The Relationship between the Conformation of Epimeric 6-Substituted 4-ene-3-Ketosteroids and their Ultraviolet and Infrared Absorption Spectra

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In the previous paper[1] an empirical rule has been presented for the absorption spectra of C_6-substituted 4-ene-3-ketosteroids. Namely, 6β-isomers have lower K-band intensities in the ultraviolet absorption spectra than the corresponding 6α-isomers. The effect was ascribed to the greater steric hindrance involved in 6β-isomers in which 6β-substituents have 1:3-X:C_{10}Me and 1:3-X:C_8H interactions[2].

Both α and β substituents in the system cause only the small wavelength displacements ($\pm\Delta\lambda\simeq 5\,\mathrm{m}\mu$) accompanied by decreases in ε. Hence, the type of spectral effects arising from the steric hindrance in the system may be associated with transitions between non-planar ground states and planar or near-planar excited states[3]. Thus the angles θ between the C_3 carbonyl groups and 4,5-unsaturated linkages in the ground state may be calculated from an equation $\cos^2\theta=\varepsilon/\varepsilon_0$, presented by Braude and Sondheimer[3], where ε_0 is the value for the unhindered compound in which $\theta=0$, if it is assumed that the 4-ene-3-keto system of 4-cholesten-3-one has uniplanar conformation. The values of θ derived in this way are given in Table I.

Table I

Ultraviolet Spectra of Epimeric 6-Substituted 4-Cholesten-3-one[4]

Compound	$\lambda_{\max}^{\mathrm{alc}}$ (mμ)	ε	$\varepsilon/\varepsilon_0$	θ°
4-cholesten-3-one	241	18,000[5]	1.	0
6α-hydroxy-	240	17,080	0.95	13
6β-hydroxy-	237	14,500	0.80	27
6α-acetoxy-	238	15,800	0.88	20
6β-acetoxy-	237	13,200	0.73	31
6α-chloro-	239	17,500	0.97	10
6β-chloro-	241	15,100	0.84	23
6α-bromo-	238	15,800	0.88	20
6β-bromo-	246	13,500	0.75	30
6α-methyl-	241	16,650	0.92	16
6β-methyl-	241	15,100	0.84	23

The greater values in the interplanar angles for the 6β-substituted 4-ene-3-ketosteroids, deduced from the difference in ultraviolet absorption, may be reflected in the infrared spectra. Unfortunately, only a limited number of the infrared spectra of these compounds have been reported[6,7,8]. In the infrared spectra of epimeric 6-acetoxy-4-cholesten-3-one[6] the location of the carbonyl band for 6β-isomer approaches that of saturated ketone more than that for 6α-isomer. A rough linear relationship[9] appears to exist between the interplanar angle θ deduced from difference in ultraviolet and $\Delta\nu/\Delta\nu_0$ where $\Delta\nu$ refers to the shift with respect to an unconjugated ketone (taken as $1713\,\mathrm{cm.}^{-1}$) and $\Delta\nu_0$ refers to the shift in the 4-cholesten-3-one (Table II).

Table II

Infrared Spectra of Epimeric 6-Acetoxy-4-Cholesten-3-one in Carbon Disulfide[4]

Compound	$\nu_{C=O}$(cm.$^{-1}$)	$\Delta\nu/\Delta\nu_0$	$\nu_{C=C}$(cm.$^{-1}$)
4-cholesten-3-one	1684	1.	1626
6α-acetoxy-	1692	0.72	1631
6β-acetoxy-	1698	0.52	—

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