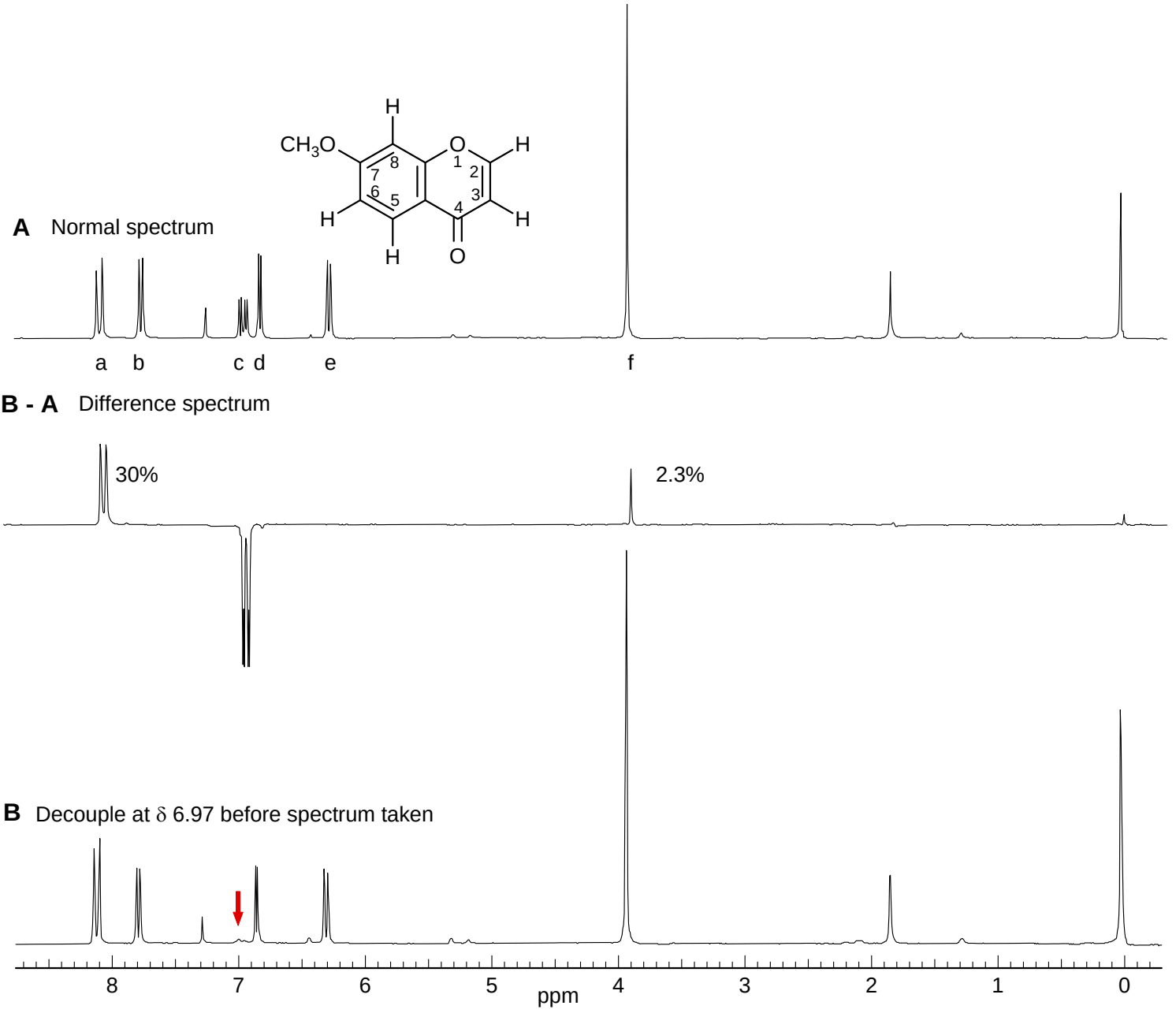
Problem R-06L ($C_{10}H_8O_3$)

200 MHz ^{1}H NMR spectrum in $CDCl_3$

Source: *Magn. Resonsn. Chem.* **1985**, *23*, 90 (Reich digitized hard copy)



PLT ex-3-2006-07-gq.plt

Problem R-06L. On the next page are reproduced three spectra of 7-methoxychromanone. Spectrum A is a normal spectrum. Spectrum B was obtained by preirradiating signal *c* with the decoupler before taking the spectrum. The decoupler was off during the acquisition. The middle spectrum is the difference between the two (B minus A) (*MRC* **1985**, *23*, 90).

(a) What kind of experiment is this?_____

(b) Assign the signals to the appropriate proton (m, *J* given). Use the numbering given on the figure.

a d, 9.3 _____ *b* d, 5.9 _____ *c* dd, 9.3, 2.7 _____

d d, 2.7 _____ *e* d, 5.9 _____ *f* s _____

(c) Explain why signal *c* disappears in Spectrum B and is negative in Spectrum B-A.

(d) Explain why Spectrum B-A has positive signals for *a* and *f*, but not for any of the others (these signals are 30% and 2.3%, respectively, of the corresponding signals in Spectrum A).

(e) Why is the increase in signal *f* so small compared to the increase in signal *a*?

(f) Irradiation of signal *d* causes a 3.1% increase in signal *f*. What does this tell you about the conformation of the methoxy group?

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Problem R-06L. On the next page are reproduced three spectra of 7-methoxychromone. Spectrum A is a normal spectrum. Spectrum B was obtained by preirradiating signal *c* with the decoupler before taking the spectrum. The decoupler was off during the acquisition. The middle spectrum is the difference between the two (B minus A) (*MRC* **1985**, *23*, 90).

2 (a) What kind of experiment is this? Homonuclear NOE (1D NOESY)

(b) Assign the signals to the appropriate proton (m, *J* given). Use the numbering given on the figure.

a d, 9.3 H^5 *b* d, 5.9 H^2 *c* dd, 9.3, 2.7 H^6

8 *d* d, 2.7 H^8 *e* d, 5.9 H^3 *f* s OCH_3

(c) Explain why signal *c* disappears in Spectrum B and is negative in Spectrum B-A.

The signal *c* has been saturated by the decoupler (α and β states equal population), hence no signal. Subtracting A (normal intensity) from B gives a negative peak for B-A.

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(d) Explain why Spectrum B-A has positive signals for *a* and *f*, but not for any of the others (these signals are 30% and 2.3%, respectively, of the corresponding signals in Spectrum A).

The *a* and *f* signals are enhanced in intensity in spectrum B by the NOE effect from signal *c*. NOE effects are
3 observed only for protons close in space to the irradiated proton (*c*). Thus *c* must be close in space to *a* and *f*.

(e) Why is the increase in signal *f* so small compared to the increase in signal *a*?

Three reasons:

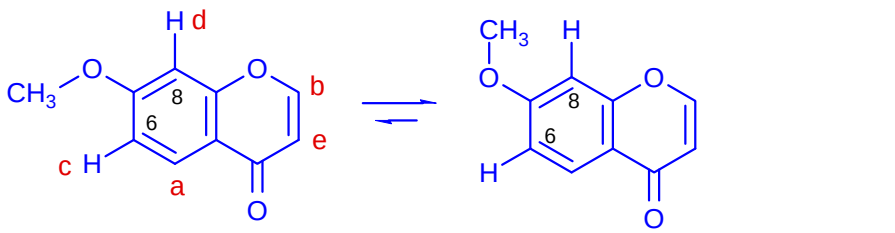
1. The protons in the methyl group principally relax each other, H_6 is thus a minor contributor to the total relaxation of the CH_3 protons.

3+2

2. The methyl group is partially relaxed by both protons H_6 and H_8 so either one of them can only contribute a smaller part.

3. Methyl groups often show substantial contributions from SR (Spin-Rotation) relaxation (τ_c is too short for effective DD relaxation). Only the fraction of relaxation caused by the DD mechanism contributes to the NOE.

(f) Irradiation of signal *d* causes a 3.1% increase in signal *f*. What does this tell you about the conformation of the methoxy group?



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2.3% NOE (H_6 -> Me) 3.1% NOE (H_8 -> Me)

Probably a little more of this conformation