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Influence of the Position of Ring Unsaturation in Steroids and Triterpenes on the Type and Formation of Mesophases II:† Influence of the Δ^7-Double Bond

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Abstract—Several sterols and triterpenes possessing a Δ^7-double bond were investigated for mesomorphic behavior. The acetates and palmitates of cholesta-5,7-dien-3β-ol and cholest-7-en-3β-ol, exhibited distinct smectic mesophases only. The acetates of 4,4,14α-trimethylcholest-7-en-3β-ol and 4,4-dimethylcholest-7-en-3β-ol showed no mesomorphism while the palmitate of the latter gave a smectic mesophase. The Δ^7-double bond seems in general to favor the formation of smectic rather than cholesteric mesophases.

1. Introduction

In a recent report† we indicated that the presence of a double bond at position 8 in a number of sterols and triterpenes markedly affects the ability of the steroid ring to form liquid crystalline states. A detailed study was therefore initiated to investigate the influence of other positions of unsaturation on mesophase formation in this class of compounds, especially those which occur naturally and form part of the biosynthetic pathways leading to cholesterol and the plant sterols. Recently we examined short and long chain fatty acid esters of 4α-methylcholest-7-en-3β-ol (lophenol, methostenol) (I) and surprisingly found that they exhibit only smectic mesophases.[1] This, coupled with the findings of Knapp and Nicholas that ergosterol (II) esters also formed smectic mesophases only,[2] prompted us to

† Part I of the series deals with the influence of the Δ^8-double bond. See Ref. 6.

examine other steroids possessing a Δ^7-double bond and structures comparable to those of otherwise differently unsaturated steroids.

2. Experimental

Materials and methods of synthesis, purification and purity tests were identical to those adopted in previous papers.[1,2,3] Phase transitions were determined under crossed polarizers. Cholesta-5,7-dien-3β-ol (III) was supplied by Sigma Chemical Co., St. Louis, Mo. Cholest-7-en-3β-ol (IV) by Schwarz-Mann Co., Orangeburg, New York. 4,4-dimethylcholest-7-en-3β-ol (V) was kindly supplied by Dr. James Gaylor, Cornell University. 4,4,14α-trimethylcholest-7-en-3β-yl acetate (VI) was obtained by hydrogenation of 4,4,14α-trimethylcholest-8-en-3β-yl acetate (dihydrolanosteryl acetate) over platinum oxide in chloroform solution for 5 hours. The resulting Δ^7-compound was separated from unreacted dihydrolanosteryl acetate by chromatography over alumina impregnated with 12% $AgNO_3$. Eluted first was dihydrolanosteryl acetate with 5% benzene in petroleum ether, followed by the acetate of the Δ^7-derivative with 10% benzene in petroleum ether.

3. Results

Esters of cholesta-5,7-dien-3β-ol-(III)

(*a*) Cholesta-5,7-dien-3β-yl Acetate: Melted at 135° to the isotropic liquid and on cooling the field became strongly birefringent at 136° with scattered zones of fan shaped structures (monotropic). Crystallization occurred at 114 °C.

(*b*) Cholesta-5,7-dien-3β-yl Palmitate: Melted at 81.5°. This compound showed an enantiotropic polymorphic smectic mesophase. It melted to a viscous, strongly birefringent fluid which became opaque at 97°. The strong birefringency reappeared at 103° and the field became isotropic at 103.5°. On cooling the isotropic liquid to 103.5° numerous large batonnets were formed, which became very crowded within 3 degrees. These batonnets coalesced into a typical large smectic focal conic structure with characteristic crosses all over the field. Further cooling to 97° caused the field to become opaque but not birefringent, a condition which can be attributed to the

formation of the smectic homeotropic state. Crystallization occurred at 75°.

Esters of Cholest-7-en-3β-ol (IV)

(*a*) Cholest-7-en-3β-yl Acetate: Melted at 120–121°. This compound formed a monotropic smectic transition on cooling at 118°, followed by crystallization at 104°.

(*b*) Cholest-7-en3β-yl Palmitate: Melted at 93–95°. The isotropic liquid was formed directly from the melting crystals. On cooling, a strongly birefringent smectic phase appeared at 92° (monotropic). Crystallization occurred at 87°.

Esters of 4,4-dimethylcholest-7-en-3β-ol (V)

(*a*) 4,4-dimethylcholest-7-en-3β-yl Acetate: Melted at 145–146°. This compound was not mesomorphic.

(*b*) 4,4-dimethylcholest-7-en-3β-yl Palmitate: Melted at 44° to a viscous birefringent liquid which became mobile and isotropic at 57°. On cooling, a very faint birefringent phase was formed, which may represent a smectic homeotropic phase. Birefringency became noted and stronger at 39° showing a perfect smectic texture. Crystallization took place at 38°.

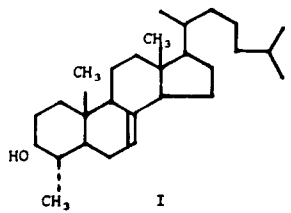
4,4,14α-trimethylcholest-7-en-3β-yl Acetate (VI)

Melted at 118°. This compound showed no mesomorphism.

4. Discussion

Whereas cholesterol (VII) readily forms both a cholesteric and a smectic mesophase when esterified with fatty acids [4], its Δ^7-isomer forms only a smectic mesophase when similarly esterified. Thus the difference in the position of the double bond in this case is coupled with a marked change in the kind of mesophase. A comparison between the properties of the esters of both Δ^5- and Δ^7-cholestenols and those of other steroidal compounds having a Δ^7-double bond (Table 1) leads to the conclusion that the Δ^7-bond inhibits the formation of cholesteric mesophases. Some studies on the influence of double bond position on mesophase formation have previously been reported. Thus Pohlmann *et al.*[5] observed that the stearates of

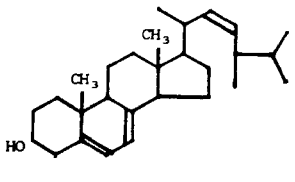
TABLE 1. Mesomorphic Behavior of Acetates and Palmitates of Some Steroids and Triterpenes



I

4α-methylcholest-7-en-3β-ol
(Lophenol)

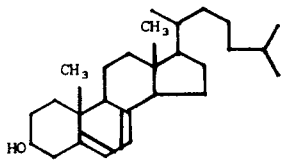
Acetate smectic
Palmitate smectic



II

Ergosta-5,7,22-trien-3β-ol
(Ergosterol)

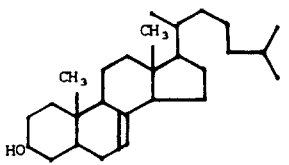
Acetate not mesomorphic
Palmitate smectic



III

Cholesta-5,7-dien-3β-ol
(7-dehydrocholesterol)

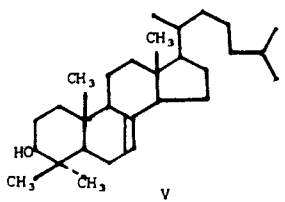
Acetate smectic
Palmitate smectic



IV

Cholest-7-en-3β-ol
(Lathosterol)

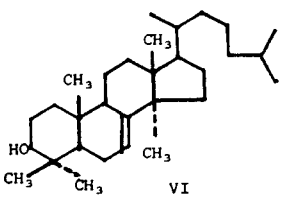
Acetate smectic
Palmitate smectic



V

4,4-dimethylcholest-7-en-3β-ol

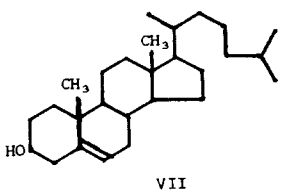
Acetate not mesomorphic
Palmitate smectic



VI

4,4,14α-trimethylcholest-7-en-3β-ol

Acetate not mesomorphic
Palmitate ——



VII

Cholest-5-en-3β-ol
(Cholesterol)

Acetate cholesteric
Palmitate smectic-cholesteric

cholest-l-en-3β-ol and cholest-4-en-3β-ol were not mesomorphic. In a recent report[6] we presented evidence that a Δ^8-double bond in the steroid nucleus could also inhibit the formation of mesophases when the corresponding compounds are esterified with fatty acids. Although Wiegand in his classical paper[7] reported mesomorphic behavior for a series of benzoates of cholesterol (VII), cholestenols and cholestadienols, he failed to specify the type of mesophases he was dealing with. Moreover he did not report the appearance of any cholesteric colors. His findings were never discussed in terms of type of mesomorphism because it was assumed at that time that a mesomorphic steroidal substance should be cholesteric.

The presence of a double bond at position 5 along with another double bond at position 7 does not seem to affect the influence of the Δ^7-double bond on preferential smectic mesophase formation. This is the case with ergosterol (II)[2] and cholesta-5,7-dien-3β-ol (III) esters. 4α-methylcholest-7-en-3β-yl acetate (lophenyl acetate) (I) forms a smectic mesophase,[1] in contrast to 4,4-dimethylcholest-7-en-3β-yl acetate (V) and 4,4,14α-trimethylcholest-7-en-3β-yl acetate (VI) which are not mesomorphic. This leads to speculation about the possibility that the number and position of methyl substituents at C_4 and C_{14} in the presence of the Δ^7-double bond may or may not have an influence on mesophase formation. Enough material of (V) and (VI) was not available to prepare a series of higher fatty acid esters for comparison with those of (I) and therefore this point cannot be clarified at the present time.

In general, since the cholesteric mesophase possesses a twisted structure, the Δ^7-double bond must therefore alter the capability of the layers of the mesomorphic compound to form the helical twist characteristic for the cholesteric mesophase. Our findings on the influence of the Δ^7- and Δ^8-double bonds[6] on mesomorphism prove that cholesterol is unique in its cholesteric behavior among other steroids of similar structure especially in regard to any possible biological significance of liquid crystals. Moreover, since other naturally occurring cholesterol biosynthetic intermediates such as 4α-methylcholest-7-en-3β-ol (lophenol) (I)[1] and cholesta-5,7-dien-3β-ol (III) have shown only smectic mesophases, this leads to speculation that if liquid crystallinity of steroids has indeed a biological aspect this aspect should be of a complex nature.

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REFERENCES

1. Atallah, A. M. and Nicholas, H. J., *Mol. Cryst. and Liq. Cryst.* **18**, 321 (1972).
2. Knapp, F. F. and Nicholas, H. J., *Mol. Cryst. and Liq. Cryst.* **10**, 173 (1970).
3. Atallah, A. M. and Nicholas, H. J., *Mol. Cryst. and Liq. Cryst.* **17**, 1 (1972).
4. Gray, G. W., in "Molecular Structure and the Properties of Liquid Crystals", 1962, Acedemic Press, New York.
5. Pohlmann, J. L. W., Elser, W. and Boyd, P. R., *Mol. Cryst. and Liq. Cryst.* **13**, 243 (1971).
6. Atallah, A. M. and Nicholas, H. J., *Mol. Cryst. and Liq. Cryst.* **18**, 339 (1972).
7. Wiegand, C., *Z. Naturforsch.* **4b**, 249 (1949).