ν_{O-H} *Absorption of Cholesterol and Epicholesterol*[1]*

By Michinori Ōki and Hiizu Iwamura

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The authors observed two ν_{O-H} absorptions with 3-buten-1-ol[2], and attributed

* Added in proof: While this paper was in press, P. von R. Schleyer, D. S. Trifan and R. Bacskai (*J. Am. Chem. Soc.*, **80**, 6691 (1958)) reported the same phenomenon for these compounds without noticing the unsymmetry of the O-H stretching band of cholesterol.

1) Part III of intramolecular interaction between hydroxyl group and π-electrons.

2) M. Ōki and H. Iwamura, This Bulletin, in press.

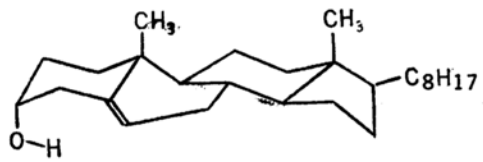
TABLE I

ν_{O-H} ABSORPTION OF CHOLESTEROL AND EPICHOLESTEROL

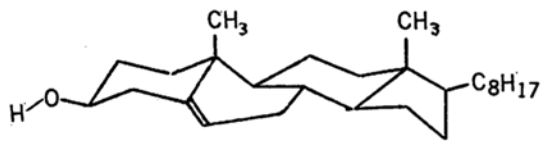
Compound	ν_{O-H} band	ν_{max} (cm^{-1})	$\Delta\nu^{a}_{1/2}$ (cm^{-1})	$A\times10^{-3}$ ($mole^{-1}\cdot liter\cdot cm^{-2}$)	$\Delta\nu_{max}$ (cm^{-1})
cholesterol	I	(3613.0)	(18.4)	(1.05)	10
	II	3623.0	16.4	3.47	
epicholesterol	I	3589.6	32.0	2.67	34.1
	II	3623.7	16.8	0.85	

one at the lower wave number (3596.1 cm^{-1}) to the intramolecular interaction between hydroxyl group and π-electrons of the double bond. Then it was naturally expected that the concept would be applicable to more complex molecules, such as steroids.

The molecular scale models indicate that the steric requirement is fulfilled for such a kind of interaction to take place in epicholesterol[3] (I), but not in cholesterol[3] (II).



I



II

Measurements of the O–H stretching absorption in the fundamental region showed that it is really the case. As shown in Fig. 1, epicholesterol gave two distinct maxima, while cholesterol a normal band for secondary alcohols, although the band can be divided into two as in the cases of other secondary alcohols[4] (Table I). The measurements and the calculation were carried out similarly as reported previously[2,5].

Comparison of the integrated intensities of band I (interacted form) and of band II (free) of epicholesterol with the corresponding values of 3-buten-1-ol shows that the number of molecules with internal interaction between hydroxyl group and the π-electrons of the double bond is much

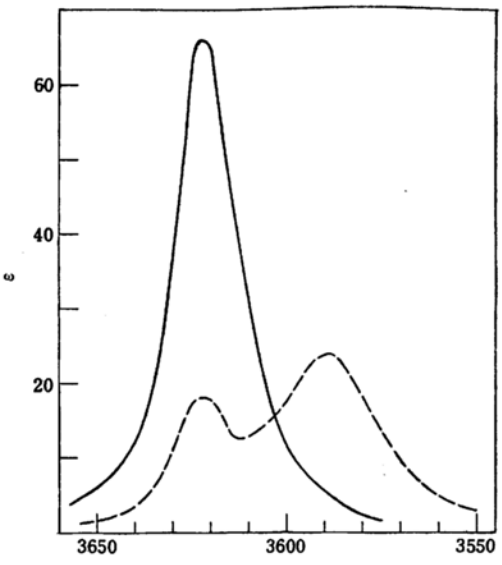
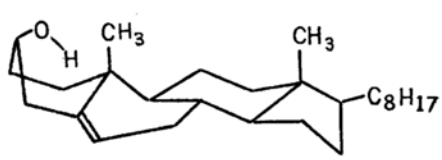


Fig. 1. ν_{O-H} absorption of cholesterol (——) and of epicholesterol (----).

greater in epicholesterol than in 3-buten-1-ol, since the integrated intensity of band I of epicholesterol is greater than that of 3-buten-1-ol (1.93×10^{3} $mole^{-1}\cdot liter\cdot cm^{-2}$) and the A_I/A_{II} value is 3.1 for epicholesterol and 0.6 for 3-buten-1-ol. The reverse in the intensities of the two bands in these compounds can be attributed to the more favorable conformation of epicholesterol than that of 3-buten-1-ol. Namely, when the interaction takes place, the conformation of C–C–C–O must be a *gauche* form which will cause greater unstability in term of energy and unfavorable entropy change in 3-buten-1-ol, while the conformation favorable for the interaction is fixed in epicholesterol.



III

3) Pure samples of these substances were kindly donated by Miss K. Mori of this laboratory, to whom the authors' thanks are due.

4) M. Ōki and H. Iwamura, This Bulletin, in press.

5) M. Ōki, H. Iwamura and Y. Urushibara, ibid., 30, 769 (1958).

The possibility for A ring of cholesterol to take a boat form (III) to some extent is denied, as far as the present data concern, because no absorption band was observed that would have been expected if cholesterol had possessed structure III favorable for the interaction.

This finding may be utilized for the analysis of epicholesterol in a mixture and similar phenomena will be observed in many other compounds of the same type. Examination of the scale models reveals that only the axial hydroxyl group is capable of forming this kind of interaction in steroids. Possibility for use in the diagnosis of the hydroxyl group is under investigation.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo