773. *Hydroxy-steroids. Part II.* The Conformations and Infrared Spectra of Steroid 3,5-Diols and Related Compounds.*

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The conformational features of a series of 3,5-dihydroxy-, 3-acetoxy-5-hydroxy-, and 5-hydroxy-3-oxo-steroids, and the corresponding decalin derivatives have been studied by infrared spectroscopy. The results of examining the O–H stretching region of dilute solutions under high dispersion are readily interpreted and give useful information about the nature and degree of interaction between the two functional groups in these compounds.

Intermolecular bonding between alcohols and esters is readily detected by infrared spectroscopy which shows that the normal mode of bonding involves the doubly bonded (carbonyl) rather than the singly bonded (alcoholic) oxygen of the ester group.[1] When the hydroxyl and the ester group are in the same molecule, bonding to the carbonyl-oxygen is still preferred [2] unless the spatial relationship between the groups favours the alternative mode of association. Such a situation arises in the monoacetates of certain cyclic *cis*-1,3-diols where bonding to the alcoholic oxygen, giving a quasi-six-membered ring, is observed: bonding to the carbonyl-oxygen would have involved an eight-membered ring.[3,4] With these compounds hydrolysis of the acetoxyl group is facilitated (as compared with the *trans*-isomers), but the original interpretation of this effect [3] has been questioned recently.[4,5]

In the present work the stereochemical (particularly conformational) features of a series of 3,5-dihydroxy-, 3-acetoxy-5-hydroxy-, and 5-hydroxy-3-oxo-steroids have been studied by examining their infrared spectra under high dispersion. It was expected that useful information would be obtained from the O–H stretching region now that the conformational factors influencing hydroxyl absorption are more fully understood.[6] The potentially more flexible bicyclic analogues [7] included in this study were kindly supplied by Professor H. B. Henbest.

Experimental

Spectroscopy.—The compounds were examined in dry carbon tetrachloride on a Unicam S.P. 100 spectrometer (prism-grating monochromator) at a spectral slit width of less than 5

* Part I, *J.*, 1962, 1566.

[1] Searles, Tamres, and Barrow, *J. Amer. Chem. Soc.*, 1953, **75**, 71.
[2] Cole and Müller, *J.*, 1959, 1224.
[3] Henbest and Lovell, *J.*, 1957, 1965.
[4] West, Korst, and Johnson, *J. Org. Chem.*, 1960, **25**, 1976.
[5] Bruice and Fife, *J. Amer. Chem. Soc.*, 1962, **84**, 1973.
[6] Dalton, Meakins, Robinson, and Zaharia, *J.*, 1962, 1566.
[7] Henbest and McEntee, (*a*) *J.*, 1961, 4478; (*b*) unpublished work.

cm.$^{-1}$ with a scanning speed of 4 min./100 cm.$^{-1}$ and a chart scale of 8 cm./100 cm.$^{-1}$. The accuracy of the $\nu_{max.}$ values is estimated to be ± 2 cm.$^{-1}$ for reasonably narrow bands and ± 5 cm.$^{-1}$ for the broader (associated hydroxyl) bands. Peak heights suitable for accurate intensity measurements were obtained as follows, the compounds containing a C=O group being investigated at two concentrations (mole/l.; cell lengths in cm.). *trans*-Hydroxy-acetates: O–H region, concn. 0·007, cell length 1, and concn. 0·07, cell 0·1; C=O region, concn. 0·007, cell 0·1 and concn. 0·07, cell 0·01. *cis*-Hydroxy-acetates: O–H region, concn. 0·0035, cell 1·0, and concn. 0·035, cell 0·1; C=O region, concn. 0·0035, cell 0·1 and concn. 0·035, cell 0·01. *trans*-Diols: O–H region, concn. 0·004, cell 1·0. *cis*-Diols, O–H region, concn. 0·0025, cell 1·0.

TABLE 1.

O–H Stretching frequencies of *trans*-diols (concn. 0·004 mole/l.).

No.	Compound	$\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$	$\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$
1	Cholestane-3β,5α-diol	3627	80	19 *	3614 sh	65	21 *
2	Cholestane-3α,5β-diol	3620	115	22			
10	(±)-9β-Methyldecalin-3β,10α-diol	3627	85	20 *	3615 sh	65	21 *
17	Ergosta-7,22-diene-3β,5α-diol	3627	70	17 *	3591	40	52 *

See text for key to this and other Tables.

TABLE 2.

O–H Stretching frequencies of *cis*-diols (concn. 0·0025 mole/l.).

No.	Compound	$\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$	$\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$
3	Cholestane-3β,5β-diol	3620	75	20	3533	110	52
4	Cholestane-3α,5α-diol	3620	60	21	3521	120	57
11	(±)-9β-Methyldecalin-3β,10β-diol	3621	65	21	3532	85	51
12	(±)-9β-Methyldecalin-3α,10α-diol	3620	55	20	3522	110	59
18	Ergosta-7,22-diene-3α,5α-diol	3621	30	20 *	3593	30	20 *
		3528	115	65			
19	Lumista-7,22-diene-3β,5β-diol	3621	45	20	3606	55	22 *
		3532	110	58 *			

TABLE 3.

trans-Hydroxy-acetates.

		Concn.	O–H Stretching			C=O Stretching		
No.	Compound	(mole/l.)	$\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$	$\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$
5	3β-Acetoxycholestan-5α-ol	0·07	3630	15	20 *	1734	450	16
			3607	35	20			
			3458	55	120	1716	230	20 *
		0·007	3630	20	20 *	1735	570	15
			3607	50	20			
			3458	20	125	1717 sh	120	—
9	5α-Acetoxycholestan-3β-ol	0·07	3622	55	22	1727	490	17
			3471	30	210	1707 sh	140	20 *
		0·007	3622	70	17	1727	570	17
6	3α-Acetoxycholestan-5β-ol	0·07	3621	40	15 *	1736	460	17
			3611 sh	35	14 *			
			3477	45	130	1717	220	20 *
		0·007	3620	50	15 *	1737	540	20
			3611 sh	40	20 *			
			3466	10	135	1718	140	20
13	(±)-3β-Acetoxy-9β-methyl-10α-decalol	0·07	3632	20	21 *	1738	510	16
			3610	40	18 *			
			3461	40	130	1719	230	17 *
		0·007	3632	25	11 *	1737	600	14
			3610	50	9 *			
			3458	15	140	1718	150	16 *
14	(±)-3α-Acetoxy-9β-methyl-10β-decalol	0·007	3620	47	12	1737	530	20
			3606 sh	40	—			
			3460	14	135	1718 sh	120	—
20	3β-Acetoxyergosta-7,22-dien-5α-ol	0·007	3592	42	40	1738	650	14
			3457	9	75 *			
21	5α-Acetoxyergosta-7,22-dien-3β-ol	0·07	3621	55	22	1731	450	23 *
			3465	35	210	1711 sh	170	—
		0·007	3621	70	22	1731	530	19

TABLE 4.

cis-Hydroxy-acetates.

No.	Compound	Concn (mole/l.)	O–H Stretching $\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$	C=O Stretching $\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$
7	3β-Acetoxycholestan-5β-ol	0·035	3596	140	27	1747	640	15
		0·0035	3596	140	27	1748	650	15
8	3α-Acetoxycholestan-5α-ol	0·035	3596	170	30	1747	660	14
		0·0035	3596	180	30	1748	680	14
15	(±)-3β-Acetoxy-9β-methyl-10β-decalol	0·035	3622	40	17 *	1740	460	21
			3599	55	30 *			
		0·0035	3622	40	17 *	1740	480	21
			3599	55	30 *			
16	(±)-3α-Acetoxy-9β-methyl-10α-decalol	0·035	3598	160	33	1745	660	14
		0·0035	3598	160	30	1746	690	14
23	3β-Acetoxylumista-7,22-dien-5β-ol	0·035	3593	140	28	1748	620	15
		0·0035	3593	140	28	1749	630	16
22	3α-Acetoxyergosta-7,22-dien-5α-ol	0·035	3597	130	29	1747	580	12 *
						1735 sh	250	—
		0·0035	3596	130	29	1748	570	12 *
						1736 sh	240	—

TABLE 5.

Hydroxy-ketones.

No.	Compound	Concn. (mole/l.)	O–H Stretching $\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$	C=O Stretching $\nu_{max.}$	$\varepsilon_{max.}$	$\Delta\nu\frac{1}{2}$
24	5α-Hydroxycholestan-3-one	0·007	3606	75	17	1720	440	20
			3504	15	85 *			
			3424	15	—			
27	5β-Hydroxycholestan-3-one	0·007	3611	70	19	1719	420	21
			3490	15	140 *			
			3424	15	—			
25	(±)-10α-Hydroxy-9β-methyl-3-decalone	0·004	3607	60	17	1719	350	15 *
			3502 sh	20	—			
			3422	40	115 *	1712 sh	310	17 *
		0·007	3607	65	17	1719	430	20
			3502 sh	15	—			
			3420	25	150 *			
28	(±)-10β-Hydroxy-9β-methyl-3-decalone	0·004	3610	60	19	1720	390	18 *
			3495 sh	15	—			
			3423	35	110	1714 sh	340	18 *
		0·007	3610	70	18	1719	430	20
			3493 sh	10	—			
			3422	25	140 *			
26	5α-Hydroxyergosta-7,22-dien-3-one	0·007	3608	55	21 *	1722	430	22
			3594	50	25 *			

Hydroxy-ketones: O–H region, concns. 0·007 and 0·004, cell 1·0; C=O region, concns. 0·007 and 0·004, cell 0·1.

The results are shown in Tables 1—5, and illustrated in Figs. 1—5. Wave-numbers of maximal absorption ($\nu_{max.}$) and apparent half-intensity band widths ($\Delta\nu\frac{1}{2}$) are in cm.$^{-1}$ units, and molecular extinction coefficients ($\varepsilon_{max.}$) are in mole^{-1} l. cm.$^{-1}$ units. For C=O compounds the letters d (dilute) and c (concentrated) refer to the concentrations given above. A dash in the $\Delta\nu\frac{1}{2}$ column indicates that overlapping of bands prevented measurement of $\Delta\nu\frac{1}{2}$: a superscript * indicates that overlapping occurred on only one side of the band, and in these cases $\Delta\nu\frac{1}{2}$ was taken to be twice the difference between $\nu_{max.}$ and the wave-number, on the "clear" side of the band, at which the intensity was equal to half $\varepsilon_{max.}$. Shoulders on neighbouring (main) bands are denoted by sh. The $\nu_{max.}$ values for the hydroxy-acetates numbered 5—8 and 22 are more accurate than those reported previously;[3,8,9] except for no. 5,[9] no $\varepsilon_{max.}$ values were given in the earlier work. Some of the results for the bicyclic compounds have already been given.[7a]

[8] Mayor and Meakins, *J.*, 1960, 2792.
[9] Henbest, Meakins, and Wrigley, *J.*, 1958, 2633.

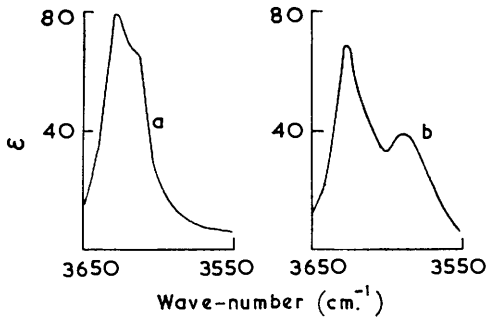


FIG. 1. (a) Cholestane-3β,5α-diol. (b) Ergosta-7,22-diene-3β,5α-diol.

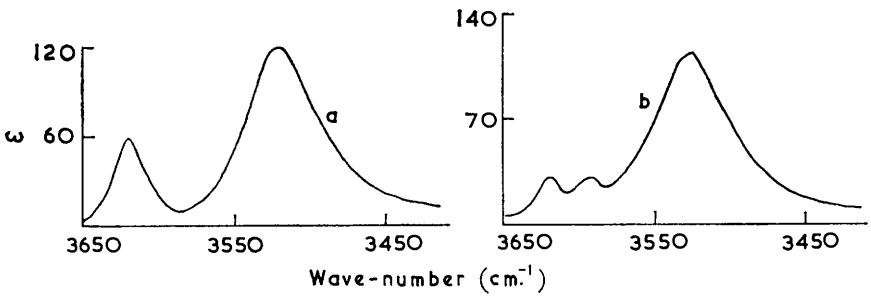


FIG. 2. (a) Cholestane-3α,5α-diol. (b) Ergosta-7,22-diene-3α,5α-diol.

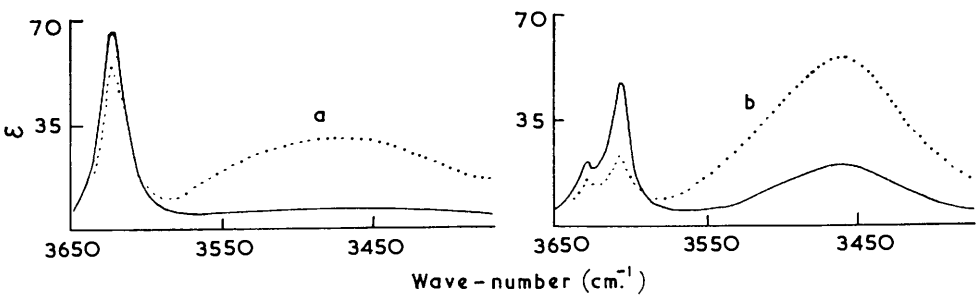


FIG. 3. (a) 5α-Acetoxycholestan-3β-ol. (b) 3β-Acetoxycholestan-5α-ol.
Full lines, 0·007M-solutions; dotted lines, 0·07M-solutions.

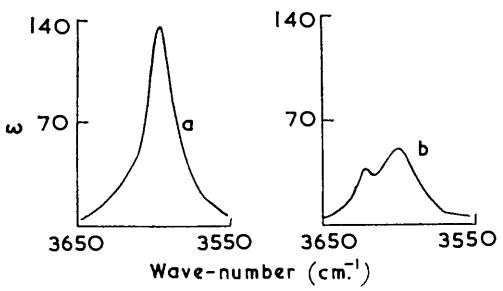


FIG. 4. (a) 3β-Acetoxycholestan-5β-ol.
(b) (±)-3β-Acetoxy-9β-methyl-10β-decalol.

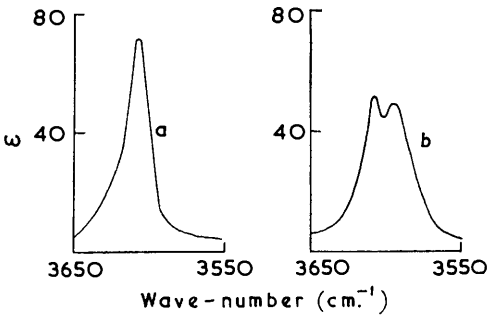


FIG. 5. (a) 5α-Hydroxycholestan-3-one.
(b) 5α-Hydroxyergosta-7,22-dien-3-one.

Materials.—The steroids (except no. **21**) were prepared by published procedures: purity was checked by examination on silica " chromatoplates." In the following list the m. p. and $[\alpha]_D$ (in chloroform) values found in this work are recorded after the numbers of the compounds. (The names of compounds corresponding to the numbers are given in the Tables.) Thus " 1,224—225°, + 21° " indicates " no. 1, cholestan-3β,5α-diol. m. p. 224—225°, $[\alpha]_D$ + 21°." References to compounds which are not described in Elsevier's " Encyclopædia of Organic Chemistry," Vol. XIV and Supplements, are given after the physical constants. The constants of the bicyclic compounds (except no. 14 [7b]) were as recorded in ref. 7*a*.

1, 224—225°, +21°.	2, 193—194°, +15°.	3, 126—127°, +34°.	4, 198—199°, +14°.
5, 185—186, +9	6, 148—149, +44.	7, 80—81, +60.	8, 137—138, −2.
9, 219—220, +44.	17, 230—233, +1.	18, 196—198, −1.[9]	19, 191—193, +.8[8]
20, 228—232, +2.	21, 158—161, +29.	22, 153—155, −22.[9]	23, 145—147, +29.[8]
24, 219—220, +44.	26, 241—244, +6.[9]	27, 157—158, +60.	

5α-*Acetoxyergosta*-7,22-*dien*-3β-*ol* (no. **21**).—A solution of 3β,5α-diacetoxyergosta-7,22-diene [10] (650 mg.; m. p. 159—161°, $[\alpha]_D$ +50°) in benzene (50 ml.) and 5% methanolic potassium hydroxide (50 ml.) was kept at 20° for 18 hr. Dilution with water and extraction with ether gave material which was chromatographed on deactivated alumina (60 g.). Light petroleum–benzene (3 : 1) eluted starting material (35 mg.). Benzene–ether (9 : 1) eluted 5α-*acetoxyergosta*-7,22-*dien*-3β-*ol* (400 mg.), m. p. 158—161° (needles from light petroleum), $[\alpha]_D$ +29° (*c* 1·3) (Found: C, 78·6; H, 10·4. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%). Ether eluted ergosta-7,22-diene-3β,5α-diol (80 mg.), m. p. 231—234° (from ethyl acetate), $[\alpha]_D$ +1° (*c* 1·2) (lit.,[11] m. p. 237—238°, $[\alpha]_D$ +0·5°).

Discussion

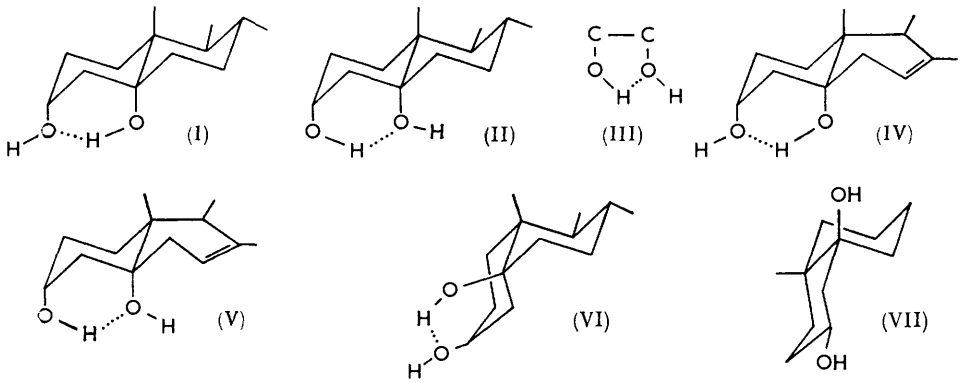
For brevity the cm.$^{-1}$ symbol is omitted from the wave-number values in the following discussion.

Examination of some of the diols at concentrations lower than those specified above did not affect their spectra, showing that the results in Tables 1 and 2 refer to molecules free from intermolecular association. The *trans*-diols, where the hydroxyl groups are too far apart for intramolecular bonding, show hydroxyl bands arising from independent absorption of the two hydroxyl groups. Thus the band (3620, ε 115) of cholestane-3α,5β-diol (no. 2) is a combination of the 3α-hydroxyl (3629, ε 69) and the 5β-hydroxyl (3619, ε 55) absorptions [6] of the monohydric alcohols. The doublet (3629, ε 28; 3611, ε 26) in cholestan-5α-ol, which arises from conformations differing in the position of the hydroxyl-hydrogen atom, superimposed on the 3β-hydroxyl band (3622, ε 61) accounts for the spectrum of cholestane-3β,5α-diol [no. 1; Fig. 1(a)]: the higher intensity of the shoulder at 3614 as compared with the 3611 band of cholestan-5α-ol is presumably caused by appreciable overlap with the main band in the diol. Similar absorption is found in the *trans*-fused bicyclic diol no. 10. Bonding of the 5α-hydroxyl group to the 7,8-double bond in the ergosterol derivative [no. 17, Fig. 1(b)] leads to the rather broad 3591 band,[6] the 3β-hydroxyl group absorbing independently at 3627.

The *cis*-diols (Table 2, Fig. 2) are markedly different in showing a strong broad band near 3530 which, in agreement with previous studies of similar 1,3-diols,[2,4,5,12,13] is ascribed to an intramolecularly bonded form. Two bonded forms can be envisaged for these compounds: for example, forms (I) and (II), favoured respectively by steric and electronic factors, are possible for cholestane-3α,5α-diol (no. 4). A decision between the somewhat similar forms arising with 1,2-diols has been made in several cases by comparing the " free " hydroxyl stretching vibration of the bonded diol (III) with the hydroxyl bands of the two corresponding monohydric alcohols.[14] However, a distinction between forms

[10] Clayton, Henbest, and Jones, *J.*, 1953, 2015.
[11] Laws, *J.*, 1953, 4185.
[12] Julia, Varech, Bürer, and Günthard, *Helv. Chim. Acta*, 1960, **43**, 1623.
[13] Schleyer, *J. Amer. Chem. Soc.*, 1961, **83**, 1368.
[14] Cole and Jefferies, *J.*, 1956, 4391; Cole, Müller, Thornton, and Willix, *J.*, 1959, 1218; Kuhn, *J. Amer. Chem. Soc.*, 1958, **80**, 5950.

(I) and (II) cannot be made entirely on the basis of the " free " hydroxyl band (3620) since both the related monohydroxy-steroids absorb near this position.[6]

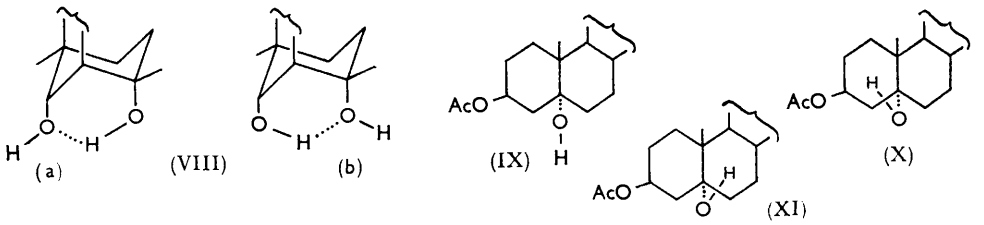


With each of the Δ^7-diols (nos. 18 and 19) two " free " hydroxyl bands appear. The 3593 absorption of the ergosterol derivative [no. 18, Fig. 2(b)] clearly corresponds to a form with the 5α-hydroxyl group oriented towards the 7,8-double bond,[6] *i.e.*, form (V). Since the intensity of the 3528 absorption is normal the second free hydroxyl band, at 3621, must arise from the alternatively bonded form (IV). Thus, in the Δ^7-compounds there is an equilibrium between comparable amounts of the two bonded forms. Comparison of the forms of the Δ^7-compound (no. 18) and the saturated diol (no. 4) shows that while forms (I) and (IV) are similar in stability, form (II) will be less stable than form (V) [the attractive interaction between the 5-hydroxyl group and the 7,8-double bond in (V) is replaced by repulsion between the hydroxyl group and the 7α-hydrogen atom in (II)]. The conclusion, that cholestane-3α,5α-diol adopts conformation (I), is supported by the wave-number (3620) of the " free " hydroxyl absorption: this band is reasonably attributed to the free 3α-hydroxyl group in form (I), but form (II) with a free 5α-hydroxyl group in the " *endo* "-form would be expected to absorb near 3610.[6] Form (VI), in which there is bonding of the 5-hydroxyl to the 3-hydroxyl group, is similarly preferred for cholestane-3β,5β-diol (no. 3). In the alternative form for this diol there would be marked repulsion between the hydrogen of the 5β-hydroxyl group and the 19-methyl group. The spectra of the bicyclic compounds (nos. 11 and 12) closely resemble those of the cholestanediols, showing that the potentially flexible *cis*-decalin derivative (no. 11) adopts a form corresponding to (VI) rather than form (VII) in which intramolecular bonding could not occur.

These results may be contrasted with those of Johnson and his collaborators [4] for certain apparently similar bicyclononene-*cis*-1,3-diols (VIII). In the latter, both bonded forms (a and b) are present although there is no double bond favourably situated for interaction with the tertiary hydroxyl group (cf. nos. 18 and 19). However, bonding of the secondary to the tertiary hydroxyl group (form b) does not here produce the unfavourable interactions of the tertiary hydroxyl group's hydrogen atom which occur in the corresponding forms of diols 3, 4, 11, and 12, and stabilisation of form b by electronic factors becomes the dominant feature.

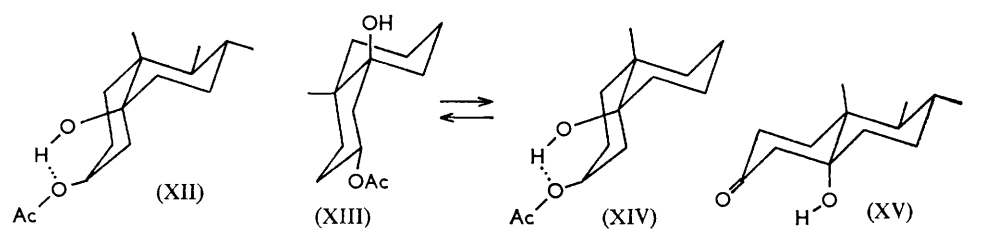
Intramolecular bonding is not possible with the *trans*-hydroxy-acetates (Table 3) and the tendency of these compounds for intermolecular association is reflected in the concentration-variable hydroxyl bands near 3460 and the C=O bands near 1715. The 5α-acetates (nos. 9 and 21) give simple spectra [Fig. 3(a)] and the bonding disappears in 0·007M-solutions. With the 3-acetates the bonding is stronger and in three cases there are two " free " hydroxyl bands [Fig. 3(b)]. In these compounds (nos. 5, 6, and 13) dilution of the solutions increases the intensities of the free hydroxyl bands as expected, but the relative intensities of the two free bands do not change appreciably. Further, the relative

intensity (*ca.* 0·4) of these bands in 3β-acetoxycholestan-5α-ol (no. 5) differs from that observed for the corresponding absorptions of cholestan-5α-ol (*ca.* 1).[6] Thus the conformations (with respect to the hydrogen atom of the hydroxyl group) of 3β-acetoxycholestan-5α-ol responsible for the doublet absorption are involved to about the same extent when intermolecular bonding occurs, but the distribution between the conformations



is influenced by the presence of the acetoxyl group. The absorption of higher wave-number (3630) arises from the "*exo*"-form (IX), and the second band (3607) from one or both of the "*endo*"-forms [(X) and (XI)].[6] Stabilisation of form (X) by the electronegative group at position 3 would explain the intensity differences between 3β-acetoxycholestan-5α-ol and cholestan-5α-ol and the slight wave-number difference between the bands of the "*endo*"-forms of the two compounds. Similar favouring of an "*endo*"-form may lead to doublet "free" hydroxyl absorption in 3α-acetoxycholestan-5β-ol (no. 6), while cholestan-5β-ol, in which the "*exo*"-form is predominant, shows only a single hydroxyl band.[6] As expected, interaction between the ethylenic centre and the hydroxyl group in the Δ^7-5α-hydroxy-compound (no. 20) leads to a reduced tendency for intermolecular association.

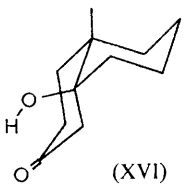
The spectra of the *cis*-hydroxy-acetates (Table 4) are not influenced by the concentrations of their solutions. Compounds 7, 8, 16, and 22 exist entirely in bonded forms, *e.g.*, (XII) for 3β-acetoxycholestan-5β-ol [no. 7, Fig. 4(a)], which exhibit unusually high acetate C=O wave-numbers as discussed previously.[3,4] With the *cis*-decalin derivative [no. 15, Fig. 4(b)] the presence of two hydroxyl bands (free hydroxyl at 3622 and bonded



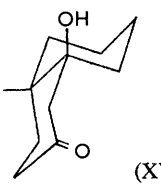
hydroxyl at 3599, neither band being affected by changing the concentration) denotes two conformations, (XIII) and (XIV). Of these forms, (XIV) is favoured by hydrogen-bonding, whereas form (XIII) is stabilised by the equatorial disposition of the acetoxyl group. The C=O band has a lower ε but a greater $\Delta\nu_{\frac{1}{2}}$ than is usual, and the wave-number (1740) is between the values expected for the two forms [(XIII), *ca.* 1735, and (XIV), *ca.* 1747]. From the hydroxyl data the equilibrium appears to be about 2 : 1 in favour of the non-bonded form (XIII). The hydroxyl band in the Δ^7-3α-acetoxy-5α-hydroxy-compound (no. 22) is somewhat less intense than those of the other steroids, and a concentration-independent shoulder appears on the main C=O absorption. These facts suggest an equilibrium between a predominant form, involving hydroxyl–acetoxyl bonding, and a less stable form in which the hydroxyl group is directed towards the 7,8-double bond. The corresponding lumisterol derivative (no. 23) shows normal absorption: here the

distance between the 5-hydroxyl group and the 7,8-double bond is increased by the unnatural stereochemistry, and only the hydroxyl-acetoxyl bonding occurs.

With one exception (no. 26) the hydroxy-ketones (Table 5) show a main hydroxyl band near 3610 and weaker bands near 3500 and 3425. The behaviour of the bicyclic compounds (nos. 25 and 28) indicates that the weak bands (and the corresponding shoulders near 1713 in the C=O region) arise from intermolecular bonding which persists even at the low concentrations used in this work. The lower intensities for the minor bands in the more bulky cholestanone derivatives (nos. 24 and 27) are, then, to be expected. The single non-associated hydroxyl band (ε 75) in 5α-hydroxycholestan-3-one (no. 24, Fig. 5(a)] is to be contrasted with the doublet (each component with ε about 30) in cholestan-5α-ol.[6] This difference, and the position of the peak (3606) in the hydroxy-ketone suggest that the hydroxyl group of 5α-hydroxycholestan-3-one adopts a preferred "*endo*"-conformation. Of the two "*endo*"-forms, one [form (XV)] will be favoured since introduction of the trigonal centre at position 3 removes a previously unfavourable interaction (that involving the 3α-hydrogen). This assignment of the 3606 absorption to form (XV) implies that alignment of the O–H and C=O bonds causes a small but definite decrease in the hydroxyl frequency. Similar forms for the hydroxy-ketones 27, 25, and 28 (Table 5) are consistent with the frequency data: the *cis*-decalin derivative (no. 28) is thus thought to adopt the "steroid" form (XVI) rather than the alternative form (XVII). The doublet absorption



(XVI)



(XVII)

of 5α-hydroxyergosta-7,22-dien-3-one (no. 26) denotes an equilibrium between forms with the hydroxyl group directed towards the carbonyl and ethylenic centres (bands at 3608 and 3594, respectively).

The preference for orientation of the hydroxyl group towards the carbonyl group in the hydroxy-ketones may arise from attraction between these groups, or from the removal of an unfavourable interaction by the trigonal centre. Since the effect on the hydroxyl frequency is so small it is not surprising that the carbonyl absorption occurs at the normal position (near 1720). Stolow[15] recently concluded from infrared measurements that there is no intramolecular interaction between the functional groups of 4-hydroxycyclohexanones. While interaction in these compounds would require boat forms and is thus less likely than the situation in our hydroxy-ketones, the spectrographic consequence of such interaction might be only a very small change in the hydroxyl wave-number.

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[15] Stolow, *J. Amer. Chem. Soc.*, 1962, **84**, 686.