The Stereochemistry of Tetralin-1-ols

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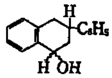
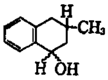
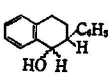
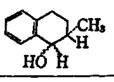
Clark-Lewis *et al.*1) and other authors2) have studied the NMR spectra of the 4α- and 4β-hydroxyflavans and their relative configurations as deduced from the coupling constants. Inoue *et al.*3) and Anjaneyulu *et al.*4) have carried out similar investigations on isoflavanols.

Tetralin-1-ols are considered to have configurations similar to those of the corresponding hydroxyflavans. One of the present authors, Hanaya, obtained 3-phenyl-1-tetralol (Ia, Ib),5) 3-methyl-1-tetralol (IIa, IIb),5) 2-phenyl-1-tetralol (IIIa, IIIb)6) and 2-methyl-1-tetralol (IVa, IVb)7) by the reduction of the corresponding α-tetralones, as is show in Table 1; he tentatively assigned a *trans* configuration to Ia, IIa, IIIb, and IVb and a *cis* configuration to Ib, IIb, IIIa, and IVa,5-7) on the basis of the mechanism of the reduction and their IR spectra.

TABLE 1

Compound		mp or bp
	Ia	mp 100—101.5°C
	Ib	mp 96—98°C
	IIa	mp 96.5—98°C
	IIb	mp 113—115°C
	IIIa	mp 66—68°C
	IIIb	mp 80—81°C
	IVa	bp 109—113°C/7 mmHg
	IVb	mp 69—70°C

In order to confirm these assignments and to decide whether or not a relationship similar to those found in the case of the hydroxyflavans exists between the coupling constants and the configurations of the tetralin-1-ols, we investigated the NMR spectra of the tetralin-1-ols.

Already, Argabright *et al.*8) have reported that IIb exhibits a triplet with $J_{1\cdot 2}=3.2$ cps in the NMR spectrum and that the hydroxyl group must be axial, while IVb exhibits a doublet with $J_{1\cdot 2}=7$ cps and both the hydroxyl and methyl groups must be of the equatorial conformation.

The experimental results are summarized in Table 2.

The hydroxyl group exists in the α-position to the phenyl or methyl group, and if it is assumed that the phenyl or methyl group is in the equatorial conformation on a half-chair ring, the Karplus relationship9) predicts that $J_{1\cdot 2}$ will be significantly smaller for 1,2-*cis* than for 1,2-*trans* isomers. In the NMR spectra of III, IV, and their acetates the $J_{1\cdot 2}$ values of IIIb and IVb are larger than those of IIIa and IVa, respectively. Therefore, these results indicate that in IIIb and IVb the phenyl or methyl group is *trans* to the hydroxyl group, and in IIIa and IVa, *cis*. These findings are consistent with the assignment proposed in preceding papers.6,7) On the other hand, when the hydroxyl group exists in the β-position to the phenyl or methyl group, the assignment based on the examination of the NMR spectra is contrary to the assignment made before.5) In the NMR spectra of I, II, and their acetates, the signal of the 1H protons of Ib and IIb appears as a triplet, while the signal of the 1H protons of Ia and IIa appears as a double doublet. Consideration of the Karplus relationship9) suggests that the 1H protons of Ib and IIb exist in a quasi-equatorial conformation, while the 1H protons of Ia and IIa exist in a quasi-axial conformation on a half-chair

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Table 2. NMR spectra of tetralin-1-ols and their acetates

Compound	Position of peaks (ppm)	No. of protons	Assignment	Remark
Ia	5.21	1	H	Double doublet $J_{1\cdot 2}=6.0$; 11.0 cps
Acetate of Ia	1.90	3	$CH_3\cdot CO\cdot O$	Singlet
	5.98	1	H	Double doublet $J_{1\cdot 2}=6.5$; 11.0 cps
Ib	5.13	1	H	Triplet, $J_{1\cdot 2}=3.0$ cps
Acetate of Ib	1.82	3	$CH_3\cdot CO\cdot O$	Singlet
	5.93	1	H	Triplet, $J_{1\cdot 2}=3.5$ cps
IIa	1.05	3	CH_3	Doublet, $J=6.0$ cps
	4.64	1	H	Double doublet $J_{1\cdot 2}=6.0$; 11.0 cps
Acetate of IIa	1.04	3	CH_3	Doublet, $J=6.0$ cps
	2.07	3	$CH_3\cdot CO\cdot O$	Singlet
	6.0	1	H	Double doublet $J_{1\cdot 2}=6.0$; 10.5 cps
IIb	1.07	3	CH_3	Doublet, $J=6.0$ cps
	4.63	1	H	Triplet, $J_{1\cdot 2}=3.0$ cps
Acetate of IIb	1.06	3	CH_3	Doublet, $J=5.6$ cps
	1.98	3	$CH_3\cdot CO\cdot O$	Singlet
	6.01	1	H	Triplet, $J_{1\cdot 2}=3.0$ cps
Acetate of IIIa	1.65	3	$CH_3\cdot CO\cdot O$	Singlet
	6.08	1	H	Doublet, $J_{1\cdot 2}=3.5$ cps
Acetate of IIIb	1.83	3	$CH_3\cdot CO\cdot O$	Singlet
	6.18	1	H	Doublet, $J_{1\cdot 2}=8.0$ cps
IVa	1.12	3	CH_3	Doublet, $J=6.0$ cps
	4.51	1	H	Doublet, $J_{1\cdot 2}=3.0$ cps
Acetate of IVa	1.00	3	CH_3	Doublet, $J=6.0$ cps
	1.95	3	$CH_3\cdot CO\cdot O$	Singlet
	5.92	1	H	Doublet, $J_{1\cdot 2}=3.0$ cps
IVb	1.08	3	CH_3	Doublet, $J=6.0$ cps
	4.25	1	H	Doublet, $J_{1\cdot 2}=6.0$ cps
Acetate of IVb	1.02	3	CH_3	Doublet, $J=6.2$ cps
	2.08	3	$CH_3\cdot CO\cdot O$	Singlet
	5.75	1	H	Doublet, $J_{1\cdot 2}=6.5$ cps

ring. The conformations of the phenyl or methyl group in the 3-position of I and II are assumed to be equatorial, as usual. Therefore, these results indicate that Ib and IIb have a *trans* relation between the phenyl or methyl group and the hydroxyl group, and that Ia and IIa have a *cis* relation.

From the above findings, the relationship between the 1,2-coupling constants and the configurations which was observed with tetralin-1-ols is similar to that seen in the case of the hydroxyflavans. Therefore, it may be concluded that the configuration of the tetralin-1-ols can be assigned on the basis of the coupling constant of the 1- and 2-protons. When the hydroxyl group exists in the β-position to the phenyl or methyl group, as has been mentioned before, the assignment based on the examination of the NMR spectra is contrary to that made on the basis of the mechanism of the reduction. This problem will be discussed in more detail later.

Experimental

Samples. The tetralin-1-ols were prepared according to the method previously reported.5-7) The acetates of the tetralin-1-ols were prepared by the acetylation of the corresponding tetralin-1-ols with acetic anhydride and pyridine at room temperature overnight. The crystal products were purified by recrystallization, while the oily products were checked by a study of their IR spectra and VPC.

The acetate of Ia, mp 74.5—76.5°C.

Found: C, 80.88; H, 6.91%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

The acetate of IIIa, mp 102—103°C.

Found: C, 81.49; H, 6.56%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

The acetate of IIIb, mp 112—113°C.

Found: C, 80.87; H, 7.15%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

NMR Measurements. The NMR spectra were measured at 60 MHz on a Varian A-60 spectrometer. The sample was dissolved in $CDCl_3$, containing TMS as the internal reference.

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