Intramolecular Hydrogen Bonds. V.[1] Aliphatic Hydroxy-carboxylates[*1]

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In a previous paper,[2] it was reported that an intramolecular hydrogen bond is formed in some α- and β-hydroxy-carboxylates in a dilute carbon tetrachloride solution, mainly on to the carbonyl-oxygen atom, rather than to the ether-oxygen of the ester group; the bonded OH-stretching frequencies were about 3540 cm^{-1} in the α-hydroxy esters and about 3559—3586 cm^{-1} in the β-hydroxy esters. In addition to this strong band, a completely resolved or an unresolved weak band or shoulder appeared in the range from ca. 3610 to 3625 cm^{-1} in both cases. It has, however, not yet been settled whether this band or shoulder is due to the free OH group or to the OH group bonded to the ether-oxygen atom. Flett[3] has suggested that it comes from the free OH group and has attributed the lowering in frequency (by ca. 10 to 20 cm^{-1} from the free OH frequencies of alcohols) to the electron-attracting effect of the ester group. This point has now been elucidated with reference to the rotational isomerism around the C–OH bond, by means of infrared measurements of a series of α- and β-hydroxy-carboxylates. Further, this paper will report on the limitation of intramolecular hydrogen bonding through the length of an alkylene chain intervening between the hydroxyl and the ester group in the ω-hydroxy $HO(CH_2)_nCOOR$ series, as well as in isomeric hydroxycyclohexane-carboxylates.

Experimental

Samples.—All the esters used are listed in Table I. The esters 1, 3, 5, 7, 9, 15, 16, 19 and 21 were those previously[2] used, while the esters 2, 4, 6, 8, 18 and 20 were prepared in similar manners. Ester No. 10 was prepared by Reformatsky reaction from acetone and methyl bromoacetate; No. 11 by the reduction of

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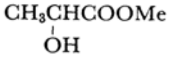
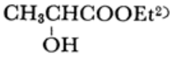
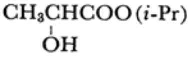
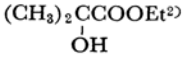
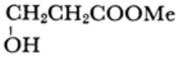
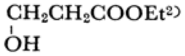
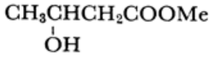
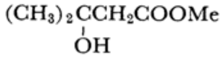
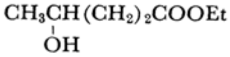
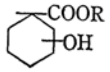
1) Part IV: N. Mori, S. Ōmura and Y. Tsuzuki, This Bulletin, **38**, 1631 (1965).

2) N. Mori, S. Ōmura, O. Yamamoto, T. Suzuki and Y. Tsuzuki, ibid., **36**, 1401 (1963).

3) M. St. C. Flett, *Spectrochimica Acta*, **10**, 21 (1957).

TABLE I. SUMMARY OF INFRARED DATA

No.	Ester	B. p., °C/mmHg (n_D^{25})	Band*	ν_{OH} cm^{-1}	D**	$\Delta\nu_{1/2}$ cm^{-1}	D_{II}/D_I
1	$\mathrm{HOCH_2COOEt}$[2]		I	3550[a]	0.68	46	
			II	3618[a]	0.13	25	0.19
2	 $\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCOOMe}$	68/46	I	3549	0.74	43	
			II	3616	0.17	32	0.23
3	 $\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCOOEt}$[2]		I	3543	0.88	44	
			II	3613	0.19	18	0.22
4	 $\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCOO(\mathit{i}\text{-}Pr)}$	74/40	I	3544	0.74	44	
			II	3614	0.15	21	0.20
5	 $\mathrm{(CH_3)_2}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{COOEt}$[2]		I	3544	0.43	48	
			II	3606	0.09	21	0.21
6	 $\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{H_2CH_2COOMe}$	74/15	I	3586	0.42	87	
			IIIa	3621	0.04	18	
			IIIb	3638	0.14	20	
7	 $\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{H_2CH_2COOEt}$[2]		I	3584[a]	0.46	110	
			IIIa	3624[a]	0.04	16	
			IIIb	3640[a]	0.17	24	
8	 $\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2COOMe}$	67/13	I	3559	0.49	82	
			II	3592	0.08	32	
			IIIab	3622	0.16	30	
9	 $\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2COOEt}$[2]		I	3560	0.58	82	
			II	3590[a]	0.08	37	
			IIIab	3626[a]	0.11	39	
10	 $\mathrm{(CH_3)_2}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{CH_2COOMe}$	67/15	I	3537	0.59	54	
			II	3588	0.04	20	
			IIIab	3613	0.06	22	
11	 $\mathrm{CH_3}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{H(CH_2)_2COOEt}$	85—87/2	I	3544	0.12	74	
			IIIa	3618	weak		
			IIIab	3628	0.13	41	
12	$\mathrm{HO(CH_2)_5COOEt}$	138/20[4]	I	3542	0.12	72	
			IIIa	3624	0.20	14	
			IIIb	3640	0.62	26	
13	$\mathrm{HO(CH_2)_6COOEt}$	145/15[4]	IIIa	3624	0.12	14	
			IIIb	3639	0.47	25	
14	$\mathrm{HO(CH_2)_8COOEt}$	131—132/2[5]	IIIa	3620	0.09	13	
			IIIb	3638	0.33	25	
15	$\mathrm{HO(CH_2)_9COOEt}$[6]		IIIa	3626[a]	0.07	16	
			IIIb	3641	0.36	24	
16	$\mathrm{HO(CH_2)_{10}COOEt}$[6]		IIIa	3620[a]	0.13	18	
			IIIb	3638	0.48	24	
							
	R Position of OH						
17	Me 1	87/10	I	3540	0.78	42	
		(1.4585)	II	3609	0.22	32	0.31
18	Me cis-2	103/14[7]	I	3544	0.60	80	
		(1.4637)	IIIab	3624	0.13	40	
19	Et cis-2[2]		I	3536[a]	0.55	76	
			IIIab	3620[a]	0.08	40	
20	Me trans-2	112.5/14[7]	I	3530	0.19	108	
		(1.4634)	II	3596	0.41	55	
			IIIab	3620	0.14	20	
21	Et trans-2[2]		I	3534[a]	0.28	102	
			II	3596[a]	0.36	63	
			IIIab	3624[a]	0.08	19	

(Continued TABLE I)

No.	R	Position of OH	B. p., °C/mmHg (n_D^{25})	Band*	ν_{OH} cm^{-1}	D**	$\Delta\nu_{1/2}$cm^{-1}	D_{II}/D_I
22	Me	cis-3	113—115/5[8] (1.4658)	IIIab	3620	0.72	24	
23	Me	trans-3	111—112/6[8] (1.4657)	IIIab	3624	0.70	26	
24	Me	cis-4	128/12[9,10] (1.4684)	IIIab	3624	0.76	28	
25	Me	trans-4	125/12[9,10] (1.4669)	IIIab	3626	0.78	26	

a) The frequencies are different from those previously[2] reported, but more exact.

* Band I denotes the band of the OH group bonded to the carbonyl-oxygen atom as in form I shown in Fig. 2, band II that of the OH group bonded to the ether-oxygen atom as in form II, and bands IIIa and IIIb are of the free OH groups as in forms IIIa and IIIb, respectively, and band IIIab consists of both the bands IIIa and IIIb.

** $D=\log I_0/I$

ethyl levulinate with sodium borohydride; Nos. 12 and 13 by the oxidation of the corresponding cycloalkanones with potassium persulfate in ethanol; No. 14 by the Bouveault-Blanc reduction of the corresponding α,ω-dicarboxylic acid monoester, followed by esterification; No. 17 by the hydrolysis of cyclohexanone-cyanohydrin followed by esterification, and Nos. 22 to 25 by the catalytic hydrogenation of the corresponding methyl hydroxybenzoates. The γ-hydroxyvalerate (11) was considerably contaminated by its lactone, which was formed during vacuum distillation. The physical constants of these esters agreed with those reported in the literature (cf. Table I).

Infrared Measurements.—These were carried out with solutions of ca. 0.004 mol./l.[*3] in carbon tetrachloride at 25°C, in the OH-stretching region from 3300 to 3700 cm,$^{-1}$ using a Perkin-Elmer 21 spectrophotometer equipped with a lithium fluoride prism and with a cell 3 cm. in length. The slit width was constantly 0.029 mm. The observed frequencies were calibrated against that of the atmospheric vapor. The OH spectra observed were apparently those of an unresolved or a resolved doublet or triplet and were graphically separated[*4] into two or three symmetric components, assuming that they consist of symmetric bands. The infrared data of the separated band-components are summarized in Table I.[*5] The frequencies of the peaks of the components were identical with those of the apparent bands, but most of their absorbances were somewhat or much lower than those of the latter bands.

Results and Discussion

The infrared data of the esters investigated are listed in Table I.

***α*-Hydroxy Esters.**—All the esters, without exception, show a strong symmetric band at 3540—3550 cm^{-1} (band I) and a weak symmetric band at 3606—3618 cm^{-1}, as Fig. 1 shows. The

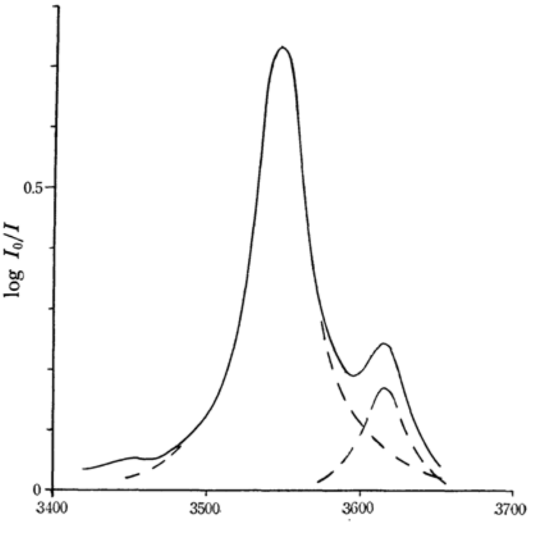


Fig. 1. OH spectrum of methyl lactate (2).

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4) R. Robinson and L. H. Smith, *J. Chem. Soc.*, **1937**, 373.

5) P. Chuit and J. Hausser, *Helv. Chim. Acta*, **12**, 466 (1929). Me ester: b. p. 137—139°C/3 mmHg.

6) N. Mori, S. Ōmura and Y. Tsuzuki, This Bulletin, **38**, 1037 (1965).

7) H. B. Henbest and B. B. Millward, *J. Chem. Soc.*, **1960**, 3575; J. Pascual, J. Sistaré and A. Regás, ibid., **1949**, 1943.

8) H. L. Goering and C. Serres, *J. Am. Chem. Soc.*, **74**, 5908 (1952); D. S. Noyce and D. B. Denney, ibid., **74**, 5912 (1952); S. Siegel, ibid., **75**, 1317 (1953).

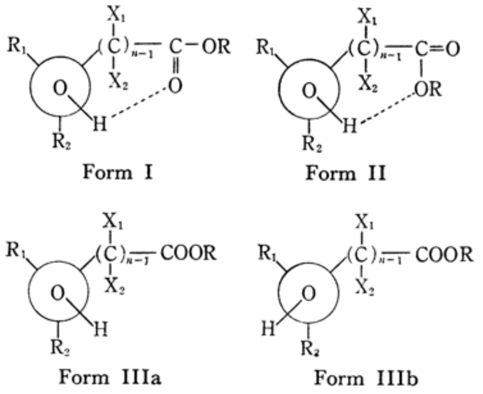
9) D. S. Noyce and H. I. Weingarten, ibid., **79**, 3098 (1957).

10) N. R. Campbell and J. H. Hunt, *J. Chem. Soc.*, **1950**, 1379.

[*3] At this concentration, intermolecular hydrogen bonding was entirely absent; a very weak band due to the overtone of a carbonyl group appeared in all the spectra at ca. 3445 cm^{-1}, in addition to the strong bands listed in Table I.

[*4] The graphical separation was made by reflecting the major component of a doublet or a triplet about the ordinate at the apparent maximum and by subtracting the mirror image from the observed spectrum. In the triplet, the residual minor part, unsymmetric on the lower or on the higher frequency side, was then similarly separated into two. The process was repeated by the trial and error method, until the components were symmetric.

[*5] Each ester in the cyclohexane series herein investigated can take two interconvertible chair-conformations; therefore, the OH band should consist of two bands due to the axial and the equatorial OH group, which are somewhat different in frequency (see A. R. H. Cole, P. R. Jefferies and G. T. A. Müller, *J. Chem. Soc.*, **1959**, 1222 and previous papers). This difference in frequency is too small to separate the observed OH band into the two components, and, at any rate, such separation is not very significant in this investigation. Accordingly, such a distinction has not drawn herein.

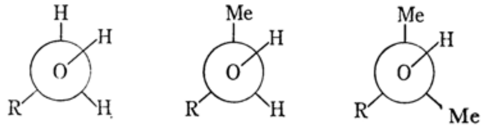


n	Ester No.	R_1	R_2	X_1	X_2
1	1	H	H		
1	2—4	Me(or H)	H(or Me)		
1	5	Me	Me		
1	17	R_1 and R_2 together form the pentamethylene group			
2	6, 7	H	H	H	H
2	8, 9	Me(or H)	H(or Me)	H	H
2	10	Me	Me	H	H
2	18, 19	R_1 and X_1 together form the tetramethylene group, and R_2 and X_2 are hydrogens.			
2	20, 21	R_1 and X_2 together form the tetramethylene group, and R_2 and X_1 are hydrogens.			
3	11	Me(or H)	H(or Me)	H	H
3	22	R_1 and X_1 on the C_1 atom together form the trimethylene group, and R_2, X_2 and the other X_1 are hydrogens.			
3	23	R_1 and X_2 on the C_1 atom together form the trimethylene group, and R_2, X_1 and the other X_2 are hydrogens.			
4	24, 25	The same with ester Nos. 22 and 23, respectively, except the trimethylene group is replaced by the ethylene group.			
5 or more	12—16	H	H	H	H

Fig. 2. Possible rotational isomers around the C-OH axis.

frequency of the latter band decreases with the increasing number of methyl groups attached to the α-carbon atom. In assigning this band, it is convenient to take into account the rotational isomers possible by rotation around the C_α–O axis, as is shown with the four possible forms, I—IIIa,b, and their mirror images, in Fig. 2. In this figure, form I is hydrogen-bonded with the carbonyl-oxygen atom, and form II, with the ether-oxygen atom, while forms IIIa and IIIb do not form any hydrogen bond.

According to the infrared study of alcohols by Ōki and Iwamura,[11] the OH frequency depends on the number of methyl groups skew to the OH group with respect to the C–O bond, as is shown by forms A—C:



ν_{OH} cm^{-1} Form A: 3640 Form B: 3627 Form C: 3617

wherein R represents a hydrogen atom or an alkyl group.

As examples of compounds capable of taking a hydrogen-bonded form such as form I (n=1 in the figure) we may mention such α-ketols as acylmethyl carbinol[12] and 2-hydroxycyclohexanones[13], whose bonded and free OH frequencies are ca. 3490 and 3615 cm^{-1} respectively. The latter frequency is lower by 12 cm^{-1} than the OH frequency of 3627 cm^{-1} in form B of alcohols; this lowering in frequency may be caused by the electron-attracting effect of the ketone group.

In the case of the α-hydroxy esters, the electron-attracting effect of the ester group exercised on the OH frequency, if there is any at all, is probably much smaller than that of the ketone group. The weak band of glycolate 1 appears at 3618 cm^{-1}, lower by 22 cm^{-1} than the OH frequency of 3640 cm^{-1} in form A of alcohols; therefore, it can not be due to the free OH group in form IIIb corresponding to form A. This indicates, further, the absence of the non-bonded form IIIa, which should be thermodynamically less stable than IIIb. Accordingly, the band must be assigned to the bonded OH group in the residual form II. In this case, the lowering in frequency is 9 cm^{-1} from the OH frequency of 3627 cm^{-1} in form B, corresponding to form II.

In the lactates 2, 3 and 4, similarly, the weak band whose frequency is lower by ca. 13 cm^{-1} than the 3627 cm^{-1} of the OH band for form B and lower by ca. 3 cm^{-1} than the 3617 cm^{-1} for form C, may consist of a major component due to the bonded OH group in form II and a minor component due to one in the less stable rotational isomer II (R_1=H; R_2=Me). With α-hydroxyisobutyrate 5 and 1-hydroxycyclohexane-carboxylate 17, since the lowering in the frequency of the weak band is ca. 10 cm^{-1} from the 3617 cm^{-1} in form C, comparable to the above cases, this band may be predominantly due to the bonded OH group in form II. Consequently, the OH group other than that in form I may hydrogen-bond with the ether-oxygen atom to a much larger extent than it remains free.

Further evidence for this assignment is provided by the fact that the frequencies of the esters 1,

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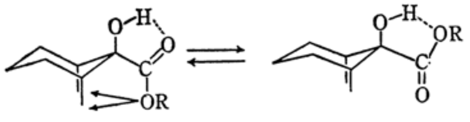
[11] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

[12] M. C. Duculot, *Compt. rend.*, **241**, 1738 (1955).

[13] A. R. H. Cole and G. T. A. Müller, *J. Chem. Soc.*, **1959**, 1224; N. H. Cromwell and R. E. Bambury, *J. Org. Chem.*, **26**, 997 (1961), and the references therein cited.

2—4 and 17 are in good agreement with the bonded OH frequencies of 3622, 3614 and 3607 cm^{-1}, respectively, of the monoacetates[14] of ethylene glycol, *trans*-cyclohexane-1, 2-diol and 1-hydroxycyclohexylcarbinol in a hydrogen-bonded form such as form II. These frequencies are higher by 10—21 cm^{-1} than the bonded OH frequencies of 3612,[15] 3602[15] and 3586[14] of the respective free diols; this rise in frequency may be attributed to the decreased electron-density on the ether-oxygen atom resulting from the resonance of the ester group. A similar finding is afforded in the case of diaxial *cis*-cyclohexane-1, 3-diols and their monoacetates.[16]

The ratio of the absorbance of the weak band to that of the strong band (D_{II}/D_I) is substantially constant in the esters, 1—5, except 17, irrespective of the number of methyl groups on the α-carbon atom, but it tends to decrease as the alcoholic alkyl portion of the ester group increases in bulk or in number of carbon atoms, as is positively shown for lactates 2, 3 and 4, The relatively high ratio of the ester 17 may be explained in terms of the possible steric repulsion between the axial hydrogens on C_2 and C_6 and the alkoxy group in form I; by this means this form can be partially converted into form II, as is shown, e. g., by the following equilibrium between conformations containing an OH group axial:



Form I Form II

β-Hydroxy Esters.—The β-hydroxy-propionates and -butyrates 6—9 show, in each case, a strong band in the range from 3559 to 3586 cm^{-1}; this band is considerably broadened on the higher frequency side, and it also has a shoulder at ca. 3620—3640 cm^{-1} on this side, as is shown in Fig. 3. On the other hand, the isovalerate 10 shows a strong, almost symmetric band at 3537 cm^{-1}, with a broad shoulder on the bottom of the band on the higher frequency side; the latter can be separated into two components, as is shown in Fig. 4. However, the spectra of the cyclic esters 18—21 are somewhat different; the cis esters show a strong band at 3544 cm^{-1}, with a weak shoulder on the higher frequency side, and the trans isomers, an unresolved triplet with a maximum at 3596 cm^{-1}, as is shown in Figs. 5 and 6.

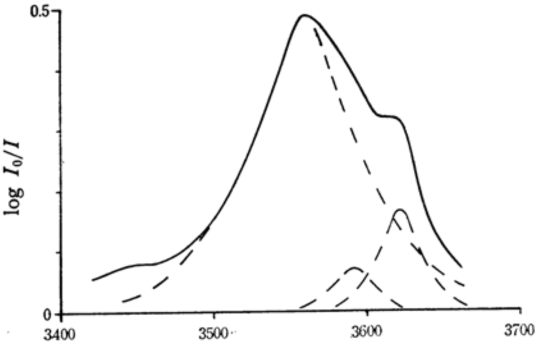


Fig. 3. OH spectrum of methyl 2-hydroxybutyrate (8).

In a previous paper,[2] which dealt with ethyl β-hydroxy-propionate and -butyrate (7 and 9), it could not be concluded whether the shoulder of the band was due to the free OH group. This point has now been solved by separating each of the complicated bands into three components, as is shown in Fig. 3. The separated components have maxima at 3585, 3622 and 3639 cm^{-1} in the case of the esters 6 and 7; the lowest frequency

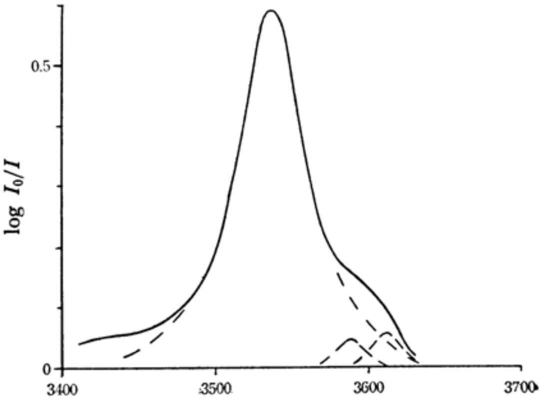


Fig. 4. OH spectrum of methyl 2-hydroxyisovalerate (10).

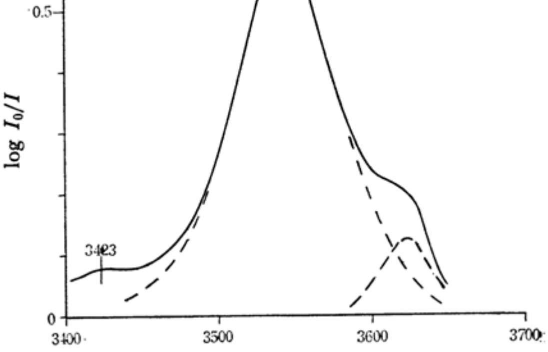


Fig. 5. OH spectrum of methyl *cis*-2-hydroxycyclohexane-carboxylate (18).

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[14] N. Mori, unpublished data.

[15] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

[16] H. B. Henbest and B. J. Lovel, *J. Chem. Soc.*, **1959**, 1965; H. B. Henbest and J. McEntee, ibid., **1961**, 4478.

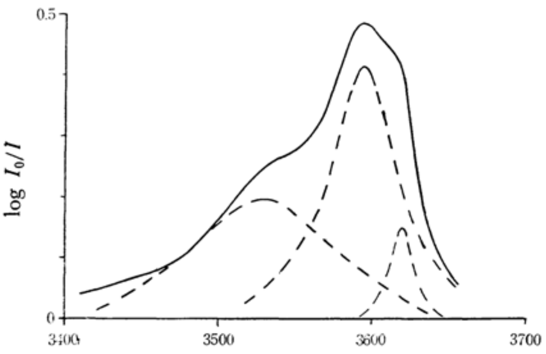

Fig. 6. OH spectrum of methy *trans*-2-hydroxy-cyclohexane-carboxylate (20).

band may be due to the bonded OH group in form I (band I). The other two may be assigned to the free OH groups in forms IIIa and IIIb, rather than to the bonded OH group in form II, because their relative intensities and frequencies are comparable to those of the other ω-hydroxy esters 12—16.

In the β-hydroxybutyrates 8 and 9, the band at 3624 cm^{-1} may consist predominantly of two bands due to the free OH groups in forms IIIa (R_1=Me ; R_2=H) and IIIb, probably with a weaker band due to the free OH in another form IIIa (R_1=H ; R_2=Me), because the frequency is comparable to the 3627 cm^{-1} of the OH group in form B corresponding to the former two forms, while it is higher than the 3617 cm^{-1} of the OH group in form C corresponding to the latter IIIa. Subsequently, the band at 3590 cm^{-1} may be due to the bonded OH group in form II. This assignment can be supported also by the fact that the intensity of this band relative to the band IIIab of 3624 cm^{-1} is higher than those of the band IIIa to IIIb for all the ω-hydroxy esters. The same assignments can be given for the separated band-components in the cyclic series, 18—21. In this series, it is of interest that the cis-esters almost exclusively take form I, while the trans-isomers prefer form II, though the reason for this is not clear.

In the β-hydroxyisovalerate 10, the three bands can similarly be assigned to two bonded groups and one free OH group, as Table I shows.

Further evidence for the assignment of band I is given by the fact3) that diacetone-alcohol and hydroacetylacetone, capable of forming a ring similar to form I through intramolecular hydrogen-bonding, exhibit the bonded OH frequencies of 3532 and 3557 cm^{-1} respectively; these frequencies are comparable to those of the esters 10 and 8. A hydrogen-bonded form similar to form II can be realized in the diaxial conformations of *cis*-1, 3-diol monoacetates in cyclohexane systems; the bonded OH frequencies are lower by ca. 20 cm^{-1} than the corresponding free OH ones;16) this affords additional support for the assignment of band II.

From the above informations and reasoning, we are led to the conclusion that the methyl groups on the β-carbon atom sterically serve to make the hydroxyl and the ester group closer together; the non-bonded forms, IIIa and IIIb, thereby decrease in proportion, and instead the hydrogen-bonded form, II, comes into existence. Further, this effect results in strengthening the hydrogen bond in form I, as is indicated by the facts that the degree of the lowering in frequency of band I resulting from the introduction of one or two methyl groups is unexpectedly large (i. e., ca. 30 cm^{-1} per methyl group) and that, simultaneously, the relative intensity of band I tends to increase. Such an effect is, however, not observed in the α-hydroxy esters.

The Other Esters.—Higher ω-hydroxy esters do not form a hydrogen bond with the ether-oxygen atom in form II. However, some of them are hydrogen-bonded with the carbonyl-oxygen atom. In the γ-hydroxyvalerate 11, the bonded OH band I has almost the same intensity as that of the free OH band, but in the ε-hydroxy ester 12 (see Fig. 7) it is very weak, and in the other ω-hydroxy esters, it entirely disappears. It is interesting that the ester 12 is hydrogen-bonded and a nine-mumbered ring is formed, although the largest ring hitherto known contains at most eight members (in 5-methoxypentanol[17] and 5-phenylpentane-1,5-diol[18]). In addition to this, these esters have, in cach case, a strong free OH band broadened on the lower frequency side; the two components separated may be due to the free OH groups in forms IIIa and IIIb respectively.

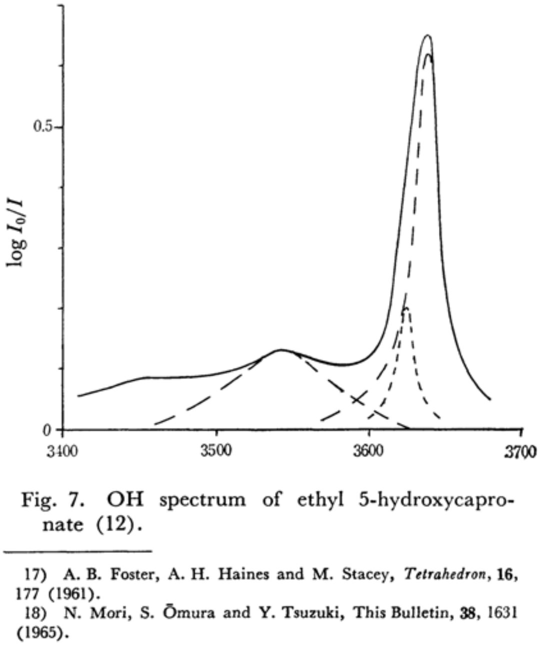

Fig. 7. OH spectrum of ethyl 5-hydroxycapronate (12).

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[17] A. B. Foster, A. H. Haines and M. Stacey, *Tetrahedron*, **16**, 177 (1961).

[18] N. Mori, S. Ōmura and Y. Tsuzuki, This Bulletin, **38**, 1631 (1965).

In the case of the ester 11, the lower frequency band is due to the free OH group in form IIIa (R_1=H ; R_2=Me), while the higher frequency band is due to that in forms IIIa (R_1=Me; R_2=H) and IIIb. The intensity ratios of band IIIa to band IIIb (or IIIab) are ca. 0.25.

3- and 4-Hydroxycyclohexane-carboxylates (22—25) are not internally hydrogen-bonded. The absence of any hydrogen bonding in the *cis*-4-hydroxy ester 24 can be explained in view of the fact that even if the hydrogen bonding were possible, the stabilization[*6] resulting from it would be much lower than the instabilization[*7] resulting from taking the boat or twist conformation required for ordinary hydrogen-bondings between 1- and 4- cis groups.[19] In the case of the *cis*-3-hydroxy ester 22, the reason for the absence of hydrogen-bonding seems to be that the orientation of the ester group in its 1, 3-diaxial chair-conformation is unfavorable for hydrogen-bonding. If the ester group could take an orientation favorable for hydrogen-bonding with the OH group, the stabilization[*6] resulting from the hydrogen-bonding could exceed the difference in free energy (ca. 2.0 kcal./mol.[*8]) between the non-bonded diaxial and the diequatorial chair-conformation and, therefore, molecules taking the diaxial conformation which is hydrogen-bonded should be present to a considerable extent.

Comparison with Other Hydrogen-bonded Systems.—As has been described above, the bonded OH frequencies may reasonably be assigned on the basis of a comparison with those of some ketols and alkane-diol monoacetates. In this paragraph, they will be compared with those of α, ω-alkane-diols[15,17] and ω-methoxyalkanols[17] of the series $RO(CH_2)_nOH$, wherein R is a hydrogen atom or a methyl group. As is shown in Table II, only when the number of members in a ring to be formed through hydrogen-bonding is equal to 5, the bonded OH frequncies I in the α-hydroxy esters are much lower, but the frequencies II are slightly higher than those of the other series. This seems to indicate this decreasing order in proton-accepting power: ester C=O>MeO>HO>ester –O–,[†] if the distances between the hydroxyl-hydrogen and the proton-accepting oxygen atoms in all the series are almost equal in such probable geometries that the OH and the ester group in the esters are oriented as in forms I and II (in I, the C=O bond almost eclipses the C_α–O bond and the C–OR bond is situated between the C_α–R_1 and the C_α–R_2 bond, while in II, the C=O bond almost eclipses the C_α–R_1 bond and the C–OR bond is skew to the C_α–O and the C_α–R_2 bond.); the OH and the OR group in both the alkanol series are skew to one another with respect to the C_α–C_β axis.

TABLE II. A COMPARISON OF BONDED OH FREQUENCIES (ν_{bondedOH} cm^{-1})

Number of ring-memers	Hydroxy ester			$RO(CH_2)_nOH$[17]	
	Ester No.	Band I	Band II	R=H	R=Me
5	1	3550	3618	3619, 3612[15]	3610
	3	3543	3613		
6	7	3584	—	3565, 3558[15]	3554
	9	3560	3590		
7	11	3544	—	3484, 3478[15]	3460
8				—	3500
9	12	3542	—	—	—

When the ring consists of six members or more, however, the frequencies I and II of the ester series are higher than those of both the alkanol series; this indicates that the OH group in the former series is more apart from the proton-accepting atoms than in the case of the latter. Further, in the hydrogen-bonded esters with $n=1-5$ (except 2,) the OH–O=C distances are almost equal and with $n=2$ it is longer, if the bonded OH frequencies directly reflect the distances, as has been recognized in the alkane-diol system.[15]

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[*6] Compared with the enthalpies of 2—3 kcal./mol. for ordinary OH-O type intramolecular hydrogen bondings.[20]

[*7] Compared with the free energy difference between the chair and the twist conformations of the cyclohexane of 4 kcal./mol.[21]

19) R. D. Stolow, P. M. McDonagh and M. M. Bonaventure, *J. Am. Chem. Soc.*, **86**, 2165 (1964), and references therein cited.

20) H. Buc and J. Néel, *Compt. rend.*, **255**, 2947 (1962); L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

21) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York, N. Y. (1962), p. 206.

[*8] Approximated by adding the corresponding values of 0.9 and 1.1 kcal./mol.[22] for an OH and an ethoxycarbonyl group, since such summation has been verified to be approximately correct in some cases.[23,24] This value is comparable to the 1.9 kcal./mol.[23] for *cis*-cyclohexane-1, 3-diol, which is strongly internally hydrogen-bonded.[15]

22) Ref. 21, p. 236.

23) S. J. Angyal and D. J. McHugh, *Chem. & Ind.*, **1956**, 1147.

24) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961); E. L. Eliel and H. Haubenstock, *J. Org. Chem.*, **26**, 3503 (1961).

[†] This order can be supported also by the 3622 cm^{-1} of ethyleneglycol monoacetate (see Ref. 14).