4	114.6		
Q37′-2	X_1 = H, X_2 = OAc	156.8	138.9	129.2	129.3	119.2	152.3	110.3	152.4	117.2	D	226
		160.3	114.4	144.4	130.2	114.2	159.6	104.8	155.4	115.0		
Q37′-3	X_1 = OMe, X_2 = OH	159.8	135.7	131.0	109.4*	145.8^{+}	150.4	102.8*	147.5	110.2	D	227,228
		160.1	113.8	144.1	129.9	113.6§	157.1	104.0§	155.1^{+}	114.4		
Q37′-4	X_1 = OMe, X_2 = OAc	160.3	140.0	129.3	105.7	149.0	155.4	112.0	142.1	116.6	C	228
		158.7	114.2	142.8	126.7	109.0	156.5	115.2	145.7	115.3		
Q37′-5	X_1 = OMe, X_2 =7-OCO-C(Me)OH-COO-(6"-O-β-D-glc*p*)	159.6	137.3	130.1	109.8	146.5	149.0	103.1	146.9	112.4	D	229
		160.1	114.1	144.2	129.9	113.8	156.9	104.6	155.2	114.7		
Q37′-6	X_1 = OMe, X_2 =[O-β-D-glc*p*-(6′′-OCO-CH_2-C(Me)OH-CH_2-COOH)]	156.7	137.0	129.7	109.5	146.2	148.7	102.9	146.6	112.2	D	222
		159.9	113.9	144.0	129.9	113.5	159.3	104.3	154.9	114.5		

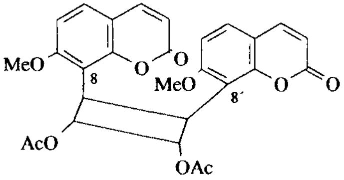


Q38′-1	161.7	112.3	144.2	129.7	129.6	160.9	97.9	154.4	111.8	C	230
	161.0	113.0	143.9	126.3	107.5	159.7	114.8	152.3	113.2		

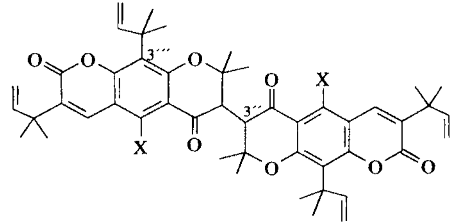
Q58´-1		160.0 160.0	108.9 111.1	139.1 145.0	148.0 128.0	104.1 112.8	155.6 159.3	112.1 110.1	152.7 152.8	101.8 111.3	D	231
Q68´-1		159.9 160.4	108.3 109.4	139.9 140.2	150.6 147.7	110.6 105.8	157.7 153.8	113.3 112.0	151.8 152.6	103.2 103.2	D	181

Q78´-1		161.4	113.5	145.6	128.2	114.6	158.7	114.8	155.3	114.0	A	232
	X = OH	161.0	112.6	145.9	129.9	115.3	163.5	114.3	153.0	112.8		
Q78´-2	X = OMe	161.4	112.3	144.1	128.2	108.0	157.3	114.0	153.8	112.4	C	232
		160.0	113.4	143.8	126.3	113.8	160.0	117.8	153.8	113.8		
Q88´-1		161.1	112.8	144.1	128.5	118.4	155.7	117.4	152.8	112.7	C	233

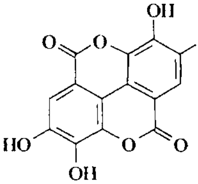
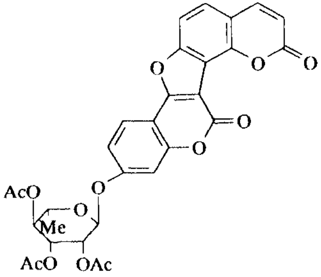
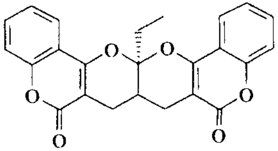
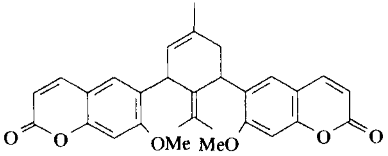
Q88´-2		161.3 110.3 138.5 155.1 90.1 161.7 107.2 154.0 103.3 161.5 110.6 138.7 155.6 90.6 162.0 107.4 154.6 103.7	C	106
Q88´-3		161.8 113.1 143.7 127.6 108.2 153.0 116.6 160.5 113.0	C	234
Q88´-4		160.6 112.7 143.8 126.7 106.3 153.4 115.0 160.3 112.5 160.4 112.4 143.7 127.5 106.6 153.3 115.0 160.2 112.4 (no assignment of the data sets to the individual coumarin moieties)	C	234

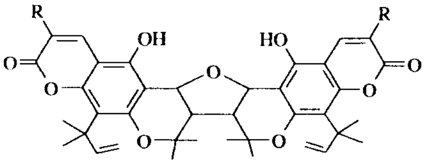


Q88´-5		160.4	112.5	143.7	127.0	106.7	153.2	115.9	160.3	112.5	C	234

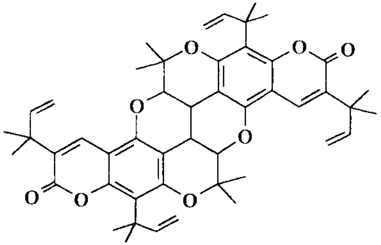


Q3´´3´´´-1	X = OH	159.2	130.1	132.4	158.6	105.2	158.9	114.3	158.8	104.1	C	190
Q3´´3´´´-2	X = Me	159.2	130.9	132.6	151.2	112.4	154.1	118.8	153.4	108.2	C	235

R-1		158.8	110.6	107.3	110.6	110.6	148.0	139.2	136.6	107.3	D	236
R-2		159.1	115.7	143.3	123.1	108.6	156.9	115.7	148.3	115.7	C	237
		159.1	103.3	160.6	126.3	114.2	159.4	104.3	155.4	106.6		
R-3		162.2	100.2	156.4	122.4	124.1	132.1	116.9	152.8	114.9	C	57
R-4		162.4	113.2	144.8	127.8	131.5	160.5	99.1	154.0	112.5	C	85
		162.3	113.0	144.5	125.0	130.8	160.2	98.6	154.0	112.1		

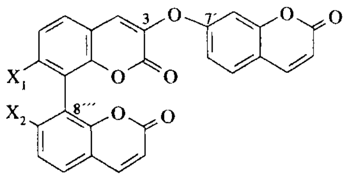


R-5	R = H	159.9	109.5	139.4	148.6	107.4	155.2	113.9	153.4	102.7				D	238
		159.8	109.9	139.8	152.1	106.6	155.0	113.3	153.7	103.8					
R-6	R = C(Me$_2$)CH=CH$_2$	158.6	127.5	132.8	148.2	107.5	154.0	112.8	152.4	102.7				D	238
		158.5	127.9	133.3	151.8	106.8	154.3	113.2	152.7	103.8					



R-7	159.7	128.7	132.3	148.1	95.8	154.2	113.1	152.8	102.8	77.8	73.2	26.0	?	239

Table 13. ^{13}C chemical shifts of tricoumarins (S)

	Substituents	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**	**C-7**	**C-8**	**C-9**	**C-10**	**Solv.**	**Reference**
												
S-37′8′′-1	$X^1 = X^2 = OH$	156.8	135.0	131.3	129.1	113.2	158.8	106.9	151.2	110.8	D	226
		159.9	113.8	143.9	129.8	113.2	159.5	103.9	154.9	114.3		
		160.4	111.0	144.9	128.8	112.8	159.4	107.1	153.4	111.3		
S-37′8′′-2	$X^1 =$ OH,	156.5	135.0	131.1	129.1	111.4	158.6	106.6	150.9	110.6	D	226
	$X^2 =$ O-α-L-rham*p*	159.9	113.8	143.9	129.9	113.0	159.4	104.2	154.8	114.3		
		160.1	113.0	144.6	129.4	113.3	157.0	109.6	152.6	113.5		
S-37′8′′-3	$X^1 =$ OH,	156.6	135.1	130.9	128.9	111.3	158.4	106.6	151.0	110.7	D	222
		159.9	113.8	144.0	129.8	112.8	159.4	104.2	154.9	114.3		
		160.1	112.8	144.6	129.2	113.1	157.4	109.5	152.6	113.1		
S-37′8′′-4	$X^1 =$ OAc,	157.0	140.3	127.2	128.5	120.3	151.2	114.0	150.5	117.2	C	222
	$X^2 =$ apio*f* triacetate	160.8	115.5	143.5	129.8	114.8	159.4	106.6	156.0	115.8		
		161.1	115.1	143.7	130.1	111.6	156.9	109.8	153.5	115.0		
S-37′8′′-5	$X^1 =$ OAc,	156.3	138.5	129.4	129.8	120.2	150.6	113.3	150.1	117.3	D	226
	$X^2 =$ O-α-L-rham*p*	159.9	113.9	144.4	130.4	114.2	159.3	104.5	155.4	115.1		
	triacetate	160.3	114.5	144.8	130.8	110.9	155.6	108.3	152.5	114.2		

References to Section 6 (Tables 5-13)

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