The N.m.r. Spectra of Some Diterpenes

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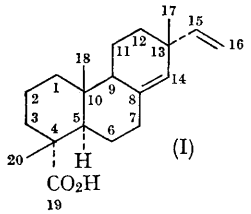
THE concepts outlined in the preceding Communication[1] concerning the calculation of chemical shifts have been applied to sandaracopimaric (I), isopimaric, and pimaric acid, and to their respective dihydro- and tetrahydro-derivatives. The chemical shifts for the C-17, C-18, and C-20 methyl groups have been calculated (Table 1) (for method see preceding Communication[1]) and the methyl resonances assigned (Table 2). Since it is well established[2–4] that the C-20 methyl groups resonate at a lower field than the C-17 and C-18 methyls, the lowest methyl signals were allocated to C-20. The mode of assigning the C-17 and C-18 methyl resonances may be illustrated by reference to sandaracopimaric acid (I). In this acid these resonances occur at 50·8 and 62·5 c./sec., in dihydrosandaracopimaric acid (II) at 48·8 and 53·5 c./sec., and in tetrahydrosandaracopimaric acid (III) at 47·8 and 53·0 c./sec., from Me_4Si at 60 Mc./sec. The shift values for (II) and (III) may be combined in four ways as follows:

	A		B		C		D	
	C–17	C–18	C–17	C–18	C–17	C–18	C–17	C–18
(II)	53·5	48·8	53·5	48·8	48·8	53·5	48·8	53·5
(III)	53·0	47·8	47·8	53·0	53·0	47·8	47·8	53·0
$\Delta\sigma_{(III)\rightarrow(II)}$	−0·5	−1·0	−5·7	+4·2	+4·2	−5·7	−1·0	−0·5

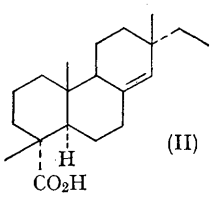
TABLE 1

Compound	Chemical shifts in c./sec. at 60 Mc./sec. C–17 Obs.	C–17 Calc.	C–18 Obs.	C–18 Calc.	C–20 Obs.	C–20 Calc.
Tetrahydropimaric acid →	−2·5		+5·7			
Dihydropimaric acid	(−0·3)	−4·2	(+3·5)	+3·0	−0·7	−0·8
Tetrahydrosandaracopimaric acid (III) → Dihydrosandaracopimaric acid (II)	−5·7	−8·3	+4·2	+5·1	−1·0	−0·8
Tetrahydro-isopimaric acid (III) → Dihydroisopimaric acid	+5·8	+3·8	−1·0	+1·7	−5·0	−4·4
Tetrahydropimaric acid → $\Delta^{8(9)}$-Dihydropimaric acid	+1·0	+1·5	−5·0	−7·6	−0·2	−2·1
Tetrahydrosandaracopimaric acid (III) → $\Delta^{8(9)}$-Dihydrosandaracopimaric acid	−0·2	+1·9	−6·5	−7·6	−1·0	−2·1
Phyllocladane (IV) → Phyllocladene			−1·2	−3·1		
Hibane → Phyllocladene			−0·6	−0·1		
Hibane → Hibaene	−2·2	−6·7	+11·8	+53·1		
Kaurane → Isokaurene			−1·7	−2·6		
Kaurane → Kaurene			−1·7	−2·3		

A negative sign indicates a shift to lower field values (deshielding) *i.e.*, an increase in c./sec. from Me_4Si. A positive sign indicates the converse.



(I)



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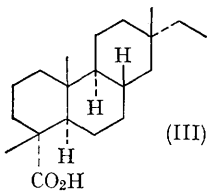

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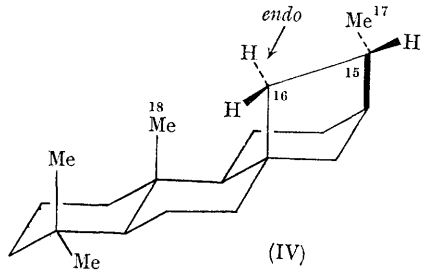

(IV)

The calculated[1] shift values for (III) → (II) are $\Delta\sigma_{C-17} = -8{\cdot}3$ c./sec., and $\Delta\sigma_{C-18} = +5{\cdot}1$ c./sec. This clearly indicates combination B to be correct. The unassigned signals at 62·5 and 50·8 c./sec. in sandaracopimaric acid (I) can be combined with the assignments for (II) as follows:

	E C–17	E C–18	F C–17	F C–18
(I)	62·5	50·8	50·8	62·5
(II)	53·5	48·8	53·5	48·8
$\Delta\sigma_{(II)\rightarrow(I)}$	−9·0	−2·0	+2·7	−13·7

Combination E is regarded as correct [and hence a complete assignment of the methyl resonances in (I), (II), and (III) follows] since, *inter alia*, (a) it is most improbable that saturation of the 15,16-double bond would have more than a marginal effect upon C-18, (b) the assignment of the lower field signal in (I) to C-17 accords with general principles (*cf.*, C-20) and (c) our method shows unequivocally that when pimaric, $\Delta^{8(9)}$-pimaric, isopimaric, and $\Delta^{8(9)}$-isopimaric acid are converted to the 15,16-dihydro-derivative $\Delta\sigma_{C-17}$ is large and negative (−9 to − 13 c./sec.) whilst $\Delta\sigma_{C-18}$ is small (~2 c./sec.).

It is inherent in our calculations of chemical-shift values that (a) the distance R must not be much less than 3 Å (*c.f.*, McConnell[5]) and (b) all parameters (*e.g.*, conformation and van der Waals effects) must be similar in both the substituted and unsubstituted compounds. It is therefore not surprising that our method fails when applied to phyllocladane (IV)/isophyllocladene. In the former compound there is a strong non-bonded interaction between the C-18 methyl group and the C-16 *endo*-proton; thus $\Delta\sigma_{C-18} = -52{\cdot}5$ (calc.) and −10·8 c./sec. (observed). The major reason for this discrepancy is undoubtedly the unjustified inclusion in the calculation of the C-16 *endo*-hydrogen bond which is about 2 Å distant from the

TABLE 2

Compound	Methyl resonance assignment (c./sec. at 60 Mc./sec.; Me_4Si internal standard.) C-20	C-18	C-17
Pimaric Acid	72·0	47·0	59·0
Dihydropimaric Acid	72·0	47·8	50·0
		(50·0*)	(47·8*)
Tetrahydropimaric Acid	71·3	53·5	47·5
Sandaracopimaric Acid (I)	72·5	50·8	62·5
Dihydrosandaracopimaric Acid (II)	71·5	48·8	53·5
Tetrahydrosandaracopimaric Acid (III)†	70·5	53·0	47·8
Isopimaric Acid	75·5	54·5	51·8
Dihydro-isopimaric Acid	75·5	54·0	42·0
$\Delta^{8(9)}$-Pimaric Acid	72·5	59·5	56·6
		(56·6*)	(59·5*)
$\Delta^{8(9)}$-Dihydropimaric Acid	71·5	58·5	46·5
$\Delta^{8(9)}$-Sandaracopimaric Acid	76·0	62·0	62·0
$\Delta^{8(9)}$-Dihydrosandaracopimaric Acid	71·5	59·5	48·0

* Alternative shift values
† Same compound as tetrahydroisopimaric acid

C-18 methyl group; thus the contribution from this bond alone to the shift value is −40·3 c./sec. An analogous situation obtains in hibane/hibaene where $\Delta\sigma_{C-18} = -53{\cdot}1$ (calc.) and −11·8 c./sec. (observed). Steric compression *per se* does not cause such discrepancies and where interactions of this kind are present in *both* compounds of the pair used to calculate a shift value, agreement between calculated and observed values is satisfactory: compare for example phyllocladane/phyllocladene and kaurane/isokaurene.

Our calculations on the diterpene acids and tetracyclic diterpenes (Table 1) lead to conclusions in general agreement with previous assignments:[2,6] satisfactory support is thus afforded for the validity of our treatment, providing the limitations in terms of R and conformational parity be observed.

The n.m.r. spectra of the diterpene acids were measured in CCl_4 and in $CDCl_3$ using a Varian A-60 spectrometer. The average of the values in these two solvents were used. Data for the tetracyclic diterpenes were taken from the relevant literature. All shift values are given for 60 Mc./sec.

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