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Conformations of 3-Alkoxycarbonyl-1-tetralols and 2-Ethoxycarbonyl-4-chromanols

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Synopsis. The 1- or 4-hydroxyl group in cis isomers of 3-alkoxycarbonyl-1-tetralols and 2-ethoxycarbonyl-4-thiochromanols are predominantly quasi-equatorial and those of the trans isomers quasi-axial. *cis*-2-Ethoxycarbonyl-4-chromanol prefers the quasi-axial OH conformation.

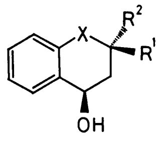
Intramolecular OH···π interaction has been used as a means of configurational and conformational studies on unsaturated alcohols.[1,2] This paper deals with the conformations of the alcohols having an alkoxycarbonyl group γ to the OH group.

The ν_{OH} absorption maxima of the alcohols examined are summarized in Table 1. Basing upon that the tetralin, chroman, and thiochroman skeletons exist preferentially as a half-chair from,[2—6] the previous studies elucidated that 1-tetralol and 4-chromanol epimers with quasi-axial OH group show each only a band around 3618 cm^{-1} and the quasi-equatorial one a doublet at 3622 and 3600 cm^{-1}, as represented by **4a**—**6a** and **4b**—**6b**, respectively, in Table 1. It is therefore readily assigned that the OH groups in **1a** and **3a** prefer the quasi-equatorial orientation and those of **1b** and **3b** the quasi-axial one. In contrast with these, **2a** showed two ν_{OH} bands at 3610 and 3596 cm^{-1}, the former band being stronger. Referring to the previous results,[3] an appearance of the two bands is ascribed to the coexistence of two conformers with quasi-axial and -equatorial OH groups, the former being predominant. This means that the conformation A with both axial OH and ester groups is more predominant than the conformation B.

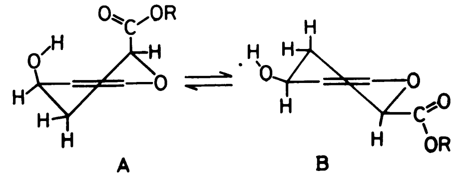
Table 1. The OH-stretching frequencies (ν_{OH}), half band-widths ($\Delta\nu_{1/2}$), and molar absorption coefficients (ε) for 1-tetralols, 4-chromanols, and 4-thiochromanols

Compound	ν_{OH}/cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	ε
1a	3621	21	21
	3599	16	52
1b	3618	17	63
2a	3610	18	42
	3596	15	31
3a	3619	12	24
	3592	13	49
3b	3617	17	47
	3600 sh	—	—
4a$^{a)}$	3622	23	37
	3600	10	66
4b$^{a)}$	3617	12	88
5a$^{a)}$	3622	23	34
	3596	14	75
5b$^{a)}$	3616	16	89
6a$^{b)}$	3625	18	32
	3594	12	52
6b$^{b)}$	3613	18	91

a) Ref. 3a. b) Ref. 3b.



1a $X=CH_2$, $R^1=COOC_2H_5$, $R^2=H$
1b $X=CH_2$, $R^1=H$, $R^2=COOC_3H_7$
2a $X=O$, $R^1=COOC_2H_5$, $R^2=H$
3a $X=S$, $R^1=COOC_2H_5$, $R^2=H$
3b $X=S$, $R^1=H$, $R^2=COOC_2H_5$
4a $X=CH_2$, $R^1=C_6H_5$, $R^2=H$
4b $X=CH_2$, $R^1=H$, $R^2=C_6H_5$
5a $X=O$, $R^1=C_6H_5$, $R^2=H$
5b $X=O$, $R^1=H$, $R^2=C_6H_5$
6a $X=S$, $R^1=CH_3$, $R^2=H$
6b $X=S$, $R^1=H$, $R^2=CH_3$



To clarify the conformational equilibrium, temperature dependence of the OH absorption was examined for **2a** and **3a** in the range 10—50 °C. The result indicated that the intensity of the lower frequency band increased with a rise in temperature for both **2a** and **3a**: the intensity ratio A_{3592}/A_{3619} of the two ν_{OH} bands at 3592 and 3619 cm^{-1} for **3a** changed from 1.3 at 10 °C to 2.2 at 50 °C. Accordingly, the quasi-axial OH conformer is more stable than the quasi-equatorial one in the equilibrium. Generally speaking, 3-hydroxycyclohexanecarboxylic acid ester do not form an intramolecular hydrogen bond.[7] If the two substituents in the cis isomer are fixed in a diaxial conformation, however, both carbonyl and alkoxyl oxygen-bonded OH species should be observed.[8] Although authors can not give a decisive explanation, the band at 3610 cm^{-1} of **2a** presumably arose from the diaxial conformation which is possible to form a hydrogen bond. Examination of the $\nu_{C=O}$ bands for **1a**, **2a**, and **3a**, however, afforded no clear sign of hydrogen-bond formation.

The above interpretation is supported by the ^{1}H-NMR measurements for **1**—**6** (Table 2). The coupling constants in Table 2 can be used to deduce the relative configurations and substituent conformations by making use of the Karplus relationship between vicinal HC-CH coupling constants and dihedral angles. A simplified method[5,6,9] can be adapted to the present cases. If the 2-substituent is in the equatorial position on half-chair dihydropyran ring and all the vicinal J's have the same sign, the value of $J_{3a\text{-}4}+J_{3e\text{-}4}$ would be significantly smaller for 2,4-*trans* than for 2,4-*cis* isomers.

TABLE 2. NMR PROTON COUPLING CONSTANTS FOR 1-TETRALOLS, 4-CHROMANOLS, AND 4-THIOCHROMANOLS

Compound	HC-CH coupling in $CDCl_3$ $J_{3a,4}+J_{3e,4}$/Hz		HC-OH coupling in DMSO $J_{\mathrm{HC-OH}}$/Hz	
	cis	trans	Quasi-equatorial OH	Quasi-axial OH
1a	15.4(d.d)		6.3	
1b		6.8(t)[a]		5.0
2a	10.0(t)			5.0
3a	12.5(d.d)[a]		5.8	
3b		7.2(d.d)		4.9
4a	17.0(d.d)[b]		7.1	
4b		6.0(t)[b]		5.3
5a	15.5—16.0(d.d)[c]		6.7	
5b		6.0—6.5(t)[c]		5.0
6a	15.3(d.d)[d]		6.3	
6b		5.9(t)[d]		5.4

a) Coupling constant of the acetate. b) Ref. 4. c) Refs. 5 and 6. d) Ref. 3b.

This explanation is assured with the data for **4**—**6** in Table 2. It is thus considered that the OH groups in **1a** and **3a** prefer the quasi-equatorial orientation and those of **1b** and **3b** the quasi-axial one. The value of $J_{3a,4}+J_{3e,4}$ (10.0 Hz) observed for **2a** is smaller than those of **1a** and **3a**, supporting the existence of the conformational equilibrium of **2a** in solution. The equilibrium is also supported by the hydroxyl ^{1}H-NMR measurements for **1**—**6** in dimethyl sulfoxide (DMSO) (Table 2).[10] The $J_{\mathrm{HC-OH}}$ of **2a** is significantly smaller than those of **1a** and **3a** and similar to those of the compounds with a quasi-axial OH group (**4b**, **5b**, and **6b**), rather than a quasi-equatorial OH group (**4a**, **5a**, and **6a**).

Experimental

3-Alkoxycarbonyl-1-tetralol (**1**),[11] 2-ethoxycarbonyl-4-chromanol (**2**),[12] and 2-ethoxycarbonyl-4-thiochromanol (**3**)[12] were prepared by reducing the corresponding ketones as reported. Since the pure *cis*-2-ethoxycarbonyl-4-thiochromanol (**3a**) was not readily isolated due to its instability, the mixture (1:1) of **3a** and **3b** was used for measurements. Then the infrared and NMR spectra of **3a** were obtained by subtracting the spectra of pure **3b** from those of the mixture.

Infrared spectra were measured using a KCl cell of 30 mm in optical length; the concentration of the CCl_4 solution was ca. 4×10^{-3} mol/dm^3. NMR spectra were measured at a probe temperature of 30 °C, using TMS as the internal standard.

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