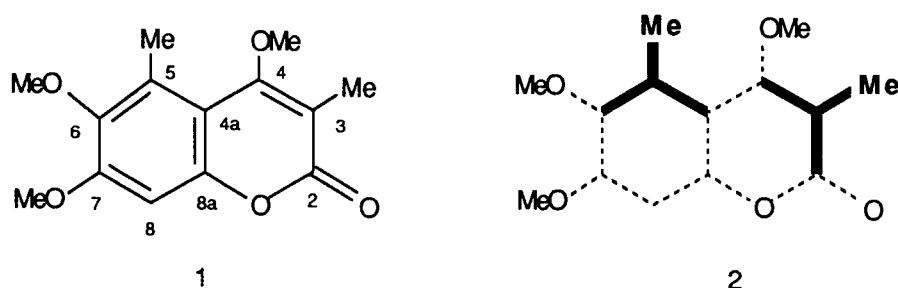


## C13 NMR ASSIGNMENTS FOR A POLYSUBSTITUTED COUMARIN FROM SHORT AND LONG-RANGE H-C CORRELATION EXPERIMENTS

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The assignment of aromatic carbon resonances in molecules with many substituents is often problematical, because the aromatic carbons are mainly quaternary and a means of distinguishing between them is not obvious. The problem has been solved in an economical and elegant manner for the coumarin 1 by a consideration of long-range H-C correlations, obtained using the FLOCK (Reynolds *et al* 1989) pulse sequence, in combination with the usual one-bond (HETCOR or H-C COSY) experiment.



To assign all the resonances it is necessary to know at the outset only that C-2, the carbonyl carbon, resonates at low field. Correlations with the protons of the methyl attached to C-3 from C-2, 3 and 4 allow these resonances to be assigned (structure 2, in bold). Correlation of 4-OMe with C-4 allows the 4-OMe proton resonance to be assigned. Having assigned the 3-Me protons it is possible to assign those for 5-Me, which show correlations with C-4a, 5 and 6 (structure 2, in bold). The 6-OMe protons correlate with C-6, which has been assigned. This leaves only C-7, 8 and 8a. The former correlates with the remaining OMe, C-8 is protonated and readily distinguished, which leaves C-8a as the remaining resonance. All that is then required is to use the one-bond correlations from H-C COSY to assign the carbon resonances for the methyl and methoxy groups, which allows the following assignments to be made: C-2, 164.4 / C-3, 110.8 / C-4, 166.9 / C-4a, 109.6 / C-5, 128.7 / C-6, 144.5 / C-7, 155.3 / C-8, 98.3 / C-8a, 151.0 / 3-Me, 10.6 / 4-OMe, 60.6 / 5-Me, 12.8 / 6-OMe, 60.6 / 7-OMe, 56.0.

In assigning the carbons, the proton resonances are also assigned, including the individual methoxy resonances. It is likely that similar procedures could be adopted for other compounds, if necessary making use of long-range correlations to aromatic protons. Coumarin 1 showed long-range correlations between H-8 and carbons C-4a, 6 and 8a which did not require to be used in the present study.

Reynolds, W.F. *et al* (1989) *Magn. Reson. Chem.* 27 : 162-164