The accuracy with which the tie-line data can be determined depends upon the accurate separation of the two phases. The two phases can be separated to within one or two drops (i.e., about 0.1 grams). In the present work, only 10 cc of the mixture was taken for the determination of the tie-line data and each phase was about 5 grams. Hence, the error involved is about 2%. The scope for such error is greater when the weight ratio of phases is large. However, the error can be minimized by taking a large quantity of the mixture. Further, in Figure 6, where a comparison of the distribution data was made between the two methods, for the acetic acid–water–ethyl butyrate system the deviation between the two methods in a few points may be due to the limitations of the proposed method and to the effect of hydrolysis and ester interchange. Maximum deviations are observed at high temperature and with large amounts of water. These are perhaps due to the effect of hydrolysis and ester interchange.

CONCLUSIONS

It has been demonstrated that phase-equilibrium and tie-line data could be satisfactorily determined adopting a new method as proposed by the authors. In the determination of the tie-line data the proposed method appears to be advantageous for, despite its limitations, it avoids the analytical procedure which may be a difficult problem in the case of certain mixtures.

NOMENCLATURE

x_c = weight % of solute
x_s = weight % of solvent
x_w = weight % of water
x_{cw} = weight % of solute in water layer
x_{cs} = weight % of solute in solvent layer
x_{ss} = weight % of solvent in solvent layer
x_{ww} = weight % of water in water layer

LITERATURE CITED

(1) Hand, D. B., *J. Phys. Chem.*, **34**, 1961 (1930).
(2) Othmer, D. F., Tobias, P., *Ind. Eng. Chem.*, **34**, 693 (1942).
(3) Othmer, D. F., White, R. E., Trugger, E., *ibid.*, **33**, 1240 (1941).
(4) Ramanarao, M. V., Dakshinamurty, P., *J. Chem. Eng. Data*, **3**, 248 (1965).
(5) Treybal, R. E., Weber, L. D., Daley, J. F., *Ind. Eng. Chem.*, **38**, 817 (1946).

RECEIVED for review April 1, 1969. Resubmitted March 5, 1971. Accepted January 24, 1972.

Proton Magnetic Resonance Studies of 4-Substituted Coumarins

RAMJI L. MITAL, RADHA R. GUPTA,[1] and SURESH K. JAIN
Chemistry Department, Rajasthan University, Jaipur-4, India

Proton magnetic resonance spectral studies of 4-methyl coumarins are reported. The position of the resonance signal, due to three protons of the methyl group at C_4, depends on the nature and position of the substituents in benzene ring of the coumarin ring system. A resonance peak at $\tau = 3.78–4.15$ indicates the presence of a proton at C_3 in the form —C=C—H. Coupling of CH_3 at C_4 exhibits allylic coupling with proton at C_3 with $J = 1.1$ Hz. Coupling constants ($J_{5,6}$) has been calculated, and its value shows ortho coupling. The resonance peak due to protons H_6 and H_8 depends on the nature of substituents in the benzene ring at C_5 and C_7. When the methyl groups at C_5 and C_7 are replaced by hydroxy groups, the resonance signal due to H_6 and H_8 splits, and these protons are rendered magnetically nonequivalent.

Although the literature is replete with studies of coumarins (*6*), there are surprisingly few data dealing with the nmr spectra of coumarin derivatives (*1, 2*). Structural studies in coumarin chemistry have been made using many instrumental techniques, and a number of difficulties have been encountered in structure elucidation of this class of compounds. The present investigation was undertaken to determine whether the application of pmr studies in the structural chemistry of coumarin derivatives would lead to some general correlations between structure and spectra in this series of heterocyclic compounds.

The coumarin derivatives involved in this study were prepared by the well-known Pechmann reaction by condensing the corresponding phenol with ethyl acetoacetate using concentrated sulfuric acid as the condensing agent. Coumarins prepared are already known (*6*) and their structures are well established. Purity of these compounds was checked by thin-layer chromatography. The nmr spectra were taken at 60 MHz on a Varian A-60 nmr spectrometer in deuterochloroform solution with the exception of 5-hydroxy-4, 7-dimethylcoumarin, which was taken in dimethyl sulfoxide. Tetramethylsilane was used as an internal standard in all cases.

For compounds I and II, resonance signals are at $\tau = 7.60$ and $\tau = 7.59$, respectively, and show the presence of a CH_3 group in the allylic form—i.e., a C=C—CH_3 linkage. Signals at $\tau = 7.43$ and $\tau = 7.45$ in compounds III and IV are also due to a CH_3 group at C_4 in the allylic form and minor shift toward lower field may be attributed to the vicinal substituent at C_5 in these compounds. Peaks at $\tau = 3.89$, 3.78, 3.98, and 4.15, respectively, in compounds I–IV are due to protons at C_3 in the form —C=C—H. Protons of CH_3 at C_4 exhibit allylic coupling with the proton at C_3 with coupling constant equal to 1.1 Hz. See Table I.

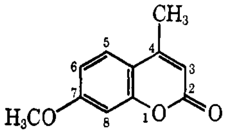
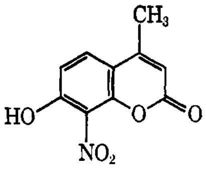
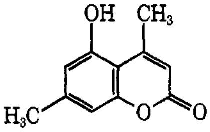
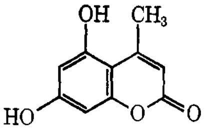
In compounds I and III peaks at $\tau = 6.13$ and $\tau = 7.70$ are due to H_3CO and CH_3 (at C_7) groups, respectively.

For compound I a quartet consisting of two doublets is ob-

---

[1] To whom correspondence should be addressed.

Table I. Proton Magnetic Resonance Spectral Data of Coumarins

	Compound	τ	H	Multiplicity	Assignment
I		7.60	3	Singlet	CH_3 group at C_4
		3.89	1	Singlet	H_3
		6.13	3	Singlet	OCH_3 group at C_7
		3.16, 2.51	2	Quartet (two doublets)	H_5 and H_6 coupled
II		3.21	1	Singlet	H_8
		7.59	3	Singlet	CH_3 group at C_4
		3.78	1	Singlet	H_3
		2.96, 2.23	2	Quartet (two doublets)	H_5 and H_6 coupled
III		7.43	3	Singlet	CH_3 group at C_4
		3.98	1	Singlet	H_3
		7.70	3	Singlet	CH_3 group at C_7
		3.40	2	Singlet	H_6 and H_8
IV		7.45	3	Singlet	CH_3 group at C_4
		4.15	1	Singlet	H_3
		3.76	1	Singlet	H_6 or H_8
		3.66	1	Singlet	H_6 or H_8

tained and form what is known as an *AB* quartet. The middle points of doublets are at 3.16 and 2.51 with a separation of 9 Hz giving $J_{AB} = 9$ Hz and $\Delta AB = 449.5 - 410.5 = 39$ Hz. Because of $\Delta AB/J_{AB} = 39/9 = 4.3$ (*3–5*), the middle points of doublets can be assigned the positions of signals due to protons *A* and *B*. A J_{AB} of 9.0 Hz shows ortho coupling. H_A and H_B are at C_5 and H_6, respectively. When we consider that H_6 absorbs at a slightly higher point ($\tau = 4.10$) (*1*) than H_5 ($\tau = 3.85$) (*1*) in the parent compound, coumarin, we can assign $\tau = 3.16$ and 2.51 to H_6 and H_5, respectively. A peak at $\tau = 3.21$ is due to H_8. Similarly a quartet in compound II with $J_{AB} = 8.5$ Hz, $\Delta_{AB} = 43$ Hz and $\Delta_{AB}/J_{AB} = 43/8.5 = 5.1$ can be interpreted. H_6 and H_5 can be assigned at $\tau = 2.96$ and 2.23 (the middle points of doublets), respectively.

In compound III, a peak at $\tau = 3.40$ representing two protons (H_6 and H_8) is obtained. In 4,5,7-trimethylcoumarin, a peak at 3.12 representing two protons (H_6 and H_8) has also been reported (*2*). Thus, the replacement of a CH_3 group of 4,5,7-trimethylcoumarin by an OH group to get 5-hydroxy-4,7-dimethylcoumarin causes a slight change (from $\tau = 3.12$ to 3.40) in the position of resonance signal due to H_6 and H_8, but H_6 and H_8 remain in the same electronic environment. If another CH_3 group of compound III is replaced by an OH group to get compound IV, surprisingly two peaks at $\tau = 3.66$ and $\lambda = 3.76$ are obtained indicating that H_6 and H_8 are no longer equivalent and meta coupling with $J_{6.8} = 1.5$ Hz is obtained. Meta coupling is also observed in compound I with $J_{6.8} = 2.5$ Hz.

LITERATURE CITED

(1) Govil, G., Kanekar, C. R., Khetrapal, C. L., Virman, Y. P., *Current Sci.*, **30**, 331 (1961).

(2) Grigg, R., Knight, J. A., Roffey, P., *Tetrahedron*, **22**, 3301 (1966).

(3) Jackman, L. M., "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," p 90, Pergamon Press, London, 1959.

(4) Mathieson, D. W., "Nuclear Magnetic Resonance for Organic Chemists," p 250, Academic Press, Ltd., London, 1967.

(5) Roberts, J. D., "Nuclear Magnetic Resonance. Applications to Problems in Organic Chemistry," p 53–5, McGraw-Hill, New York, NY, 1959.

(6) Sethna, S., Phadke, R., "Organic Reactions," Vol. VII, p 1, Roger Adams, Ed., Wiley, New York, NY, 1953.

RECEIVED for review January 4, 1971. Accepted March 2, 1972.