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Short communication

CARBON-13 NMR SPECTROSCOPY OF HETEROCYCLIC COMPOUNDS

Part VII. The characterisation of 7-fluorocoumarin from a 20-MHz study of chemical shifts, carbon—proton and carbon—fluorine coupling constants

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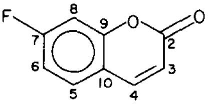
Almost no investigations have been made of compounds containing the 2-*H*-1-benzopyran-2-one ring system with a fluorine substituent. The only monofluorocoumarin so far described appears to be the 3-derivative [1]. No monosubstituted coumarins bearing a fluorine in the benzenoid ring have hitherto been reported, although the synthesis of 6- and 7-fluoro-4-hydroxycoumarin has been described [2].

Since the coumarins are an important class of compounds, many investigations have aimed at discovering suitable techniques for investigating the nature and position of substituents. The general application of ^{1}H-NMR spectroscopy in this field has been summarised in a recent book [3]. However, while signals from the protons in the heterocyclic ring are widely separated and readily identified, those from the carbocyclic ring are often found to have closely similar chemical shifts, which give rise to complex 'second order' spectra difficult to analyse in terms of molecular substitution patterns.

In previous papers [4] we have demonstrated the convenient use of carbon-13 spectroscopy for approaching problems of molecular structure in a range of variously substituted coumarins. Shift data, and information on both short- and long-range C—H coupling constants can allow an unambiguous assignment of structure relying only to a minimal extent on correlations with data derived from dissimilar skeletal systems. Here a synthesis is given for 7-fluorocoumarin (I), and the ease with which the structure is assigned using ^{13}C-NMR rather than a traditional ^{1}H-NMR approach is illustrated.



I

The synthesis was achieved by a parallel reaction to that for 7-bromocoumarin [5] using *m*-fluorophenol, and afforded a somewhat higher yield than the former. Proton-NMR spectroscopy gave a spectrum on which the only readily identifiable features were the signals from H_3 and H_4, plus a complex second-order three-proton signal. Conversely, carbon spectra obtained with and without proton-noise-decoupling proved simple to interpret. The derived carbon chemical shifts, together with $^{13}C—^{1}H$ and $^{13}C—^{19}F$ coupling constants are summarised in Table 1.

The proton-noise-decoupled spectrum consists of nine signals, all but one of which are doublets owing to the presence of carbon—fluorine coupling. Four signals are identified as arising from carbons bearing no proton substituent by virtue of their lower intrinsic intensities and from the absence of a large one-bond $^{13}C—^{1}H$ coupling constant on the proton-coupled spectrum. The signal at 163.6δ is assigned to C_7 by virtue of a large (251.5 Hz) $^{1}J(CF)$ coupling (compare 245.3 Hz in fluorobenzene [6]). The carbonyl carbon, at 159.2δ, can be recognised [4] both by characteristic couplings to H_3 and H_4 and by its typical chemical shift. The other quaternary carbons, C_9 and C_{10}, are individually assigned by analogy with their observed shifts in other coumarins. Signals for C_3 and C_4 are known [4] to be relatively unperturbed by substituents in the carbocyclic ring and can be assigned accordingly. Their relative positions and coupling patterns are typical; there is an inter-ring C_4H_5 coupling of 5 Hz. It is interesting to note that $^{6}J(C_3F_7)$ is larger than $^{5}J(C_4F_7)$.

TABLE 1

Spectral parameters for 7-fluorocoumarin

	δ[a]	C—H couplings[b]		C—F couplings[b]	
C_2	159.2	C_2H_3 C_2H_4	5.0 11.5	—	
C_3	114.7	C_3H_3	174.0	C_3F_7	3
C_4	143.3	C_4H_4 C_4H_5	167.5 5.0	C_4F_7	ca. 1
C_5	130.1	C_5H_4 C_5H_4	3.5 167.5	C_5F_7	10.5
C_6	111.9	C_6H_6 C_6H_8	169.0 4.0	C_6F_7	23.0
C_7	163.6	C_7H_5 C_7H_6 C_7H_8	13.0 5.0 4.0	C_7F_7	251.5
C_8	103.5	C_8H_6 C_8H_8	3.5 169.0	C_8F_7	25.5
C_9	154.6	c		C_9F_7	13.0
C_{10}	115.5	d		$C_{10}F_7$	3.0

[a] In p.p.m. from TMS as a secondary reference (± 0.1 p.p.m.). [b] Given to the nearest 0.5 Hz. [c] Complex multiplet, unresolved. [d] Obscured by part of the signal from C_8.

The signs of couplings are undetermined; it is probable that in the latter case two contributing mechanisms are present, with opposite signs, while in the F_7—H_3 interaction these mechanisms are of like sign and reinforce each other.

The assignments remaining are for C_5, C_6 and C_8. Examination of shift data for fluorobenzene [7] suggests that substituent chemical shifts (SCS) follow an alternating pattern relative to the carbon signal for benzene (C_3 + 35.1, C_o − 14.1, C_m + 1.6, C_p − 4.4 p.p.m.). The CF couplings in fluorobenzene [6] are $^2J = 21.0$, $^3J = 7.7$ and $^4J = 3.3$ Hz; these data readily permit the assignments given in Table 1. SCS values for 7-fluorocoumarin relative to coumarin are given in Table 2. It is seen that an alternating shift perturbation relative to the parent compound is again present, but with values of slightly diminished magnitudes. Relative to the parameters for fluorobenzene, all CF couplings in the carbocyclic ring except for the *para* interaction are conversely slightly enhanced.

In several respects these data parallel those for 7-hydroxycoumarin [4]. The SCS values are similar, while the long-range couplings C_6H_8 and C_8H_6 across the substituent are reduced in magnitude relative to the values in coumarin, and that from the substituent carbon C_7 to H_5 is noticeably enhanced. The assignment of C_5 is further reinforced by the presence of a small transannular coupling to H_4.

It may be concluded that assignments of carbon signals and thence determination of structure for fluoroheterocycles of this general type can be made quite readily. The use of proton-coupled spectra gives ^{13}C—^1H couplings which are of particular value and significance as are the ^{13}C—^{19}F interactions directly obtainable from proton-noise-decoupled spectra.

Carbon spectra were determined as previously [4]. In order to maximise digital resolution, coupled spectra were permitted to "fold". Spectra were recorded using DMSO-d_6 and referenced to the solvent signal, the known separation from TMS being employed in order to present chemical shift data in the conventional manner.

7-Fluorocoumarin

m-Fluorophenol (11.2 g) was dissolved in concentrated H_2SO_4 (25 ml) and warmed to 120°C with stirring. Malic acid (13.4 g) was added in small portions,

TABLE 2

Substituent chemical shift (SCS) values

Carbon	2	3	4	5	6	7	8	9	10
Substituent chemical shift[a]	−0.4	−1.2	−0.4	+2.0	−12.2	+32.2	−12.4	+1.2	−3.0

[a] SCS values are given as changes in shifts, expressed in p.p.m., between coumarin and 7-fluorocoumarin, both in DMSO as solvent.

and the mixture stirred for a further 0.5 h, then allowed to cool. The golden solution was poured into ice, when a yellowish precipitate formed. This suspension was recovered by steam distillation, yielding a white solid (1.2 g). This was recrystallised (EtOH); yield 0.97 g, m.p. 137°C. Found: C, 65.6; H, 3.2; F, 11.7; $C_9H_5FO_2$ requires: C, 65.85; H, 3.05; F, 11.6% [8].

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