# An Abnormal Deshielding Effect on a Methine Proton by a Neighbouring Acetyl Group

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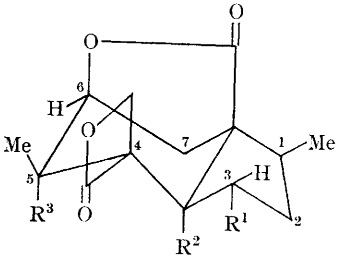
IN an n.m.r. spectrum a methine proton on carbon bonded to hydroxyl exhibits a characteristic shift of *ca.* 1·1 p.p.m. to lower field when the alcohol is acylated.[1] This effect is widely applied as an easy method of characterizing secondary alcohols. During the structural studies of anisatin[2] and neoanisatin,[3] it was found that a methine proton moves similarly by *ca.* 1·1 p.p.m. to lower field on acetylation of a vicinal hydroxyl group. Acetylation† of noranisatin (I) gave noranisatin diacetate (II). The n.m.r. spectra of (I) and (II) show that the signal of the C-3 proton moves to lower field (from 4·60 p.p.m. to 5·67 p.p.m.) on acetylation of the secondary hydroxyl as expected, whilst the signal of the C-6 methine also moves by *ca.* 1·1 p.p.m. to lower field on acetylation of the tertiary hydroxyl group on C-5. The latter deshielding effect is due to the nonbonded interaction between the acetoxy-group and the methine rather than interactions through chemical bonds. This shift value is unusually large for the anisotropic effect of an acetoxy-group to the best of our knowledge. Other derivatives of anisatin and neoanisatin exhibit a similar deshielding influence by acetylation of the tertiary hydroxyl group on C-5. A few examples from our result are listed in the Table. The feature of these compounds is that an equatorial proton deshielded by acetylation is vicinal to the axial tertiary hydroxyl to which another tertiary hydroxyl function is disposed in a 1,3-diaxial relationship.



(I) Noranisatin: R$^1$ = R$^2$ = R$^3$ = OH
(II) Noranisatin diacetate: R$^1$ = R$^3$ = OAc, R$^2$ = OH
(III) Norneoanisatin: R$^1$ = H, R$^2$ = R$^3$ = OH
(IV) Norneoanisatin monoacetate: R$^1$ = H, R$^2$ = OH, R$^3$ = OAc
(V) Noranisatin carbonate: R$^1$,R$^2$ = –O·CO·O–, R$^3$ = OH
(VI) Noranisatin carbonate acetate: R$^1$, R$^2$ = –O·CO·O–, R$^3$ = OAc

TABLE‡

| Compound | Chemical shift of C-6 proton | Compound | Chemical shift of C-6 proton | Shift value |
|---|---|---|---|---|
| (I) | 4·31 (d) | (II) | 5·43 (d) | 1·12 |
| (III) | 4·28 (d) | (IV) | 5·39 (q) | 1·11 |
| (V) | 4·59 (d) | (VI) | 5·48 (q) | 0·89 |

‡ p.p.m. from tetramethylsilane in $CDCl_3$(I–IV) and $CD_3{\cdot}CO{\cdot}CD_3$ (V, VI) solution; d = doublet, q = quartet.

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† The position of the tertiary acetoxy-group was firmly established by spectral evidence (n.m.r. and i.r.), which will be reported in a separate paper. Satisfactory analyses were obtained for all new compounds in this paper.

[1] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London, 1959, p. 55.

[2] (a) K. Yamada, S. Takada, S. Nakamura, and Y. Hirata, *Tetrahedron Letters*, 1965, 4785; (b) N. Sakabe, Y. Hirata, A. Furusaki, Y. Tomiie, and I. Nitta, *ibid.*, 1965, 4795; (c) K. Yamada, S. Takada, S. Nakamura, and Y. Hirata, *ibid.*, 1965, 4797.

[3] S. Takada, S. Nakamura, K. Yamada, and Y. Hirata, *Tetrahedron Letters*, 1966, 4739.