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VIBRATIONAL CIRCULAR DICHROISM OF THE OH STRETCHING VIBRATIONS IN METHYL 3-HYDROXYBUTYRATE AND METHYL LACTATE

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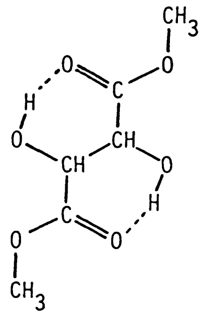
The vibrational circular dichroism associated with the OH stretching vibrations of methyl 3-hydroxybutyrate and methyl lactate has been measured in the CCl_4 solutions. The bisignate feature of VCD observed in methyl 3-hydroxybutyrate has been interpreted as the coexistence of rotational isomers in intramolecularly hydrogen bonded species.

Vibrational circular dichroism (VCD) has emerged and evolved over the past decade as a new spectroscopy, and is presently beginning to make a practical application to deducing the molecular structure and molecular dynamics of chiral molecules.1)

The VCD associated with the OH stretching vibration of dimethyl tartrate $[-CH(OH)COOCH_3]_2$ has been measured by Keiderling and Stephens.2) They interpreted the observed bisignate feature on the basis of a coupled-oscillator theory. This interpretation was subsequently questioned and an alternative explanation was proposed by Marcott et al.3) that the observed bisignate VCD was due to the two molecular species in intramolecularly hydrogen bonded structures, e.g., a six-membered ring hydrogen bond 1 and a five-membered ring hydrogen bond structure 2, on the basis of the result that the VCD of methyl mandelate $[C_6H_5CH(OH)COOCH_3]$ gave a monosignate peak in the OH stretching region. Su and Keiderling reported the temperature dependance of the OH stretching VCD and the deuteration effect of the OH and OD stretching VCD in dimethyl tartrate,4) and they concluded that the coupled-oscillator model was consistent with their new experimental data. In the present study the VCD spectra of methyl 3-hydroxybutyrate $[CH_3CH(OH)CH_2COOCH_3]$ and methyl lactate $[CH_3CH(OH)COOCH_3]$ were measured which are regarded as model compounds of the six-membered 1 and five-membered 2 ring hydrogen bond structures, respectively.



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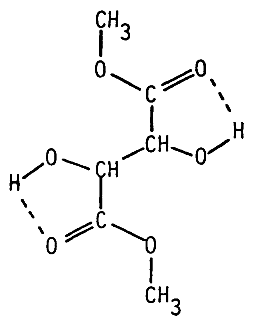

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The (-)-(R) and (+)-(S) isomers of methyl 3-hydroxybutyrate were obtained from Wako Chemical Co., and (-)-(S)- and DL-methyl lactate were obtained from

Aldrich Chemical Co. and Tokyo Kasei Co. They were used without further purification as dilute solutions in spectroscopic grade CCl_4. VCD spectra were measured with a JASCO (Japan Spectroscopic Co., Ltd.) J-200E infrared spectropolarimeter which is a modified instrument of a JASCO J-200D near-infrared spectropolarimeter. Major modifications are substitutions of a Barnes InSb detector with a large area (7 mm diameter) for a Judson's one, a Hinds CaF_2 modulator for a quartz one, and a wire-grid polarizer for a Glan-Taylor prism. This VCD unit was interfaced to a personal computer (NEC PC-9801) which allows data acquisition and subsequent data processing. The instrument was constantly flushed with nitrogen gas to reduce interfering atmospheric H_2O absorption.

In Fig. 1 are shown the VCD and absorption spectra of methyl 3-hydroxybutyrate and methyl lactate in the CCl_4 solutions. The intermolecular associations were negligible in such dilute solutions studied. The strong absorption band at 3565 cm^{-1} and the shoulder at 3630 cm^{-1} of the dilute solution of methyl 3-hydroxybutyrate are assigned to the intramolecularly hydrogen bonded and hydrogen-bond free OH stretching vibrations, respectively, according to Mori et al.[5)] The strong band at 3555 cm^{-1} and the weaker band at 3615 cm^{-1} of methyl lactate are assignable to the OH stretching vibrations of the intramolecular hydrogen bonds with the carbonyl and methoxy oxygen atoms, respectively.[5)] One should notice that the band width at 3565 cm^{-1} of methyl 3-hydroxybutyrate (85 cm^{-1}) is much broader than that at 3555 cm^{-1} of methyl lactate (40 cm^{-1}).

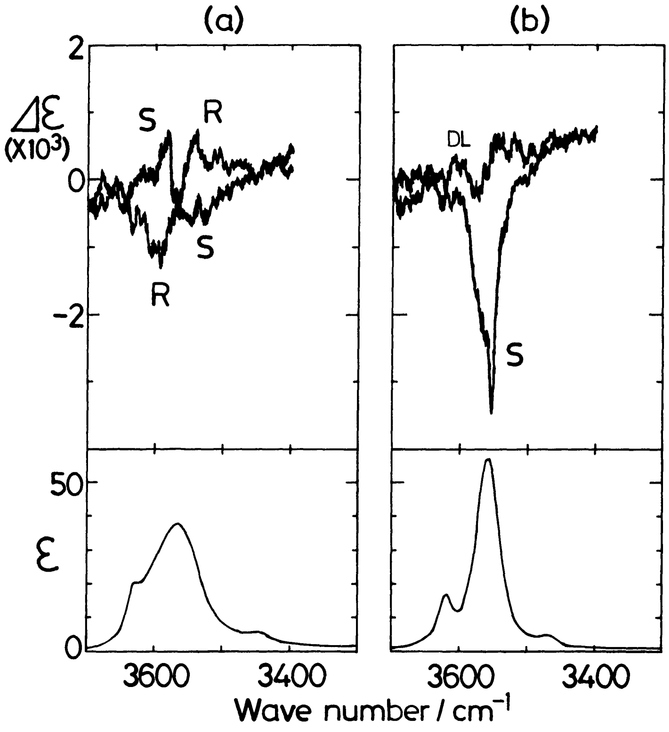
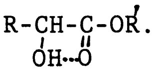
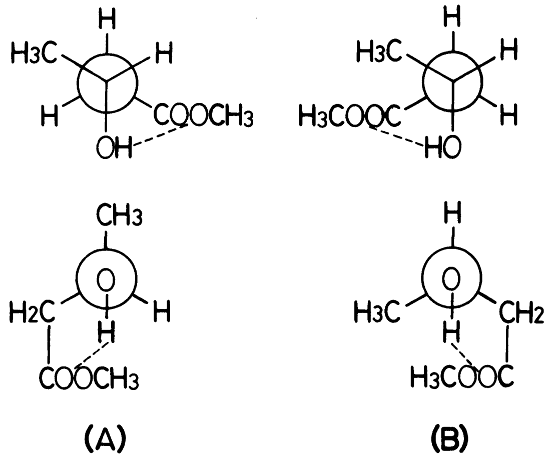


Fig. 1. VCD and absorption spectra of (a) methyl 3-hydroxybutyrate 8 mM (1 M=1 mol dm^{-3}), resolution 15 cm^{-1}, (b) methyl lactate 6 mM, resolution 18 cm^{-1}, in CCl_4 solutions at room temperature.

The VCD spectra of methyl 3-hydroxybutyrate exhibit a bisignate feature centered at 3565 cm^{-1} which corresponds to the intramolecularly hydrogen bonded OH stretching band maximum of the absorption spectrum. The CD spectrum of the R enantiomer shows negative and positive peaks from higher wave number, and the magnitudes of both lobes are approximately equal. The rotational strength of each lobe is $\pm 0.2 \times 10^{-43}$ (esu cm)^2. In methyl lactate only the monosignate VCD was observed for the absorption band at 3555 cm^{-1}, the OH stretching band of the intramolecular hydrogen bond with the carbonyl oxygen atom. The rotational strength of this band for the (S)-isomer is -1.1×10^{-43} (esu cm)^2. The VCD sign for the intramolecularly hydrogen bonded OH stretching of (S)-methyl lactate is the same as that of (S)-methyl mandelate[3)] with the same absolute configuration. Then the negative VCD observed in (S)-methyl lactate would be characteristic for the OH stretching VCD in the intramolecularly hydrogen bonded structure with the five membered ring 2 of the (S)-α-hydroxyesters



$R\text{-}\underset{\text{OH}\cdots}{CH}\text{-}\underset{\text{O}}{\overset{}{C}}\text{-}OR'$.



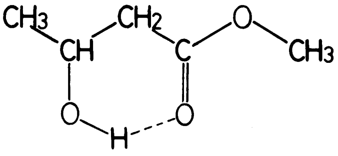


Fig. 2. Possible conformations of intramolecular hydrogen bonds in methyl 3-hydroxybutyrate.

Methyl 3-hydroxybutyrate has only one OH group and there is no possibility of a degenerate coupled-oscillator contribution to the CD band of the OH stretching vibration. Then we conclude that the observed bisignate feature comes from two molecular species which give rise to oppositely signed CD signals each other. A possible intramolecular hydrogen bond structure in methyl 3-hydroxybutyrate is a six-membered ring structure 1. The two conformations as shown in Fig. 2 could be possible as the six-membered ring strucure 1 with an intramolecular hydrogen bond. In those structures the conformation about the CH_2 -CH bond should take a gauche (G) or gauche' (G') form with reference to the CH-O and CH_2-COO bonds in order to make an intramolecular hydrogen bond.

In the structures (A) and (B) in Fig. 2 the environment of the OH group (the perturbation by ester group) would be approximately mirror-image relationship each other. Then it is plausible that these two structures give rise to the OH stretching VCD with opposite sign. Also one may expect these two structures to have slightly different OH stretching frequencies. According to the correlation of the OH stretching frequency and conformation about the C-O bond in secondary alcohol[6)] one might expect the structure (A) exhibits a slightly higher frequencies than the structure (B) in Fig. 2. Accordingly we tentatively assign the higher frequency lobe in VCD to the structure (A) and the lower one to the structure (B) in Fig. 2, respectively.

The smaller VCD intensity of methyl 3-hydroxybutyrate compared with methyl lactate is suggestive of some cancellation due to overlapping of the oppositely signed bands. The broader absorption band width of methyl 3-hydroxybutyrate compared with methyl lactate further implies close overlapping of two bands in frequency. Roughly the same intensity of two oppositely signed peaks in VCD suggests that two molecular species of conformations (A) and (B) of methyl 3-hydroxybutyrate as shown in Fig. 2 exist in roughly equal concentration. This is further supported by our analysis of the vicinal proton coupling constants $^3J_{HH}$ in ^{1}H-NMR.$^{7)}$

From the above discussion the similar rotational isomerism might be expected and contribute to the bisignate feature in dimethyl tartrate. The S-configuration in methyl 3-hydroxybutyrate corresponds to the R,R-configuration in dimethyl tartrate if the former could be regarded as a model compound of the latter by the substitution of the CH_3- group for the CH_3OCO-group on an asymmetric carbon atom. However, the bisignate structure observed in (2R,3R)-dimethyl tartrate is opposite sign of that in (S)-methyl 3-hydroxybutyrate and the band width in dimethyl tartrate (40 cm^{-1}) is about the same as that of methyl lactate and methyl mandelate but quite narrower than that of methyl 3-hydroxybutyrate. Then the origin of VCD in dimethyl tartrate might be different from methyl 3-hydroxybutyrate. The relative intensity of the two lobes in methyl 3-hydroxybutyrate would change with conformer population by variation of temperature and/or solvents. We are currently pursuing more extensive experiments to obtain more detailed information.

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