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$\nu_{O\text{-}H}$ Absorptions and Conformations of Epimeric 1-Tetralols and Chroman-4-ols

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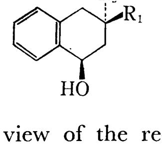
The O–H stretching IR absorptions of epimeric 1-tetralols and chroman-4-ols were examined in dilute carbon tetrachloride solutions. The absorption pattern was found to be related to the conformation of the hydroxyl group; the epimers with the quasi-axial OH group showed a singlet ν_{O-H} at 3618 cm^{-1}, while those with the quasi-equatorial hydroxyl had doublet absorption at 3622 and 3600 cm^{-1}. Based on these findings 1-tetralol itself was shown to exist preferentially in the OH axial conformation. The bands at 3618 and 3600 cm^{-1} were assigned severally to the hydroxyl groups bonding to the π-electrons on the benzene ring. When an additional aryl group is present β to the hydroxyl, another O–H$\cdots\pi$ bonding to the aryl group becomes possible in addition to that between the OH group and the benzene ring of the tetralin and the chroman skeletons. The conformation of the aryl substituents was deduced by applying the empirical correlation relating the geometry of the molecule to the bonded ν_{O-H} frequency in a wide variety of aromatic alcohols which incorporate β-arylethanol moiety.

In connection with the stereochemical study of the reduction of α-tetralones, one of the present authors proposed previously a tentative configurational assignment of the resulting 1-tetralol epimers based on their different intramolecular O–H$\cdots\pi$ bonding as revealed by the O–H stretching (ν_{O-H}) absorption spectra.[1,2] A part of the conclusion was, however, found later to be contradictory to that derived from the NMR study and the mechanistic reasoning of their formation by the reductive reactions.[3] Thus the epimers of **1** (mp 96—98°C) and **2** (mp 113—115°C) which were established to be *trans* by the latter studies had been assigned to the contrary because they did not show the apparent O–H$\cdots\pi$ bonding absorption which was expected to be stronger for the *trans* epimer with the axial hydroxyl group.



1a R_1=Ph, R_2=H
1b R_1=H, R_2=Ph
2a R_1=CH_3, R_2=H
2b R_1=H, R_2=CH_3

In view of the recent successful application of the intramolecular O–H$\cdots\pi$ bonding to the structural elucidation,[4,5] the consideration of the above controversy is intriguing. It is the purpose of the present paper to develop a more careful discussion relating the ν_{O-H} data to the conformation of tetralols and chroman-4-ols.

Results

In Table 1 are listed ν_{O-H} maxima of the 1-tetralols and chroman-4-ols, whose configurations have been established on the basis of both the dependence of the vicinal proton coupling constant on the dihedral angle due to the Karplus type equation and the mechanism of their formation.[3] Some of the typical IR absorption traces are reproduced in Figs. 1 and 2. From the data in Table 1 the following conclusions can be derived directly. (1) In a series of the alcohols with the substituent γ to the hydroxyl (**1**, **2**, **5** and **6**), the *cis* epimer has the doublet ν_{O-H} at 3622 and 3600 cm^{-1}, while the *trans* epimer has a skew singlet at 3618 cm^{-1}. (2) In a pair of **4**'s the above correlation between the ν_{O-H} pattern and the configuration is reversed: it is the *cis* isomer which shows a singlet ν_{O-H}. (3) 1-Tetralol itself has a doublet ν_{O-H} more like those with *cis*- γ- or *trans*-β-methyl substituent. The relative intensity of the two bands are, however, reversed. (4) When there is an aryl substituent β to the hydroxyl (**3**, **7**, **8** and **9**), the *trans* epimer gives the doublet absorption at 3614 and 3600 cm^{-1}, while the *cis* at 3616 and 3582 cm^{-1}.

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[1] K. Hanaya, *Nippon Kagaku Zasshi*, **87**, 745 (1966).

[2] K. Hanaya, *ibid.*, **87**, 995 (1966).

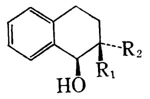
[3] S. Mitsui, A. Kasahara and K. Hanaya, This Bulletin, **41**, 2526 (1968).

[4] M. Tichý, "Advances in Organic Chemistry: Methods and Results", Vol. 5, R. A. Raphael, E. C. Taylor and H. Wynberg, Ed., John Wiley & Sons, Inc., New York, N. Y. (1965), p. 115.

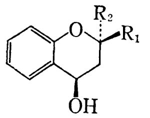
[5] M. Ōki, H. Iwamura, T. Onoda and M. Iwamura, *Tetrahedron*, **24**, 1905 (1968).

Table 1. ν_{O-H} absorption of 1-tetralols and chroman-4-ols

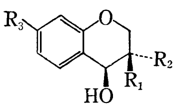
Compound	ν_{max}	$\Delta\nu^{a}_{1/2}$	ε
1-Tetralol	3618	18	63
	3601	11	36
1a	3622	23	37
	3600	10	66
1b	3617	12	88
2a	3625	24	30
	3602	7	65
2b	3618	15	88
3a	3615	17	45
	3585	24	34
3b	3615	16	30
	3600	17	71
4a	3620	18	69
4b	3617	22	37
	3598	11	59
5a	3623	23	34
	3596	14	75
5b	3616	16	89
6a	3621	23	38
	3596	12	65
6b	3618	14	86
7a	3616	19	51
	3582	30	34
7b	3614	16	59
	3600	19	64
8a	3615	18	60
	3582	31	42
8b	3613	15	57
	3600	18	53
9a	3617	18	55
	3575	25	43
9b	3615	14	61
	3598	20	63



3a $R_1=Ph$, $R_2=H$
3b $R_1=H$, $R_2=Ph$
4a $R_1=CH_3$, $R_2=H$
4b $R_1=H$, $R_2=CH_3$



5a $R_1=Ph$, $R_2=H$
5b $R_1=H$, $R_2=Ph$
6a $R_1=CH_3$, $R_2=H$
6b $R_1=H$, $R_2=CH_3$



7a $R_1=Ph$, $R_2=R_3=H$
7b $R_1=R_3=H$, $R_2=Ph$
8a $R_1=Ph$, $R_2=H$, $R_3=OCH_3$
8b $R_1=H$, $R_2=Ph$, $R_3=OCH_3$
9a $R_1=p\text{-}CH_3OC_6H_4$, $R_2=H$, $R_3=OCH_3$
9b $R_1=H$, $R_2=p\text{-}CH_3OC_6H_4$, $R_3=OCH_3$

Discussion

There is enough rationalization in regarding the conformation of the cyclohexene moiety of 1-tetralols as a half-chair.[6] As for the chroman skeleton, no direct evidence seems to have been presented for the half-chair conformation of the dihydropyran. Although the sofa conformation in which all the atoms of the ring except $C_{(2)}$ are coplanar has once been proposed,[7] the half-chair model seems to be more consistent with the NMR data.[8] The observed difference in the ν_{O-H} pattern between the epimers means that the benzylic hydroxyl groups should never be equally inclined to the plane of the benzene ring in both cases, and the striking similarity in the IR absorptions with the corresponding 1-tetralol epimers as shown in Table 1 may be considered as another support for the half-chair conformation of

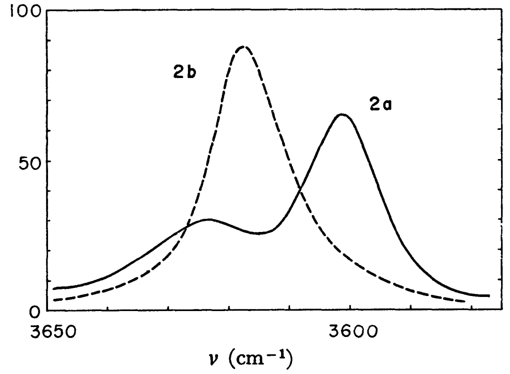


Fig. 1. ν_{O-H} Absorptions of *cis*- and *trans*-3-methyl-1-tetralols.

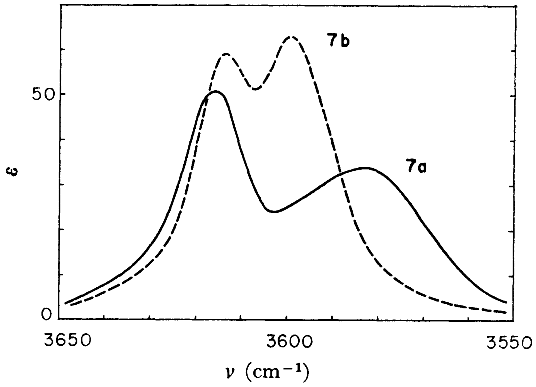


Fig. 2. ν_{O-H} Absorptions of 3-phenylchroman-4-ols.

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[6] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, **77**, 2505 (1955); E. L. Eliel, N. L. Allinger and G. A. Morrison, "Conformational Analysis", Interscience Publishers, New York, (1965); N. L. Allinger, J. A. Hirsch, M. A. Miller and I. J. Tyminski, *J. Amer. Chem. Soc.*, **90**, 5773 (1968); J. F. Chiang and S. H. Bauer, *ibid.*, **91**, 1898 (1969).

[7] E. M. Philbin and T. S. Wheeler, *Proc. Chem. Soc.*, **1959**, 167.

[8] J. W. Clark-Lewis, *Rev. Pure and Appl. Chem.*, **12**, 96 (1962); J. W. Clark-Lewis, L. M. Jackman and T. M. Spotwood, *Aust. J. Chem.*, **17**, 632 (1964).

the chroman nucleus.

Due to the conformational preference of the phenyl and the methyl groups over the hydroxyl,[9] the former groups may well be considered to assume preferentially the equatorial disposition on the 1-tetralol and chroman-4-ol skeletons. The conformation of the hydroxyl group should consequently be determined by its configuration with respect to the other substituents. Thus the *cis*- and *trans*-γ-substituted alcohols are expected to have the equatorial and axial hydroxyl groups, respectively. The 1-tetralols and chroman-4-ols with the *cis*- and *trans*-β-substituents are considered to have the axial and equatorial OH groups, respectively. Then the rules (1) and (2) derived in the preceding section can be restated as follows. It is the epimer with the quasi-equatorial benzylic hydroxyl group that shows the doublet absorption at 3622 and 3600 cm^{-1}. The OH quasi-axial epimer, to the contrary, displays only a 3618 cm^{-1} singlet.[11]

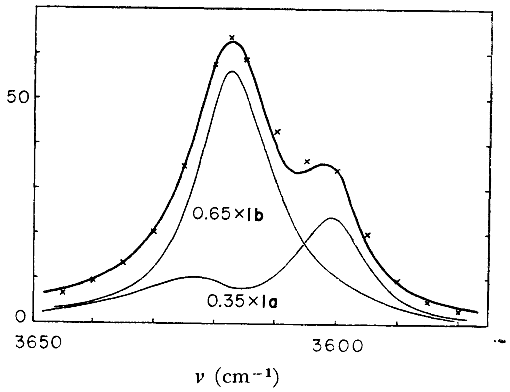

Fig. 3. ν_{O-H} Absorptions of 1-tetralol, **1a** and **1b**.

—— 1-tetralol (observed)

XX 0.35×**1a**+0.65×**1b**

It is instructive to note that graphical superposition of the spectra of **1a** and **1b**, or **2a** and **2b**, reproduces the apparent ν_{O-H} curve of 1-tetralol itself (Fig. 3) when the ratio of mixing is 0.54 to 1.[11a] Thus it is concluded that in 1-tetralol the OH quasi-axial conformation predominates and the apparent conformational energy ($-\Delta G_{25°}$) of the benzylic OH group is calculated to be -0.37 kcal/mol. This is not necessarily due to the O–H···π bonding energy because the steric hindrance between the equatorially oriented OH group and the parallelly disposed aromatic hydrogen atom is expected to be more serious than one 1,3-diaxial H–OH interaction in the cyclohexene ring. An analogous situation may be found in the allylic $A^{(1,2)}$ strain proposed by Johnson and Malhotra[12] for the 2,3-disubstituted cyclohexenes in which the substituent at the allylic 3 position often prefers the axial conformation.

Turning now to the interpretation of the ν_{O-H} frequencies, we could assign the bands at 3622 and 3618 cm^{-1} to the free OH group and only the low-frequency band at 3600 cm^{-1} to the one which is O–H···π bonded, by applying the naive concept of the effect of the hydrogen bonding on ν_{O-H} frequency. The assignment would be, however, rather confusing because it is at first glance the epimer with quasi-axial hydroxyl group which looks more advantageous for internal O–H···π bonding due to the perpendicular approach of the hydroxyl hydrogen to the π-electron cloud on the benzene ring. The interaction of the quasi-equatorial hydroxyl group with the benzene ring might be more horizontal. This is the reason why the opposite configurational assignment was made previously.[1,2] Therefore the truth must be either that the 3622 and/or 3618 cm^{-1} bands are not due to the free ν_{O-H} or that the quasi-axial hydroxyl group is not so favorably disposed for the internal O–H···π bonding as the quasi-equatorial epimer.

According to the conformational theory of the multiplicity of the ν_{O-H} absorptions,[13] the free ν_{O-H} frequencies of a pair of the epimeric alcohols under consideration may be expected to be as listed in the first column of Table 2 depending on the conformation of the OH group with respect to the C–O bond. The contribution of the type **a** conformation in which the OH bond is directed towards the center of the cyclohexene and dihydropyran ring may be smaller in the OH quasi-axial epimer because of the 1,3-diaxial interaction.[14] Therefore the singlet absorption at

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[9] The conformational energies ($-\Delta G_{25°}$) in the cyclohexyl derivatives are 3.1, 1.7 and 0.6 kcal/mol for the phenyl, methyl and hydroxyl groups, respectively.[10]

[10] E. L. Eliel, *Angew. Chem.*, **77**, 784 (1965).

[11] The same phenomenon has been observed in the epimeric pairs of conformationally fixed cyclohexen-3-ols in which nothing is different from the present system but the benzene ring is replaced by the ethylenic double bond.[5] This apparent reversal in the ν_{O-H} absorption patterns may in general be termed as the anomaly in the benzylic and allylic O–H···π bonding.

[11a] G. F. Katekar and A. G. Moritz, *Aust. J. Chem.*, **22**, 2337 (1969).

[12] F. Johnson and S. K. Malhotra, *J. Amer. Chem. Soc.*, **87**, 5492 (1965); S. K. Malhotra and F. Johnson *ibid.*, **87**, 5493 (1965).

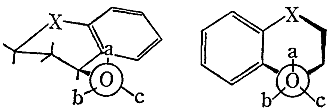
[13] a) M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959); b) R. Piccolini and S. Winstein, *Tetrahedron Lett.*, **1959**, 4; c) F. Dalton, G. D. Meakins, J. H. Robinson and W. Zaharia, *J. Chem. Soc.*, **1962**, 1566; d) P. J. Krueger and M. D. Mettee, *Can. J. Chem.*, **42**, 347 (1964); e) J. Weinman, *Bull. Soc. Chim. Fr.*, **1967**, 4259; f) L. Joris, P. von R. Schleyer and E. Osawa, *Tetrahedron*, **24**, 4759 (1968).

[14] H. S. Aaron and C. P. Rader, *J. Amer. Chem. Soc.*, **85**, 3046 (1963); H. S. Aaron, C. P. Ferguson and C. P. Rader, *ibid.*, **89**, 1431 (1967).

TABLE 2. ASSIGNMENT OF THE ν_{O-H} ABSORPTIONS IN 1-TETRALOLS AND CHROMAN-4-OLS

Conformation of the OH group	Type	O-H bond staggered between	Free ν_{O-H}[13] expected	Bonded ν_{O-H} observed	$\Delta\nu_{O-H}$
Quasi-axial	**a**	C-C and C-C	3618	—	—
	b	C-C and C-H	3627	3618	9
	c[a]	C-C and C-H	3627	—	—
Quasi-equatorial	**a**	C-C and C-C	3618	3600	18
	b[a]	C-C and C-H	3627	—	—
	c	C-C and C-H	3627	3622	5

a) OH Group is not directed towards the π-electrons in these conformations.



$X=CH_2$ or O

3618 cm^{-1} of the axial epimers is too low in frequency to be assigned to the free ν_{O-H}. Actually it corresponds well to the reported bonding ν_{O-H} of benzyl alcohols[15] in which the C–O bond has been estimated to be "axial" with respect to the plane of the benzene ring.[16] Thus it is more reasonable to regard this singlet absorption as the O–H···π bonded ν_{O-H}. The shift of ν_{O-H} as the result of the interaction ($\Delta\nu_{O-H}$) will be estimated to be 9 cm^{-1} (=3627−3618). In the quasi-equatorial alcohols, it is the type **a** conformation with the O–H bond staggered between the two C–C bonds which is expected to give relatively large ν_{O-H} shift. The OH hydrogen atom in this conformation is shown by molecular models to be favorably situated to overlap with the π-electrons on the benzene ring, while the hydroxyl group stays free in the **b** and lies close to the nodal plane of the π-orbitals on the benzene ring in the **c** conformations, respectively. Therefore the band at 3600 cm^{-1} should be regarded as the bonding ν_{O-H} in the **a** conformation. The second band at 3622 cm^{-1} may be an unresolved overlap of the free and weakly-bonded bands in the conformation **b** and **c**, respectively.[17]

Since the proposal by Badger and Bauer[18] it has been well-documented that $\Delta\nu_{O-H}$ provides a good measure of the strength of the hydrogen bonding especially when the closely related proton donors on the one hand and the acceptors on the other are compared.[19] In the previous papers[5,20] it has been shown that the strength of the O–H···π bonding is governed by the amount of overlap between the orbitals of the π-electrons and the hydroxyl group when a series of compounds with nearly equivalent basicity of the π-electrons and the acidity of the OH groups are compared. As one of the possible measures indicating the overlap between the interacting groups, the overlap integral *S* between the Slater's hydrogen 1*s* and the carbon 2*p* atomic orbitals has been shown to be appropriate.[5,20] In Table 3 are compared these parameters in each interacting conformation based on the geometry which was scaled on a Dreiding model. Although correlation with the observed $\Delta\nu_{OH}$ data is far from quantitative linearity, it is still the type **a** conformation of the quasi-equatorial hydroxyl which has the largest *S* as expected from the largest $\Delta\nu_{O-H}$. In this conformation, the O–H dipole is disposed anti-parallel to that of the 2*p*π lobe on the adjacent carbon atoms in the benzene ring. The electrostatic force between the dipoles might also be contributing to effecting the largest $\Delta\nu_{O-H}$ shift in addition to the effect of the electron delocalization roughly estimated from *S*.

In the alcohols with β-aryl substituent (**3, 7, 8**

TABLE 3. OVERLAP BETWEEN THE HYDROXYL GROUP AND THE π-ELECTRONS ON THE BENZENE RING

Conformation of the OH group	Type	$\sum S$[a]	$\Delta\nu_{O-H}$ observed
Quasi-axial	**b**	0.099	9
Quasi-equatorial	**a**	0.110	18
	c	0.050	5

a) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

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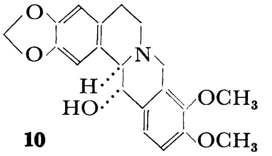
15) M. Ōki and H. Iwamura, This Bulletin, **32**, 955 (1969).

16) J. C. Evans, *Spectrochim. Acta*, **17**, 129 (1961).

17) 13-Epiophiocarpin (**10**) is reported to give ν_{O-H}'s at 3625(shoulder) and 3597 cm^{-1} (M. Ohta, H. Tani and S. Morozumi, *Tetrahedron Lett.*, **1963**, 859. Contrary to the original interpretation, the latter band may be due to the bonded ν_{O-H} characteristic of the equatorial benzylic alcohols.



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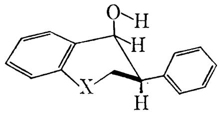
18) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

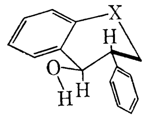
19) G. C. Pimentel and A. L. McClellan, "Hydrogen Bond", W. H. Freeman & Co., San Francisco (1960), p. 82.

20) M. Ōki and H. Iwamura, *J. Amer. Chem. Soc.*, **89**, 576 (1967).

and **9**), the internal bonding of the hydroxyl group with the π-electrons of the aryl group has to be taken into account in addition to the benzylic interaction discussed above. As the result of the preferentially equatorial disposition of the aryl group on the cyclohexene and the dihydropyran nuclei, the hydroxyl group should be quasi-axial in the *cis* epimers. The doublet absorptions at 3616 and 3582 cm^{-1} must have arisen from the O-H$\cdots\pi$ bonding to the benzo-ring and the aryl group (see **11**), respectively. This assignment may be confirmed by the observation that the *p*-methoxyl substitution in the aryl group shifts the latter absorption to the still lower frequency (*ca.* 3582 cm^{-1} in **3a**, **7a** and **8a** to 3575 cm^{-1} in **9a**) by enhancing the basicity of the aryl π-electrons.[15,21] In the *trans*-β-aryl substituted series, **3b, 7b, 8b** and **9b,** the quasi-equatorial OH group can interact either with the benzo-benzene ring to exhibit 3600 cm^{-1} band as in the γ-substituted cases or with the β-aryl group to produce the new absorption at 3614 cm^{-1} in the type **b** conformation of the hydroxyl group (see **12**). Alternatively the band at 3600 cm^{-1} might be considered to be an overlap between the two kinds of the bonded bands. The relative intensity of the 3614 cm^{-1} bands is, however, almost unity and too high to be assigned to the hydroxyl group in the **c** type conformation which should be populated one third at best.



11 3582 cm^{-1}



12 3614 cm^{-1}

In an attempt to delineate the spatial configuration of the plane of the aryl group relative to the rest of the molecule in **11** and **12,** it seemed intriguing to examine the ν_{O-H} absorptions in a wide variety of conformationally-fixed β-phenethyl alcohols. As summarized in Table 4, the bonded ν_{O-H} frequencies range from 3616 cm^{-1} down to 3560 cm^{-1}. It is rather apparent from molecular models that the larger ν_{O-H} shift in compounds **17** to **22** may be derived from the geometry which permits closer approach of the hydroxyl group to the π-electrons on the aromatic ring. In compounds **13** and **14,** on the contrary, the hydroxyl hydrogen lies close to the nodal plane of the carbon $2p\pi$ orbitals of the benzene ring with result of the smallest shift in the ν_{O-H} frequency.[22] When alcohols with the same framework are compared, their ν_{O-H}'s fall within the experimetal errors and support the idea that the geometrical factors are playing the major role in determining the absorption frequency.[23] As in the previous treatment,[5,20] one could compute the Slater overlap integral between the hydrogen 1*s* and the carbon 2*p* orbitals to represent the extent of overlap between the two interacting groups in each alcohol, but the dihedral angle θ made by the plane of the aromatic ring and the plane defined by the three carbon atoms, C_α,C_β and C_1 of the benzene ring has now been employed as a convenient measure expressing the geometrical relationship between the OH and the aromatic π-electrons. It is shown in Fig. 4 that it is by definition the quadrant described by θ and not the supplementary angle of θ which should contain the OH group. For each alcohol the angle θ was measured on a Dreiding model and/or estimated on the basis of the geometry of the partial structure when this is known. Thus the exact dimension of cyclopentene[24] was assumed for **15** and **24.** The consistent value of $\theta = 144°$ was also obtained for **17** and **22** from the structure of norbornane and norbornadiene determined by the electron diffraction study.[25] The results are included in Table 4. It is not always proper to regard the apparent difference in frequencies of the doublet absorption peaks as the ν_{O-H} shift, because the conformational environment of the hydroxyl group which is well-documented[13] with its influence on the ν_{O-H} frequency does not necessarily coincide in the free and the bonded forms. To avoid ambiguity in

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[21] M. Ōki and H. Iwamura, This Bulletin, **32**, 1135 (1959).

[22] To the authors knowledge, only one attempt has so far been presented which is partly successful in correlating ν_{O-H} data with the distance r between the hydroxyl hydrogen and the carbon atom carrying the π-electrons pertaining to the interaction (Y. Matsui, M. Takasuka and T. Kubota, *Shionogi Kenkyusho Nempo* (*Ann. Rept. Shionogi Res. Lab.*), **15** 125 (1965); T. Kubota, M. Takasuka and Y. Matsui, *ibid.*, **16**, 63 (1966)). This approach is, however, too approximate to be applied to conformational analysis.

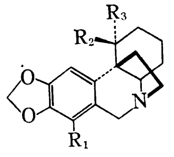
[23] It is noted by comparing pairs of **13a** and **13b**, **13c** and **13d**, and **8a** and **9a** that the methoxyl group produces further low frequency shift by 0, 3 and 7 cm^{-1} at 3616, 3600 and 3582 cm^{-1}, respectively, of the ν_{O-H} frequencies of the unsubstituted alcohols. The lowest frequency of 3560 cm^{-1} observed for epihaemanthamine **21** must be partly due to this electronic effect produced by the methylenedioxy group on the aromatic ring which is known to increase the basicity of the π-electron system just as the methoxyl group does. For the purpose of conformational discussion, it is necessary to eliminate from the observed ν_{O-H} value contribution of the electronic effect. By considering approximately twice as much shift as one methoxyl group, the corrected frequency for the unsubstituted homolog of **21** would be about 3574 ($=3560 + 2 \times 7$) cm^{-1}.

[24] G. W. Rathjens, *J. Chem. Phys.*, **36**, 2401 (1962); S. S. Butcher and C. C. Costain, *J. Mol. Spectroscopy*, **15**, 40 (1965); J. Laane and R. C. Lord, *J. Chem. Phys.*, **47**, 4941 (1967).

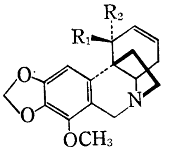
[25] Y. Morino, K. Kuchitsu and A. Yokozeki, This Bulletin, **40**, 1552 (1967).

TABLE 4. ν_{O-H} ABSORPTIONS AND GEOMETRIES OF CONFORMATIONALLY-FIXED β-PHENYLETHANOLS

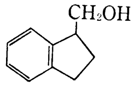
Compound	Free ν_{O-H}	Bonded ν_{O-H}	θ °	Ref.
Demethoxyepidihydrobuphanamine **13a**		3616	15	26
Epidihydrobuphanamine **13b**		3616	15	26
Epibuphanamine **14a**		3614	20	26
Indane-1-methanol **15**	3638	3605	65	27
β-Phenylethanol	3636	3606		21
cis-2-Phenylcyclohexanol **16a**	3627	3600		This work
trans-2-Phenylcyclohexanol **16b**	(3622)	3599		This work, 28, 29
1,2,5,7,7,8-Hexamethyl-3,4-benzotricyclo-[3.3.0.0^{2,8}] oct-3-en-6(*syn*)-ol **18**		3580	110	30
1,2,3,4-Tetrahydro-1,4-methanonaphthalen-2(*syn*)-ol **17**	3624	3576	115	This work, 22
Epihaemanthamine **21**		3560	115	31
1,2,3,4-Tetrahydro-1,4-ethanonaphthalen-2(*syn*)-ol **19**	3618	3586	120	This work, 32
1,4-Dihydro-1,2,3,4,10,10-hexamethyl-1,4-ethanonaphthalen-9(*syn*)-ol **20**	3635	3580	120	33
1,2,3,4-Tetrahydro-1, 4-methanonaphthalen-9(*syn*)-ol **22a**	3619	3575	145	34, 22
9(*anti*)-Methyl-1,2,3,4-tetrahydro-1,4-methanonaphthalen-9(*syn*)-ol **22b**	3625	3576	145	22
β-2,5-Dimethyl-9-hydroxy-2'-methoxy-6,7-benzomorphan **23a**	3634	3591	155	35
β-9-Hydroxy-2'-methoxy-2,5,9-trimethyl-6,7-benzomorphan **23b**	3622	3586	155	36
β-5-Ethyl-9-hydroxy-2'-methoxy-2-methyl-6,7-benzomorphan **23c**	3625	3595	155	37
β-2,9-Dimethyl-5-ethyl-9-hydroxy-2'-methoxy-6,7-benzomorphan **23d**	3610	3591	155	37
Buphanamine **14b**	3613	3584	160	26
Indan-2-ol **24**	3620	3592	165	38
Demethoxydihydrobuphanamine **13c**	(3620)	3602	165	26
Dihydrobuphanamine **13d**	(3620)	3599	165	26



13a $R_1=H, R_2=OH, R_3=H$
13b $R_1=OCH_3, R_2=OH, R_3=H$
13c $R_1=H, R_2=H, R_3=OH$
13d $R_1=OCH_3, R_2=H, R_3=OH$



14a $R_1=OH, R_2=H$
14b $R_1=H, R_2=OH$



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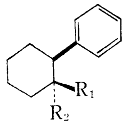
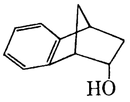


16a $R_1=OH, R_2=H$
16b $R_1=H, R_2=OH$



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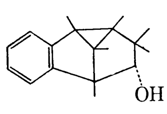

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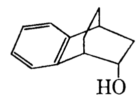

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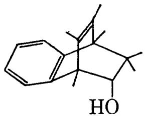

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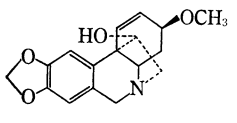

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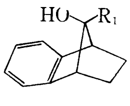
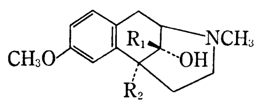
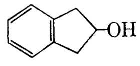


22a $R_1=H$
22b $R_1=CH_3$



23a $R_1=H$, $R_2=CH_3$
23b $R_1=CH_3$, $R_2=CH_3$
23c $R_1=H$, $R_2=C_2H_5$
23d $R_1=CH_3$, $R_2=CH_5$



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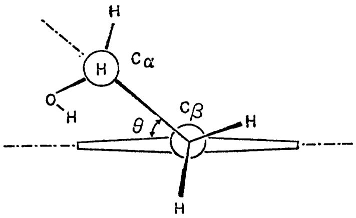

Fig. 4. Definition of the dihedral angle θ in β-phenylethanols.

evaluating the free ν_{O-H} which would be expected for the bonded conformer when it has not O–H···π bonding, the bonded frequency itself is tentatively to be compared without reference to the free ν_{O-H}. It is apparent that the lower the bonded O–H frequency the stronger the O–H···π bonding. Graphic presentation gives reasonably smooth bonded ν_{O-H} *versus* θ curve as shown in Fig. 5. The correlation may well be rationalized by inspection of molecular models (see Fig. 4) in such a way that when $\theta=120°$ the OH hydrogen is situated right above the π-cloud of the C_1 atom on the benzene ring and the overlap between the hydroxyl and the π-electrons is expected to be maximal. At $\theta=30°$ the hydroxyl hydrogen lies on the plane of the benzene ring, pointing the node of the π-electrons with result of no effective bonding at all. Correspondingly ν_{O-H}'s appear at the normal free ν_{O-H} region of 3620—3627 cm^{-1}. The argument is based on the assumption that in most of the bonded conformations of β-phenylethanols the C_α–O bond is staggered with the C_β–C_1 bond; the dihedral angle between the plane of O–C_α–C_β and that of C_α–C_β–C_1 is approximately 60°.

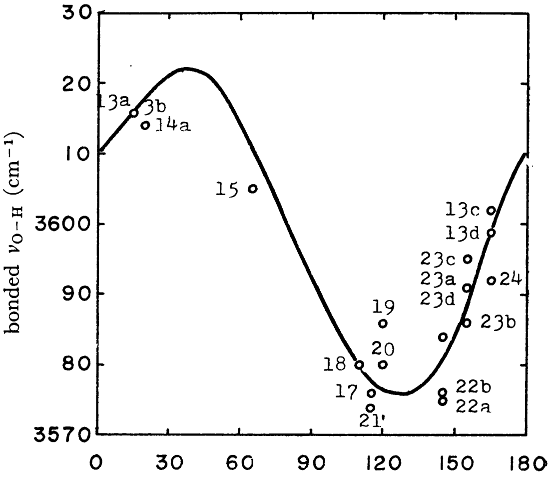

Fig. 5. Angular dependence of the observed ν_{O-H}.

The curve in Fig. 5 could be approximated by Eq. (1) and will be of great use in conformational study of β-phenylethanols. Thus it is possible

$$\nu_{O-H}^{bonded}\,(\mathrm{cm}^{-1}) = 3625 - 50\cos 2(\theta-30°) \qquad (1)$$

to estimate that in the bonded conformation of **11** θ must be about 120°. In **12** θ is estimated to be *ca.* 60°. Geometrically these conditions are satisfied in either epimer by fixing the plane of the benzene ring so that the $C_{(2)}$–$C_{(3)}$ bond of the chroman skeleton (bold lined in **11** and **12**) eclipses the plane. Analogously for 2-phenylcyclohexanols (**16a** and **16b**) $\theta=90°$; the $C_{(1)}$–$C_{(2)}$ bond in the cyclohexyl moiety is projected perpendicular to the plane of the benzene ring. This is not consistent with that proposed for phenylcyclohexane itself. The benzene ring has been estimated to be perpendicular to the plane defined by the $C_{(1)}$–$C_{(2)}$–$C_{(3)}$ atoms of the cyclohexane ring.[39] If the latter conformation were kept in **16**, markedly different ν_{O-H} frequencies should at least have been observed for **16a** and **16b**, because the spatial relation between the OH and the aromatic ring is quite different in both epimers. The θ defined as above amounts to 60° and 120° for the *cis* and the *trans* epimers, and the bonded ν_{O-H} of *ca.* 3615 and 3580 cm^{-1} should have been observed, respectively.

As another example on this line, mention should be made of the reported conformation of (+)-catechin teramethyl ether. Birch colaborated with Cole[40] concluded the 2-aryl-3-OH-diaxial

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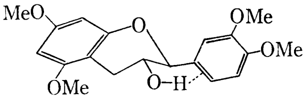
[39] E. W. Garbisch and D. B. Patterson, *J. Amer. Chem. Soc.*, **85**, 3228 (1963); N. L. Allinger, J. Allinger, M. A. DaRooge and S. Greenberg, *J. Org. Chem.*, **27**, 4603 (1962).

[40] A. J. Birch, J. W. Clark-Lewis and A. V. Robertson, *J. Chem. Soc.*, **1957**, 3586.



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conformation on the assumption that the observed $\nu_{\text{O-H}}$ at 3594 cm^{-1} might be due to the internal hydrogen bonding to the ring oxygen of the chroman skeleton. The conclusion is, however, incompatible with the conformational energy of the axial aryl group.[9,10] Even stabilization of the OH axial conformation by the O–H···O hydrogen bonding does not seem to be enough to allow predominantly axial hydroxyl, because in the case of tetrahydropyran-3-ol the conformer with the equatorial OH group is still present in an appreciable concentration.[41] Therefore the preferred conformation of (+)-catechin tetramethyl ether would better be considered as 2,3-diequatorial with the hydroxyl group bonded to the π-electrons on the aryl group (**25**). The observed frequency of 3594 cm^{-1} is reasonably understood when the electron-donating effect of the two methoxyl substituents on the aryl ring is taken into account[23] in reference to 3599 cm^{-1} observed for the structurally analogous *trans*-2-phenylcyclohexanol (**16b**).[42]

Experimental

The infrared absorptions were measured either on a Perkin-Elmer 125 double beam or a 112G single beam grating high resolution IR spectrometer, the spectral slit width being 1.0 cm^{-1} in the region concerned. A quartz cell of 20 mm and a KCl cell of 30 mm in optical length were used. The concentration of the solutions was *ca.* 5 mmol/*l* in carbon tetrachloride distilled over phosphorus pentoxide at which dilution the band due to intermolecular hydrogen bonding was not observed. Sometimes $\nu_{\text{O-H}}$ absorptions were accompanied by a weak shoulder at 3630 cm^{-1} which was found later to be due to poor cancellation of the absorptions of water vapor in the optical path especially with a double beam spectrometer.

1-Tetralols and chroman-4-ols were prepared by reduction of the corresponding α-tetralones and γ-chromanones according to the literature.[2,43] We are indebted to Prof. N. Inoue who kindly supplied samples of 3-phenylchroman-4-ols.

As to the $\nu_{\text{O-H}}$ data quoted from the literature, reliable ones were carefully picked up which have been explicitly mentioned to have been measured in dilute carbon tetrachloride solutions on the IR spectrometer equipped with a grating or a fluoride prism.

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[41] S. A. Barker, J. S. Brimacombe, A. B. Foster, D. H. Whiffen and G. Zweifel, *Tetrahedron*, **7**, 10 (1959).

[42] The corresponding hydroxyl groups in *cis*- and *trans*-flavan-3,4-diols are reported (E. M. Philbin, T. S. Wheeler, F. V. Brutcher, Jr., and W. Bauer, Jr., *J. Org. Chem.*, **27**, 4114 (1962)) to absorb at 3606 and 3608 cm^{-1}, respectively. Shift to higher frequency by several cm^{-1} when compared with those of **25** and **16b** might somehow be ascribed to the effect of the second 4-OH group which is bonding to the 3-OH consecutively.

[43] S. Mitsui and A. Kasahara, *Nippon Kagaku Zasshi* **79**, 1382 (1958); K. Hanaya and K. Kose, *ibid.*, **89**, 1002 (1968).