Intramolecular Hydrogen Bonds. VI.[1] The Characteristic Infrared OH Spectra of Isomeric Ethyl α, β-Dihydroxy-carboxylates and Their Geometries

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The threo and the erythro isomers of any compound of the RCH(OH)CH(A)R′ series, wherein R and R′ are alkyl groups and A is a proton-accepting group, show characteristic infrared OH spectra in a dilute carbon tetrachloride solution; the apparent relative intensities of the bonded and the free OH bands[2] and, in some cases, also the separations between the two bands $(\Delta\nu)$[3,4] are useful as important criteria for the configurational assignment. Such characteristic features, however, are not observed in ethyl dextro- and meso-tartrates, in which the apparent OH spectra are almost identical.[5]

In this investigation, we have found that isomeric α, β-dihydroxy-carboxylates of the $CH_3(CH_2)_n$-CH(OH)CH(OH)COOEt series, wherein n is an integer of 0, 1 and 2, exhibit some characteristic features which differ from the above statement in their OH spectra. The spectra were measured at 25°C according to a method previously[1] described. The concentrations were ca. 0.004 mol./l. in carbon tetrachloride, at which point intermolecular hydrogen bonding was absent. The erythro esters show identical OH spectra, composed of two peaks with nearly the same intensities, the higher frequency band being broadened on the higher frequency side. The threo isomers show a partially-resolved doublet with an additional shoulder at ca. 3625 cm^{-1}. In addition to these bands, both the isomers show a very weak band at ca. 3445 cm^{-1} due to the overtone of a carbonyl group.[6] Typical spectra are shown in Fig. 1, while the data on the apparent OH bands are summarized in Table I.

As is shown in the table, the lowest frequencies

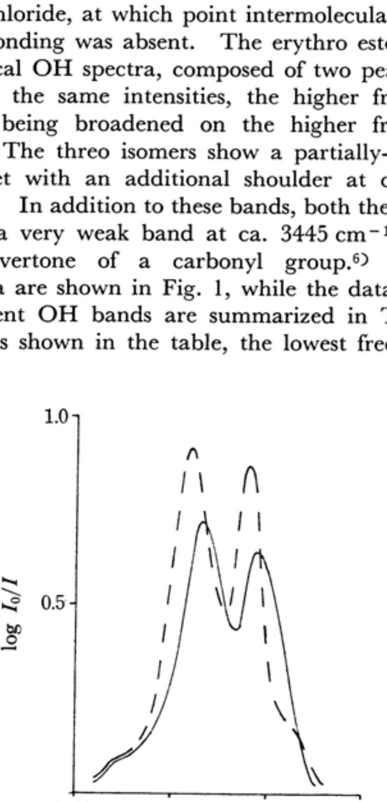

Fig. 1. OH spectra of ethyl α, β-dihydroxyvalerates.
Threo: ----; Erythro: ——

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TABLE I. SUMMARY OF INFRARED DATA OF THE ESTERS $CH_3(CH_2)_nCH(OH)CH(OH)COOEt$

	n	B. p. °C/mmHg	ν_{OH} cm^{-1} (D)[*1]				$\Delta\nu$ cm^{-1} (II−I)	D_I/D_{II}
			I	II	III	IV		
Threo	0	116/17	3522 (0.83)	3585 (0.79)	—	3622[*2]	63	1.05
Threo	1	99.5/5	3520 (0.94)	3579 (0.88)	—	3626[*2]	59	1.07
Threo	2	95/7	3521 (0.87)	3581 (0.76)	—	3626[*2]	60	1.14
Erythro	0	113.5/10	3533 (0.91)	3588 (0.83)	weak[*3]	—	55	1.09
Erythro	1	115/8	3532 (0.73)	3588 (0.64)	weak[*3]	—	56	1.14
Erythro	2	114—115/6	3532 (0.63)	3589 (0.60)	weak[*3]	—	57	1.05
Butane-2, 3-diol[3]								
Threo			—	3583	—	3632		
Erythro			—	3591	—	3633		
Ethyl lactate[1]			3543 (0.88)	—	3613 (0.19)	—		
Ethyl β-hydroxybutyrate[1]			3560 (0.58)	—	3590 (0.09)	3626 (0.09)		

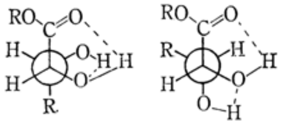
[*1] $D=\log I_0/I$ for the apparent bands.

[*2] These are of the shoulder of band.

[*3] Presumed from the broadening on the higher frequency side of band II.

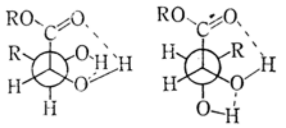
(ca. 3521 and 3532 cm^{-1} (band I)) and the separations between the strong peaks (ca. 61 and 56 cm^{-1}) are characteristic of the threo and the erythro esters respectively, but their relative intensities are indiscriminate. The additional OH absorption on the higher frequency side is, in both cases, very weak, yet it can serve as another indicator for a configurational assignment.

The α-OH group and the β-OH group can form hydrogen-bonds with one another and with the carbonyl- and the ether-oxygen atom of the ester group. According to the findings on intramolecular hydrogen bonding in α- and β-hydroxycarboxylates previously[1] reported, the hydrogen bond with the carbonyl-oxygen atom is stronger in the α-series than in the β-series; the extent of this hydrogen-bonding is very high compared with that of the hydrogen-bonding with the ether-oxygen atom in both series. Evidence for the type of hydrogen-bonding between the OH groups has already been given for ethylene-glycols.[3] On the basis of this, band I may almost exclusively be due to the α-OH group bonded to the carbonyl-oxygen, and band II may be due to the β-OH group bonded to the oxygen atom of the above bonded α-OH group, since the free OH band IV does not appear or is only slightly present. In the erythro esters, the broadening on the higher frequency side of band II may be caused by an additional weak absorption of OH groups bonded to the ether-oxygen atom. Accordingly the OH groups assigned to bands I and II must be skew to one another in respect to the C_α–C_β bond, as is shown in geometries I—IV:



I II

Threo form



III IV

Erythro form

In the NMR spectra* of the threo and the erythro ester with $n=1$ in solutions of 5 v.% in carbon tetrachloride, the resonance line of the α-methine proton appears at −3.98 p.p.m. from TMS as a doublet ($J_{\alpha\beta}=2.3$ c.p.s.) for the threo ester and at −4.09 p. p. m. as a doublet ($J_{\alpha\beta}=3.8$ c. p. s.) for the erythro isomer. The J values indicate in each case that the two methine-hydrogens are skew to one another in respect to the C_α–C_β bond.[7] Since such an orientation of the hydrogens is considered to be probable also in a concentration

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* The spectra were measured at ca. 25°C in the concentration range from 5 to 20 v.% in carbon tetrachloride, using a Varian A-60 spectrometer on pre-calibrated chart paper; TMS was used as the internal standard. The δ values of the α-methine protons in both the esters were somewhat dependent on the concentrations, but the J values were not.

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as low as 0.004 mol./l., form I seems to be most favorable for the threo esters in a dilute carbon tetrachloride solution, and form III and/or form IV for the erythro isomers.

Experimental

The threo and the erythro esters were prepared by Fischer's method of esterification from the respective α, β-dihydroxy-carboxylic acids,[8] which had been obtained by the oxidation of the corresponding *trans*-olefinic acids[9] with silver chlorate in the presence of osmium tetroxide and with perbenzoic acid respectively. The threo forms of the free dihydroxy-acids with $n=0$, 1 and 2 melted at 74, 75 and 107°C respectively, and the erythro isomers, at 80, 105 and 98°C. The boiling points of the ethyl esters are shown in Table I.

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