

THE ASSIGNMENT OF STEREOCHEMISTRY AT C-9 IN GIBBANE DERIVATIVES

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One of the problems encountered in syntheses leading to gibberellins is the determination of stereochemistry at C-9 in gibbane intermediates. Stereochemical assignment has hitherto been made on the basis of (a) preferred cis ring fusion in hydrofluorene intermediates,¹ and (b) the stereospecific reduction of $\Delta^{9,11}$ gibbenes governed by the orientation of a C-6 substituent.^{2a,2b,3} We present here spectroscopic methods for assignment of C-9 stereochemistry in gibbanes which offers, in part, a solution to this problem.

In the C-9 α gibbanes (I and III) the respective C-6 methylene protons resonate at higher field than those of the isomeric C-9 β gibbanes (II and IV) (see Table 1). This effect may arise, in the C-9 β isomers, by greater deshielding of the C-6 protons by the C-8, C-15 and C-8, C-14 σ -bonds with which they are separately coplanar (θ 0°). Also the small difference (1.5 Hz) in chemical shift of the methoxyl resonances in (I) and (II) enables the isomer composition from the reduction of the corresponding $\Delta^{9,11}$ gibbene to be readily determined (61:39); so far (I) and (II) have not been resolved on g.l.c.

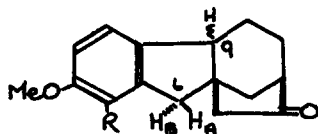


Table 1.

Compound	R	H-9	δ_A	- C-6 -	δ_B	JAB
(I)	H	α	2.53		2.23 ^a	14
(II)	H	β	2.71		2.33 ^a	16
(III)	CO ₂ Me	α	3.06		2.85 ^b	16
(IV)	CO ₂ Me	β	3.18		2.88 ^b	16

a) In C₆D₆ at 100 MHz;

b) in CDCl₃ at 60 MHz.

In gibban-16-ones having ester functionality at C-4 or C-6 it is apparent from our work, and from data extant in the literature,^{3,4} that there is a tendency for C-9 α isomers to exhibit C-16 carbonyl absorption in the infrared near 1740 cm^{-1} whereas C-9 β isomers absorb nearer 1730 cm^{-1} (Table 2).

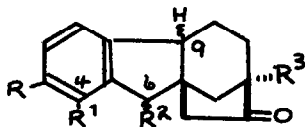


Table 2.

H-9	R	R ¹	R ²	R ³	ν C=O	Phase	Ref.
α	H	CH ₃	β -CO ₂ Me	CH ₃	1745	Nujol	3
α	MeO	CO ₂ Me	β CH ₃	H	1746	CCl ₄	
β	H	CH ₃	α -CO ₂ Me	CH ₃	1736	Nujol	3
β	H	CH ₃	β -CO ₂ Me	CH ₃	1735	Nujol	3
α	H	H	-CHO	CH ₃	1745	CCl ₄	4
α	MeO	CO ₂ Me	H	H	1742	KBr	5
β	MeO	CO ₂ Me	H	H	1735	KBr	

We have, so far, been unable to derive C-9 stereochemistry directly by n.m.r. since the C-9 proton, which subtends similar dihedral angles with the C-11 protons in both α and β isomers, has a very similar chemical shift (2.536) in both isomers (e.g. I and II).

References

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