

# THE PROTON MAGNETIC RESONANCE SPECTRA OF DITERPENE ALCOHOLS. SPIN-SPIN COUPLING THROUGH FOUR SINGLE BONDS\*

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The steric dependence of proton magnetic resonance spin-spin coupling through two saturated bonds<sup>1</sup> and through three saturated bonds<sup>2</sup> is well known. Recently the steric dependence of coupling through four<sup>3</sup> and five<sup>4</sup> bond systems containing carbon-carbon double bonds has also been reported. Much less work has been recorded concerning the geometrical dependence of coupling through four single bonds and only a few examples appear in the literature.<sup>5</sup>

Recently we<sup>6</sup> have examined the proton magnetic resonance spectra of agathadiol (I) and communol (II) and find in both these compounds an interesting example of coupling through four single bonds. The proton magnetic resonance curve of the axial C(19) hydroxymethyl group in these compounds is shown in the

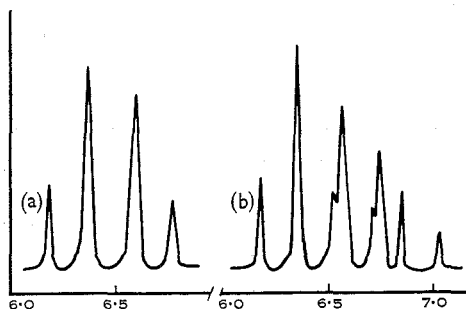


Fig. 1.—The 6-7  $\tau$  region of the proton magnetic resonance spectra of (a) agathadiol and (b) communol.

figure. The two protons at C(19) in agathadiol (Fig. 1(a)) occur at different field positions owing to restricted rotation about the C(4)–C(19) bond. The two protons then form an AB system where  $H_A = 6.28 \tau$ ,  $H_B = 6.62 \tau$ ,  $\delta_{AB} = 20.5$  c/s, and  $J_{AB} = 11.5$  c/s. These values are very close to those recorded by Wenkert and Beak<sup>7</sup> for axial hydroxymethyl groups in similar compounds.

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<sup>1</sup> Gutowsky, H. S., Karplus, M., and Grant, D. M., *J. Chem. Phys.*, 1959, **31**, 1278.

<sup>2</sup> Karplus, M., *J. Chem. Phys.*, 1959, **30**, 11.

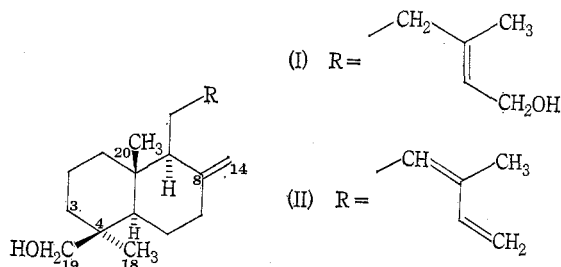
<sup>3</sup> Wittstruck, T. A., Malhotra, S. K., and Ringold, H. J., *J. Amer. Chem. Soc.*, 1963, **85**, 1699; Collins, D. J., Hobbs, J. J., and Sternhell, S., *Tetrahedron Letters*, 1963, 197.

<sup>4</sup> Pinhey, J. T., and Sternhell, S., *Tetrahedron Letters*, 1963, 275.

<sup>5</sup> Hall, L. D., and Hough, L., *Proc. Chem. Soc.*, 1962, 382, and references reported therein.

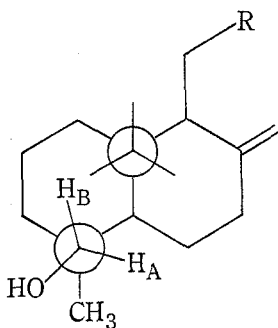
<sup>6</sup> Dennis, N., and Carman, R. M., *Aust. J. Chem.*, 1964, **17**, 390; Carman, R. M., 1964, **17**, 393.

<sup>7</sup> Wenkert, E., and Beak, P., *Tetrahedron Letters*, 1961, 358.



The spectrum of an isolated AB system should be symmetrical about the centre position at  $\frac{1}{2}(H_A + H_B)$ . However, in agathadiol the two peaks due to the B proton at higher field are distinctly broadened and suffer a consequent reduction in height. This broadening must be due to coupling of the B proton with a further proton or protons. Deuteration, or elevation of the temperature to 70°, did not materially affect the broadening or the complexity of the spectrum. Thus the hydroxyl group is not responsible for the observed coupling. It follows that the broadening must be due to a coupling through at least four single bonds. The signals from the A proton, though not broadened to the same extent as those from the B proton, also show some broadening when compared with reference peaks. Thus the band width at half-height for the peaks due to the A proton is 2.1 c/s, and for the B proton 2.3 c/s (average for 10 observations). Since the coupling of the two protons is different, it follows that this coupling must have some steric requirements. A somewhat similar example of this type of steric-dependent coupling over four single bonds has already been reported.<sup>8</sup>

It is difficult to predict with certainty which of the C(19) protons will occur at higher field. However, models show that, assuming ring A to be a chair, and assuming normal bond lengths and angles with the least number of undesirable



interactions, the most favourable conformation is probably the slightly skewed structure (III). The atom labelled  $H_B$  is then in a position above ring A and close to the C(20) methyl group where it would be expected to suffer more diamagnetic shielding, and therefore occur at higher field, than  $H_A$ . In conformation (III) the stereochemical relationship of protons A and B to protons four bonds distant is of interest.  $H_B$  is practically coplanar with C(19), C(4), and C(18), and is *trans* (about C(19)–C(4)) to C(18), and this type of geometry has been reported to show coupling in methyl  $\alpha,\beta$ -dibromoisobutyrate.<sup>8</sup> Furthermore  $H_A$  is coplanar with C(19), C(4), C(3), and H(3 $\alpha$ ) (axial), with the two hydrogen atoms on the same side of the system, and

it is this geometry, in a fused conformation, which has been found by Hall and Hough<sup>5</sup> to give maximum 1,3 coupling. It is therefore suggested that the chief causes of broadening in the signals of the A and B protons may be the C(3 $\alpha$ ) proton and the C(18) methyl group\* respectively.

\* Both the C(18) and the C(20) methyl groups show a band width at half-height of 1.3 c/s.

<sup>8</sup> Davis, D. R., Lutz, R. P., and Roberts, J. D., *J. Amer. Chem. Soc.*, 1961, **83**, 246.

Communol (II) showed eight lines in the 6.0–7.0  $\tau$  region (Fig. 1 (b)). These could be separated into two AB sets where the first quartet due to A'B' was about three times as strong as the second quartet (A''B'' protons) and where

$$H_{A'} = 6.27 \tau, H_{B'} = 6.63 \tau, \delta_{A'B'} = 21.1 \text{ c/s}, J_{A'B'} = 10.5 \text{ c/s},$$

$$H_{A''} = 6.64 \tau, H_{B''} = 6.90 \tau, \delta_{A''B''} = 16.1 \text{ c/s}, J_{A''B''} = 11.0 \text{ c/s}.$$

Change of temperature or deuteration again did not alter the pattern. Therefore it is unlikely that the two AB systems are due to two conformations of the same compound, but rather that they are due to 75% of the major compound communol (II), together with 25% of an impurity. The presence of an impurity in the communol is not surprising, even though the methyl communate from which it was prepared was pure: communol is a liquid, and the high molecular weight, together with the conjugated diene system and labile exocyclic double bond, make it extremely difficult to purify. An examination of the region above 8.5  $\tau$  of the proton magnetic resonance spectrum showed extraneous weak methyl peaks confirming the presence of an impurity. The close similarity in mode of preparation and in physical properties of our communol<sup>6</sup> with that reported in the literature<sup>9</sup> suggests that other workers may also have failed to obtain pure communol. The high  $\tau$  value of  $H_{B''}$  indicates that the impurity may possibly have formed through a migration of a double bond during either the formation or purification of the alcohol.

The AB spectrum due to communol (A'B') was again unsymmetrical with the two lines at higher field assigned to the B proton broadened and of reduced height when compared with the lines due to the A proton. This broadening is interpreted as for agathadiol.

### Experimental

The proton magnetic resonance curves were obtained on a Varian A60 spectrometer which had previously been calibrated against an audio-frequency oscillator in the normal manner. The spectra are recorded in  $\text{CDCl}_3$  solution containing tetramethylsilane as an internal standard. The agathadiol and communol were of the analytical purity described previously.<sup>6</sup>

<sup>9</sup> Arya, V. P., Erdtman, H., and Kubota, T., *Tetrahedron*, 1961, **16**, 255.