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THE NMR SPECTRA OF FUTOENONE AND DERIVATIVES: PARTIAL DECOUPLING AS AN AID IN THE ASSIGNMENT OF COMPLEX SPECTRA, AND FURTHER OBSERVATIONS OF OVERHAUSER EFFECTS

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Derivation of the structure of futoenone (I), reported in the preceding paper[1], is based largely on a complete and unambiguous assignment of the NMR spectrum of futoenone. As can be seen from Fig. 1, the six-proton group of signals appearing in the 1.0 to 3.0 ppm region of the 100 Mc spectrum is too complicated to be assigned by inspection, although the multiplicities of at least three proton-signals ($H_{7\alpha}$, $H_{9\alpha}$, $H_{10\beta}$) can be deduced from a comparison of the spectra run in different solvents [cf. Figs. 1(a), 1(e), and 1(g)].

Strong irradiation of the secondary-methyl signal at 0.50 ppm (85% C_6D_6-$CDCl_3$ solution) converts the 11α-proton signal into a doublet with 11.2 cps splitting [see Fig. 1(c)]; while complete decoupling of $H_{8\alpha}$ (a broad doublet of doublets at 4.67 ppm) causes two of the multiplets near 2 ppm ($H_{7\beta}$ and $H_{9\beta}$) to become what appears to be a doublet of doublets ($H_{7\beta}$), with splittings of 1.7 and 11.5 cps, and a doublet of doublets of doublets ($H_{9\beta}$), with splittings of 14, 5 and 1.7 cps, respectively, and, in addition, sharpens the broad doublet of doublets ($H_{9\alpha}$) near 1.4 ppm [see Figs. 1(b) and 1(e)].

From these decoupling experiments, it is now possible to deduce by a first-order analysis the multiplicities of all proton signals in the 1.0-3.0 ppm region. However, because five proton-signals ($H_{7\alpha}$, $H_{7\beta}$, $H_{9\alpha}$, $H_{10\beta}$, $H_{11\alpha}$) share a common splitting of ca 11.5 cps, it is not possible at this stage to make an unambiguous assignment of the couplings.

Adverse δ/J ratios make it difficult if not impossible to completely decouple, one from

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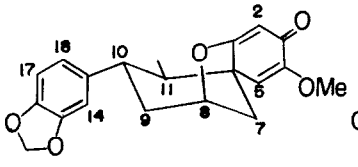
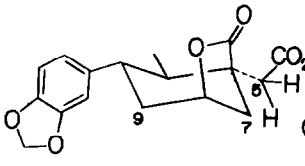
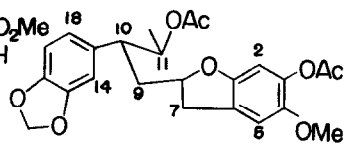
another, any of the protons appearing in the 1.0-3.0 ppm region, but do not prevent the use of partial decoupling or spin-perturbation[2] to determine which proton is coupled to which. For



I



XII



IV

example, if one or more of the lines in the multiplet due to $H_{10\beta}$ (see structure I) were to be irradiated, the signals due to $H_{9\alpha}$, $H_{9\beta}$, and $H_{11\alpha}$ would be expected to show some sort of perturbation[2], whereas those due to $H_{7\alpha}$ and $H_{7\beta}$ should remain unchanged. That this is in fact what happens can be seen from Fig. I(f). Similarly, irradiation of the 9α-proton signal [see Fig. 1(d)] causes perturbation of the signals from $H_{9\beta}$ and $H_{10\beta}$ but does not affect the $H_{7\alpha}$, $H_{7\beta}$, or $H_{11\alpha}$-signals.

In order to confirm the above findings, a similar analysis was made of the 100 Mc spectrum of the lactone XII (see Fig. 2). The results of completely decoupling $H_{8\alpha}$ [Fig. 2 (d)] or the 11-Me [Fig. 2(b)], and of partially decoupling $H_{9\alpha}$ [Figs. 2(h) and 2(f)] or $H_{10\beta}$ [Fig. 2(i)], are completely analogous to those obtained in the case of futoenone.

Long-range couplings and Overhauser Effects: The structure of the benzo-dihydrofuran moiety in the diacetate (IV) was established by the presence of the following small couplings: $J_{5,7a}$= $J_{5,7b}$=0.8, $J_{2,7a}$=$J_{2,7b}$=ca 0.1, $J_{5,OMe}$=ca 0.2 cps. The decoupling experiments which provided the magnitudes of these couplings are indicated in Figs. 3 and 4.

H_5 in futoenone also shows a long-range coupling to the methoxyl protons and, in common with the signals from many other ethylenic protons in the grouping -CH=C(OMe)-[3], exhibits an Overhauser effect[4] when the methoxyl signal is irradiated (Fig. 5).

The spectrum of futoenone also shows evidence of a small coupling (ca 0.5 cps) between H_2 and $H_{7\alpha}$. Irradiation of the 7α-H signal causes the H_2 singlet to sharpen appreciably [see Figs. 6(a) and 6(b); decrease in half-band width = 0.45 cps], and irradiation of H_2 causes a similar sharpening of the $H_{7\alpha}$ signal. Since integration of the H_2-signal, both before and during irradiation of $H_{7\alpha}$, shows no significant area increase [Fig. 6(c)], these protons are not

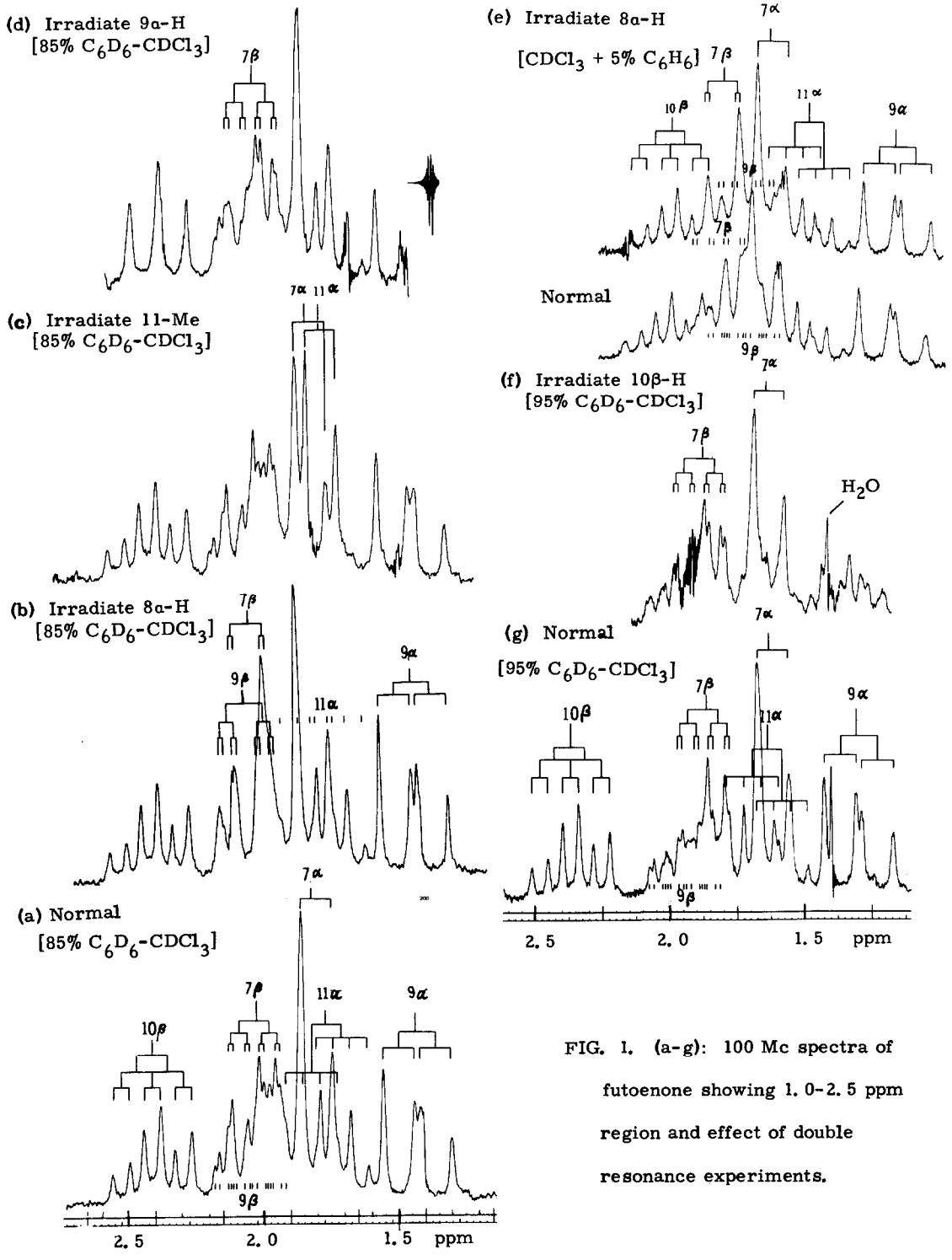


FIG. 1. (a-g): 100 Mc spectra of futoenone showing 1.0-2.5 ppm region and effect of double resonance experiments.

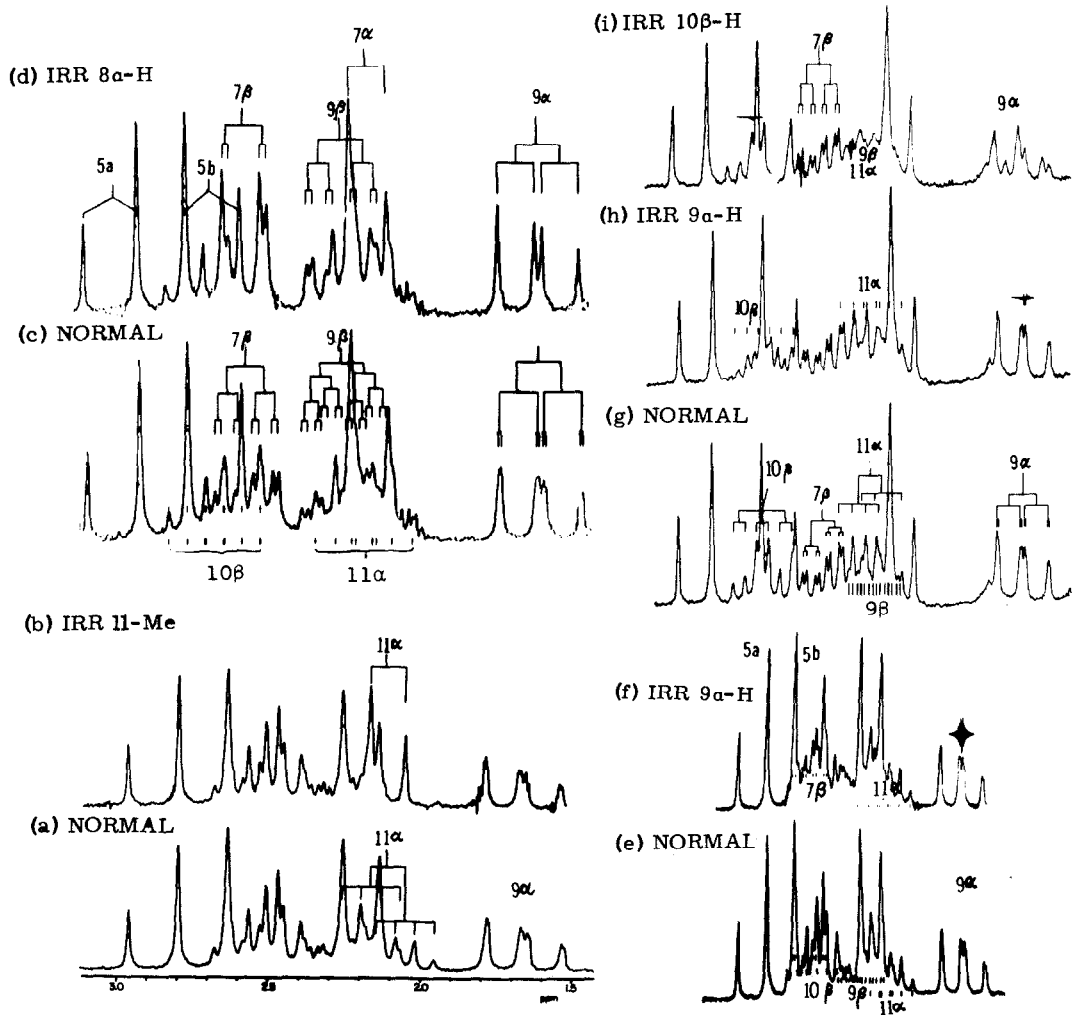


FIG. 2. 100 Mc spectra of the lactone XII.

(a) normal ($CDCl_3$)

(b) complete decoupling of 11-Me

(c) normal (30% C_6D_6-$CDCl_3$)

(d) complete decoupling of 8a-H

(e) normal ($CDCl_3$)

(f) partial decoupling of 9a-H

(g) normal (C_6D_6)

(h) partial decoupling of 10β-H

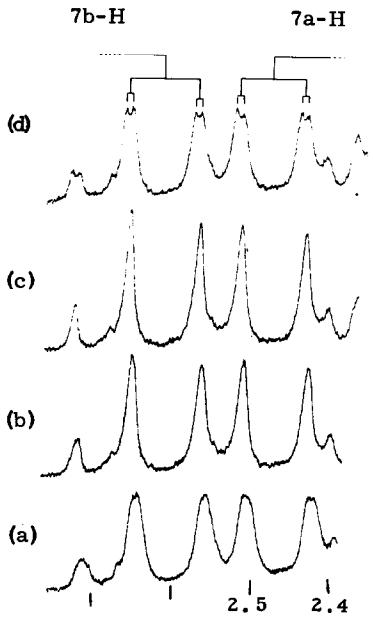


FIG. 3.

NMR of Diacetate IV in C_6D_6
(a) normal (b) IRR 5-H
(c) IRR 2-H and 5-H (d) IRR 2-H

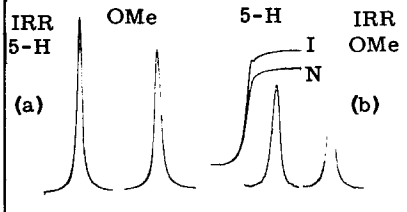


FIG. 5. NMR of Futoenone

(a) OMe with and without irradiation of 5-H
(b) 5-H with and without irradiation of OMe
Integral-N is without irradiation of OMe
Integral-I is with irradiation of OMe

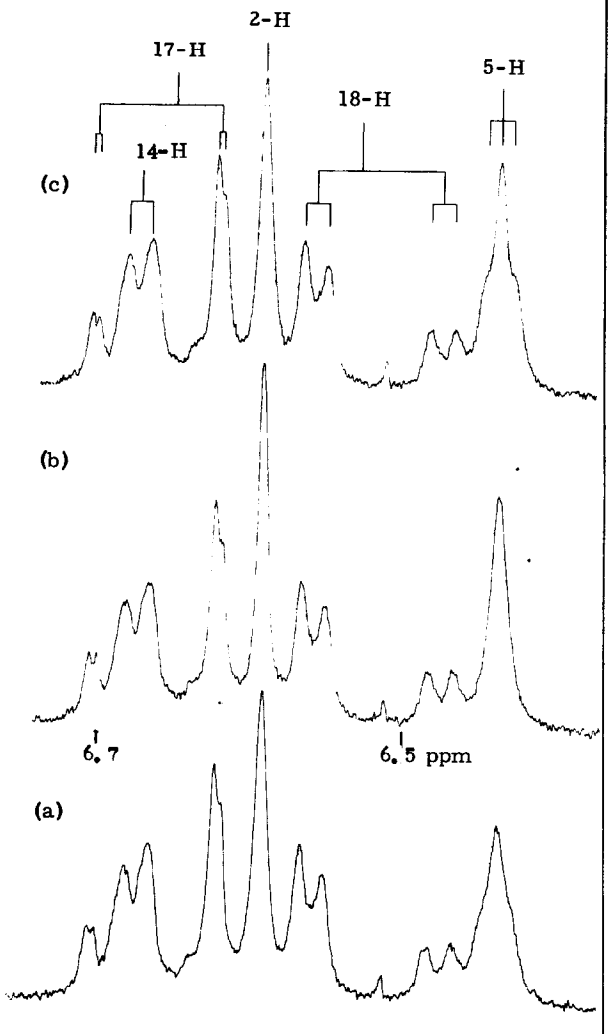


FIG. 4. NMR of Diacetate IV in 87%-C_6D_6
(a) normal (b) IRR 7a-H and 7b-H (c) IRR OMe

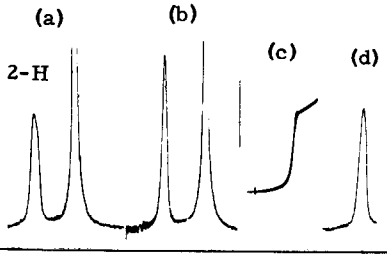


FIG. 6. NMR of futoenone in 85% C_6D_6-$CDCl_3$

(a) normal 2-H signal
(b) 2-H signal with irradiation of 7α-H
(c) superimposed integrals of 2-H,
with and without irradiation of 7α-H
(d) 2-H signal with irradiation of 7β-H

involved in an Overhauser effect[4]. As can be seen from a comparison of Fig. 6(d) with Figs. 6(a) and 6(b), $J_{2,7\alpha}$ (ca 0.5 cps) is significantly larger than $J_{2,7\beta}$ (ca 0.1 cps), which indicates that this five-bond coupling is stereospecific.

As noted earlier[1], $H_{7\beta}$ and $H_{9\beta}$ show typical W-type coupling across four bonds[5].

When the H_{14} and H_{18} protons in futoenone or the lactone XII are irradiated, the signals due to $H_{11\alpha}$, $H_{9\alpha}$ and $H_{10\beta}$ show small (ca 10%) increases in height, whereas $H_{9\beta}$ appears to be unaffected; $H_{10\beta}$ also shows some reduction in half-band width due to the removal of a small benzylic coupling[5]. Irradiation of $H_{10\beta}$, in futoenone or the lactone XII, affects H_{18} (ca 0.2-0.3 cps reduction in half-band width; ca 7% increase in signal area) more than H_{14} (ca 0.1 cps reduction in half-band width; ca 7% increase in signal area). On the other hand, irradiation of $H_{11\alpha}$ produces a greater effect on H_{14} (ca 17% increase in signal height) than on H_{18} (ca 9% increase), whereas irradiation of the $H_{9\alpha}$ or $H_{9\beta}$ signals causes small (ca 5%) increases in the heights of both the H_{14} and H_{18} signals. Although these effects are small, they are significant since irradiation of $H_{9\alpha}$, $H_{9\beta}$, $H_{10\beta}$ or $H_{11\alpha}$ produces no detectable effect in the H_{17} signal which was used as a check on instrument stability during these measurements.

REFERENCES

1) Preceding paper: Tetrahedron Letters.

2) R. Freeman and W. A. Anderson [J. Chem. Phys. 37, 2053 (1962)] have discussed the use of weak perturbing fields ("spin tickling") in nuclear magnetic double resonance experiments. The strength of the perturbing field used in the partial-decoupling described herein is intermediate between that used for "spin-tickling" and the power required for complete decoupling. Spectra were measured on a Varian HA-100 spectrometer utilizing frequency sweep and field-frequency stabilization.

3) The couplings and Overhauser effects which are exhibited by protons in the grouping -CH=C(OMe)- will be discussed elsewhere.

4) F. A. L. Anet and A. J. R. Bourn, J. Am. Chem. Soc., 87, 5250 (1965); M. C. Woods, I. Miura, Y. Nakadaira, A. Terahara, M. Maruyama, and K. Nakanishi, Tetrahedron Letters, 321 (1967).

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