Preferred Axial Conformation of the Pendant Substituent in 1-Aryldihydronaphthalenes and Aryltetralones

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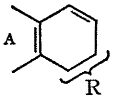
Summary The axial preference in dihydronaphthalene (III) and in a tetralone (VI) has been established by n.m.r. spectroscopy; the conformational equilibrium in the ketone was detected by c.d. measurements.

A RECENT study[1] has shown that pseudo-axial positions are preferred for substituents in 1,2-dihydronaphthalenes (I) and we report on concurrent findings in lignan chemistry.

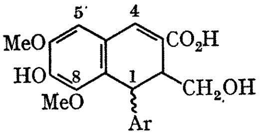
Wallis[2] showed that the low chemical shift of an 8-methoxy-substituent in the ^{1}H n.m.r. spectrum of a 1-aryl-1,2-dihydronaphthalene (lignan nomenclature) resulted from the axial character of the pendant ring. This result, and a communication from us, led Seikel and her collaborators to revise the configuration (II; *cis*-1,2) originally suggested[3] for thomasic acid to that (II; *trans*-1,2) now confirmed.[4]

The configuration of methyl α-apopicropodophyllate (III) is certain[5] and in its ^{1}H n.m.r. spectrum the value of 4Hz for $J_{1,2}$ is only compatible with a small dihedral angle between 1-H and 2-H; this reveals (IVA) another example[6] of axial preference for the pendant ring.

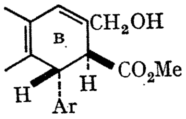
The 100 MHz. ^{1}H n.m.r. spectra of the epimeric ketones,[7] podophyllotoxone (V) and picropodophyllone (VI) were recorded by Mr. P. N. Jenkins at Imperial College and assignments were confirmed by the IPDOR method. In the spectrum of (V), which has a rigid structure, values of $J_{1,2}$ 4 Hz. and $J_{2,3}$ 16 Hz. were evaluated; these are consistent with the Karplus relation[8] and show that it can be applied with confidence to compounds of this type [*e.g.* to (III)]. Comparison of the spectra of (V) and (VI) in the region τ 2·5—4·0 shows that the only significant difference is a shift of 20 Hz. in the peak due to the two protons on the pendant ring of the latter. This must result from a contribution by the axially substituted conformer (VI) where the ring protons rotate within the shielding cone of the ketone-carbonyl group. The distinct difference in the colour of the two ketones (V) and (VI) must arise from differences in the geometry of ring B, which affect the extent of conjugation with ring A. The c.d. curves have been determined by Mr. P. B. Hulbert of this Department. In the ketonic region, podophyllotoxone (V) has one symmetrical maximum at 331 nm., and picropodophyllone (VI) has two maxima at 336 and 345 nm.; although the carbonyl groups have equal rotational strengths, since the areas under the two curves in this region are equal. The twin maxima are unusual in that they must be due to different absorption maxima in the two conformers of picropodophyllone (VI) and the ratio of their intensity is *ca.* 45 : 55 which gives an indication of the position of equilibrium at room temperature.



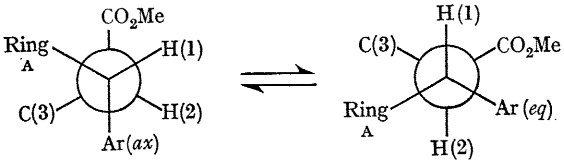
(I)



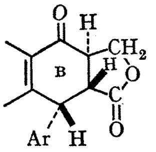
(II)



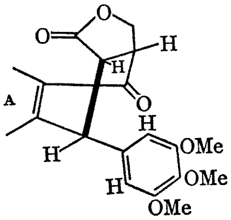
(III)



(IVA) (IVB)



(V)



(VI)

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