

TETRANORTRITERPENOID—V¹

[BICYCLONONANOLIDES III]

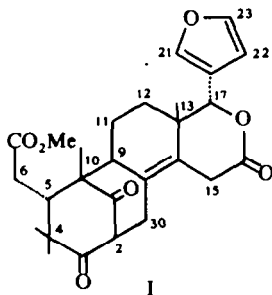
THE PMR SPECTRUM OF MEXICANOLIDE

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Abstract—The PMR spectrum of mexicanolide (I) has been examined in detail. In particular the complex spin systems arising from the protons attached to (C-5, C-6) and (C-2, C-30, C-15) have been analysed, using spin-decoupling, spin-tickling and solvent-shift procedures.

IN THE course of our investigations on the constitution of mexicanolide we had the opportunity to examine its PMR spectrum in some detail. These studies, which complement the chemical work discussed in the preceding paper¹ and have been segregated here for the sake of clarity, provided firm support for the conclusions reached on chemical grounds.



The discussion, again for clarity of exposition, starts from the constitution and stereochemistry of mexicanolide as depicted in I. Simple inspection of the PMR spectrum at 100 MHz (Fig. 1) shows the following familiar features: two α -furanic protons (2 diffuse singlets, 1H each τ 2.44, 2.61), one β -furanic proton (diffuse *s*, 1H, τ 3.52); H-17 (*s*, 1H, τ 4.75); $-\text{CO}_2\text{CH}_3$ (*s*, 3H, τ 6.28); tertiary Me's (sharp singlets: 3H, τ 8.77; 6H, τ 9.00; 3H, τ 9.12).

The remaining thirteen protons form three virtually distinct spin-systems. Two of these are analysed in the sequel with the aid of spin-decoupling, spin-tickling and solvent shifts. The system arising from protons H-9, H-11(2) and H-12(2) was not investigated.

ABX system (H-2, H-30, H-30). Double irradiation locates the AB part (H-2, 1 H-30) at τ 6.8 (*m*) and X (1 H-30) at τ 7.7 (*q*); X is further coupled (bisallylic coupling) to one or both protons at τ 6.5 (diffuse *s*; 2 H-15). Thus on irradiation (H_2) at τ 7.7 (X) the multiplet at τ 6.8 collapses to a doublet and the singlet at τ 6.5 sharpens

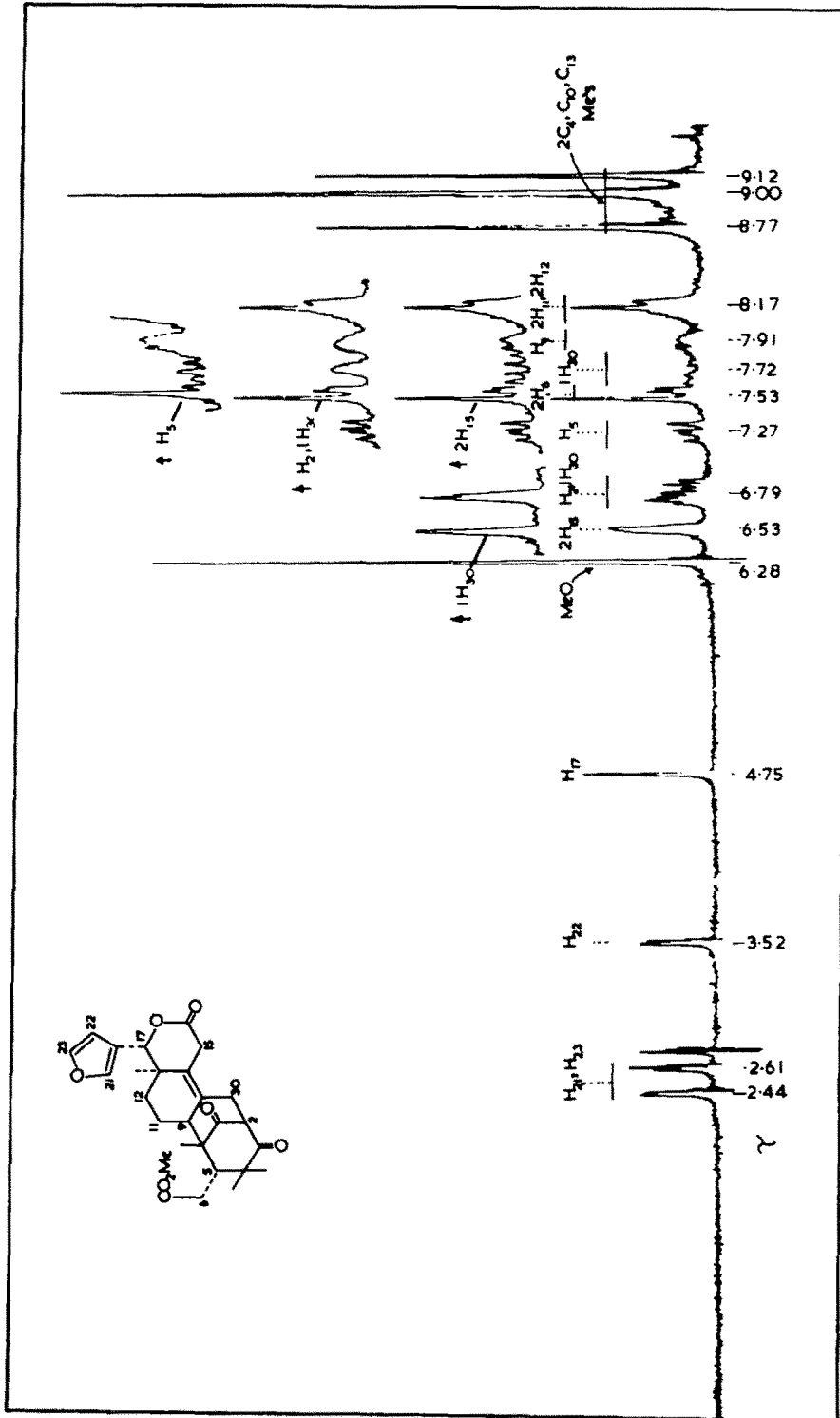


FIG. 1. NMR Single and Double Resonance Spectra at 100 MHz of Mexicanolide (I).

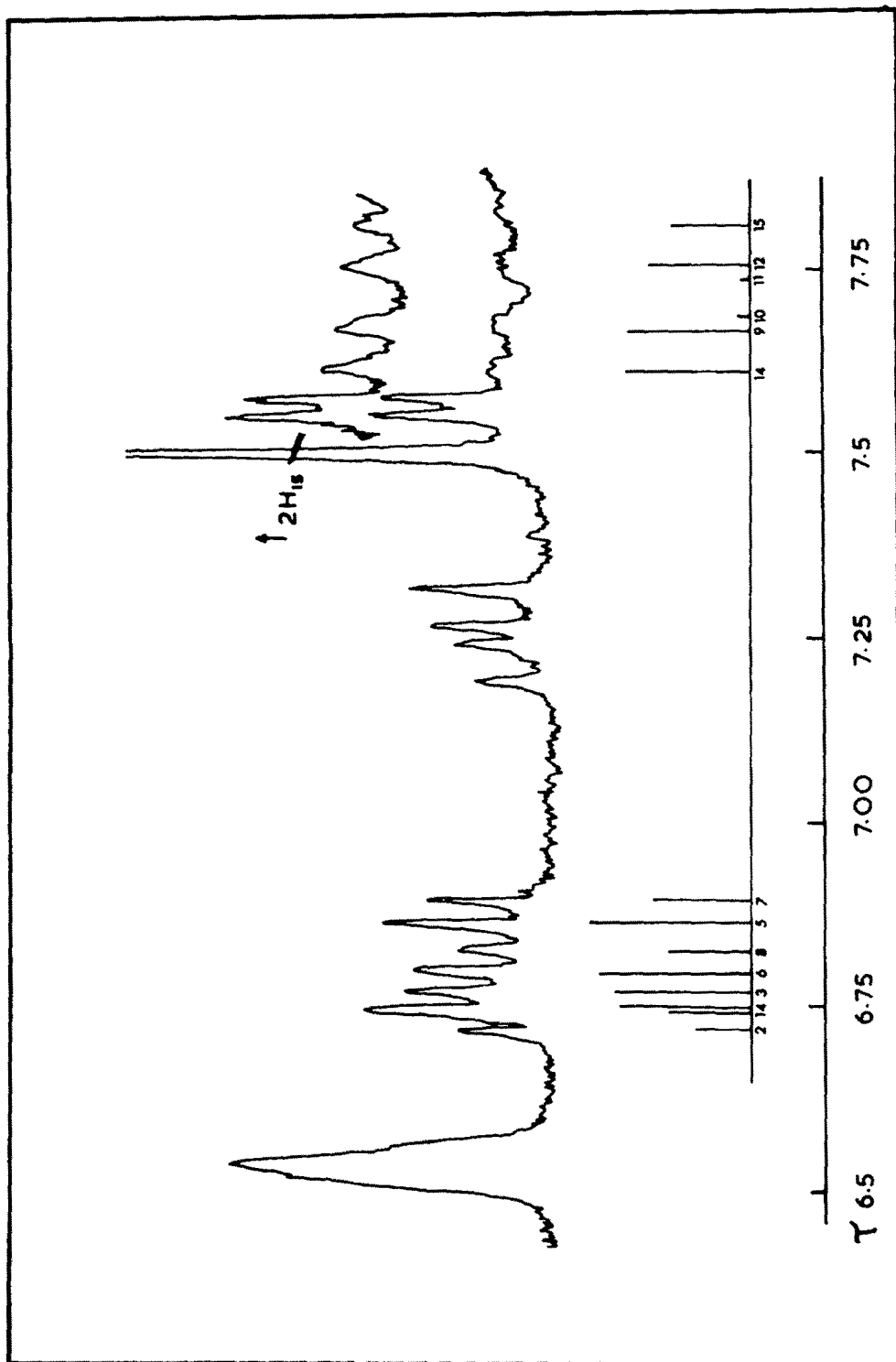


FIG. 2. Calculated and Observed NMR Spectra at 100 MHz of the ABX System in Mexicanolide. The line notation used follows that in reference 2 although strictly this should not be applied to such a closely coupled system.

simultaneously. Conversely, with H_2 at τ 6.5 (2 H-15) the X region sharpens to a clean quartet, while with H_2 at 6.8 (AB region), it is transformed to a broad singlet.

The actual δ and J values for this system were derived as follows. From direct inspection, $J_{AB} = 3.0$ Hz and X has its origin at τ 7.72. δ_{AB} , J_{AX} and J_{BX} were evaluated from line frequencies and line intensities, using the expressions appropriate to ABX systems.² The combination transitions of the X part of the spectrum were strikingly intense. This occurs when $(\delta_B - \delta_A)$ becomes small but, more important, when J_{AX} is opposite in sign to J_{BX} . Of the possible solutions, the most plausible, for the system under consideration appeared to be the following: $\delta_B - \delta_A = 2.6$ Hz: hence $\delta_B = 6.81$ τ ; $\delta_A = 6.78$ τ . $J_{AX} = 5.4$ Hz; $J_{BX} = -13.8$ Hz. As $J_{AB} = 3.0$ Hz (*v.s.*), these values are reasonable for vicinal (J_{AB} and J_{AX}) and geminal (J_{BX}) couplings.

The calculated (NMR Programme FREQUINT IV) and observed spectra for this system (Fig. 2) exhibit acceptable fit when allowance is made for band overlap and line width.

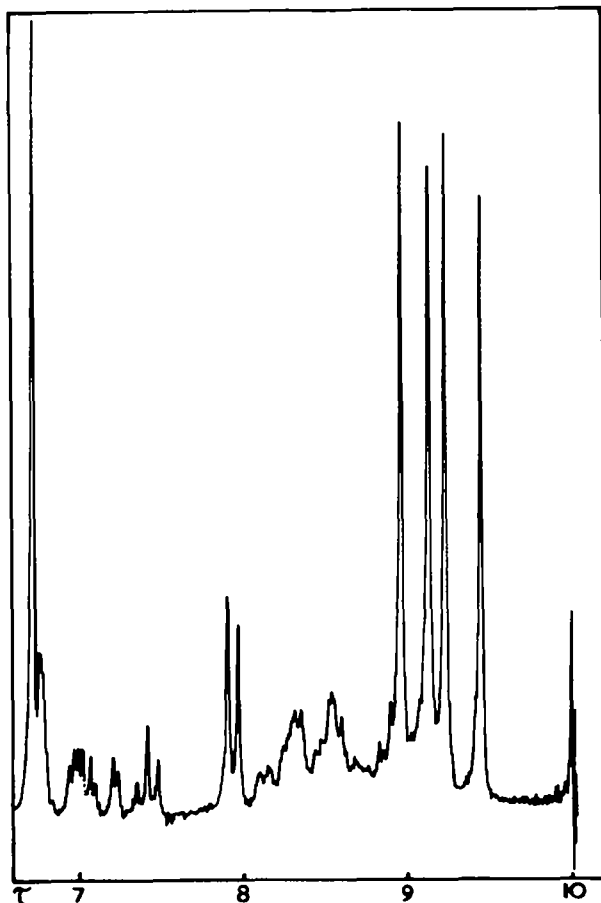


FIG. 3. NMR Spectrum of Mexicanolide at 100 MHz in Benzene- $CDCl_3$ (4:1).

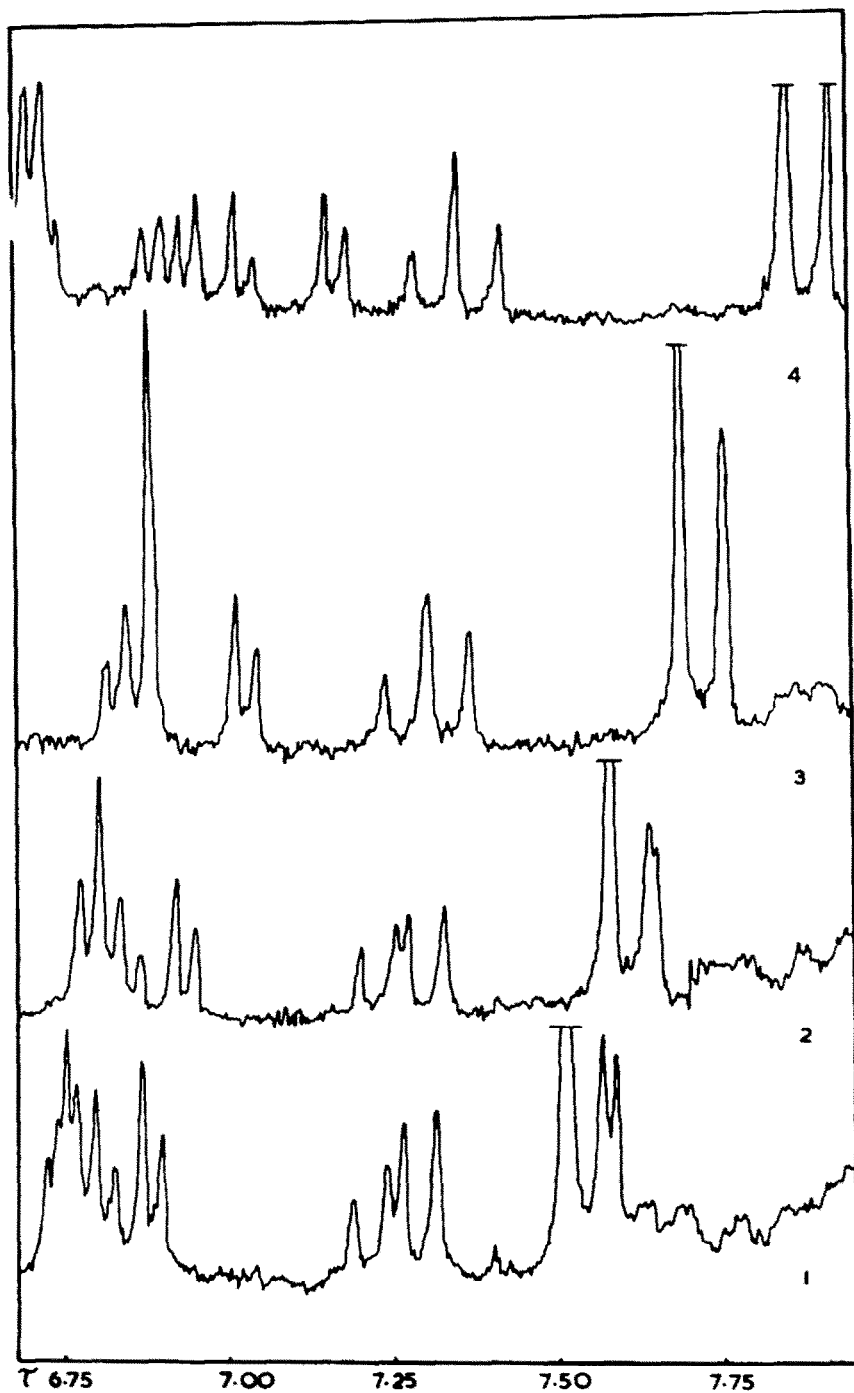


FIG. 4. AB(X) and AB₂ systems of Mexicanolide at 100 MHz in

1. Benzene-CDCl₃ (1:19)
2. Benzene-CDCl₃ (1:3)
3. Benzene-CDCl₃ (1:1)
4. Benzene-CDCl₃ (4:1).

It was possible from the derived J and δ values to assign the lines in the observed spectrum to the theoretical transition energies (Fig. 2). These assignments could be further supported by spin-tickling. Thus, tickling in turn at the four peaks of the X portion led to collapse of each of the appropriate³ lines in the AB portion of the spectrum to a broadened singlet. These were further resolved, as required by theory, into doublets when a third irradiating field (strong) was applied* at τ 6.53 (H-15), removing the complication of bisallylic coupling.

AB_2 (or ABB')† system (H-5, 2H-6). Simple spin decoupling located an isolated AB_2 (or ABB') system: A (H-5) at τ 7.3 and B_2 (2H-6) at τ 7.5 (B_2 collapses on irradiation at A). The line pattern is typically that of a common type of AB_2 spectrum.

Calculations² of more precise δ and J values gave for δ_A 7.27 τ , δ_B 7.53 τ ; J_{AB} (or average of J_{AB} and $J_{AB'}$) 6.8 Hz.

Solvent induced shifts. Several instructive points emerged when the PMR spectrum of mexicanolide was examined in a series of solvent mixtures in which the proportion of benzene in deuteriochloroform increased from 0% to 80%. (Mexicanolide becomes too insoluble when the benzene concentration rises above 80%.)

It is immediately apparent (Fig. 3) that in 80% benzene the four tertiary C-Me groups are well separated, which is not the case in deuteriochloroform.

ABX system. As the J_{AB}/δ_{AB} changes from 1.1 ($CDCl_3$) to 0.18 (80% benzene) the AB part of this system goes through a series of interesting, but expected,⁴ changes (Fig. 4). In 80% benzene the following values were evaluated² from the spectrum, $J_{AB} = 3.0$ Hz; $J_{AX} = 5.4$ Hz; $J_{BX} = -14.2$ Hz.

AB_2 (or ABB') system. Reference to Fig. 4 will show that, as the proportion of benzene increases, the original (in $CDCl_3$) AB_2 (or ABB') system, gradually changes and approaches an AX_2 (or AXX') system.

EXPERIMENTAL

The NMR spectra were recorded at a frequency of 100 MHz on a Varian HA-100 spectrometer with internal proton stabilisation (TMS) using dilute solns (approx. 3 mole %) in $CDCl_3$, unless otherwise stated, at a probe temp of 33°. The calibration of the spectrometer was checked using a Hewlett-Packard electronic counter (5212A) and double resonance experiments were performed with a Muirhead Oscillator (D-890-A). The data for the analysis of the ABX and AB_2 systems were derived from 5 recordings on an expanded scale (2 Hz/cm). Chemical shift values should be accurate to ± 0.01 ppm and coupling constants to ± 0.1 Hz. The ABX spectrum was calculated on an English Electric KDF 9 computer using the programme FREQUINT IVa (translated from FORTRAN by R. Kaptein and extensively modified by D. A. Morton-Blake).

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* Dr. J. Feeney, Varian Associates Ltd., kindly carried out these experiments.

† If rotation about the C-5, C-6 bond is hindered and the two B protons are accidentally equivalent.