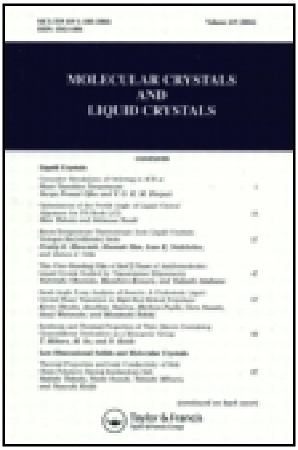

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Synthesis and Liquid Crystal Properties of Some 3-Arylcholest-2 enes and 3-Arylcholest-3,5-dienes

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Synthesis and Liquid Crystal Properties of Some 3-Arylcholest-2-enes and 3-Arylcholest-3,5-dienes

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A series of mesogenic 3-arylcholest-2-enes and 3-arylcholest-3,5-dienes were prepared. All members of the monoene and diene steroid series exhibited enantiotropic cholesteric mesophases. The broadest mesophase range was 90°, found for *para*-methoxyphenylcholest-2-ene.

INTRODUCTION

Of the three broad categories of liquid crystals, smectic, nematic, and twisted nematic or cholesteric, the unusual molecular arrangement of the latter class has led to a wide variety of applications.

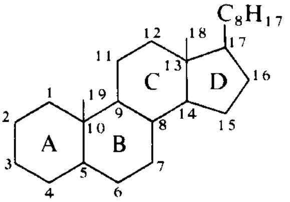
A useful model of the cholesteric mesophase is that of a layered nematic liquid twisted about an axis at right angles to the molecular layers in such a way that a gradual change in molecular orientation occurs along the twist axis, imparting a helical macrostructure to the liquid. The axis of the helix is thus perpendicular to the molecular axis. The uniaxial negative optical character of cholesteric liquids derives from the fact that the optical axis is perpendicular to the molecular axis and corresponds to the direction of the helix axis.[1]

Its helical macrostructure and uniaxial negative optical behavior give the cholesteric mesophase many of its unique properties which have been exploited in such diverse applications as "field effect" display devices,[2] temperature sensors,[3] and as chiral solvents in asymmetric reactions[4] and for induced circular dichroism.[5]

Cholesteric mesophases have been found primarily in cholesterol and related steriods, although several examples of nonsteroidal mesogens exhibiting cholesteric phases are known.[6] A requirement of the latter type to exhibit a cholesteric phase is the presence of an optically active center.

The first reported liquid crystal, cholesteryl benzoate,[7] typifies the class of cholesteric liquid crystals of which approximately 500 members have been reported.[6]

Since Reinitzer's initial report,[7] there has been considerable interest in the effect of changes in the steroid nucleus on mesomorphic properties. Numbering of the basic steroid ring system is shown below.



In 1949, Wiegand[8] reported that several mesogenic 3β-derivatives of cholestanol did *not* show liquid crystal behavior when the 3-substituent was changed to the α-orientation in which the bond is axial nor when the A-ring was changed from *cis*-fused rather than the usual *trans*-fused. Wiegand further reported a number of steroidal benzoates in which the skeletal structure had been modified by movement of the double bond from the 5–6 position of cholesterol to other ring positions and also by the introduction of a second double bond. Benzoate esters having the double bond in either the 7–8, 8–9, 8–14 or 14–15 positions and diene derivatives possessing a 5–6 and 7–8, 6–7 and 8–9, and 7–8 and 14–15 double bonds were found to give cholesteric mesophases, except when a 14–15 double bond was present. Benzoate esters with a 14–15 double bond were not mesogenic.[8]

Wiegand found that movement of the double bond(s) had small effects on the phase transition temperatures except in the case of the 8–14 benzoate isomer. For this compound, the transition temperatures were about 35° lower than those of the corresponding cholesterol derivatives.

This effect was exploited by Chu[9] in the preparation of a series of mesogenic 3β-aliphatic esters of 5α-cholest-8(14)-ene in which the transition temperatures were found to be considerably lower than those of the corresponding cholesterol derivatives.

We present here the results of a study of a monoene, 5α-cholest-2-ene and a diene, cholest-3, 5-diene, in which a *para*-substituted phenyl ring is attached directly to the unsaturated center at C–3.

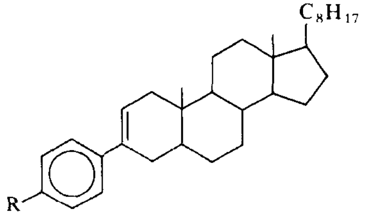
RESULTS

A series of 3-(*para*-substituted phenyl)-5α-cholest-2-enes were prepared by Grignard addition of the appropriate *para*-substituted bromobenzene to 5α-cholestan-3-one, followed by perchloric acid-catalyzed dehydration. The diene series was prepared from cholest-5-ene-3-one and the appropriate Grignard reagent, followed by acid-catalyzed dehydration to give the 3-(*para*-substituted phenyl)-cholest-3,5-dienes. The intermediate 3-aryl-3-hydroxysteroids were not isolated but were dehydrated directly to the corresponding monoene or diene.

All of the compounds in both our series exhibited enantiotropic cholesteric mesophases. For some derivatives, the mesophases persisted over a range of 80 to 90°. The data are presented in Tables I and II.

TABLE I

Transition temperature data for *para*-substituted-3-phenylcholest-2-enes[a]



Compound No.	R[b]	Phase transitions and temperatures,[c] °C	Cholesteric Range, Δt
1	H	K 140.5 C 146.5 I[d]	6.0
2	CH_3	K 160 C 209 I	49
3	C_2H_5	K 133 C 149 I	16
4	C_4H_9	K 128 C 181 I	53
5	CH_3O	K 120 C 210 I	90
6	C_2H_5O	K 105 C 172 I	67
7	C_3H_7O	K 110 C 160 I	50
8	C_4H_9O	K 98 C 169 I	71
9	$C_5H_{11}O$	K 128 C 160 I	32
10	$C_6H_{13}O$	K 130 C 154 I	24

[a] All compounds gave satisfactory elemental analyses.

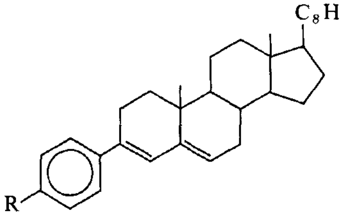
[b] Alkyl groups are normal.

[c] The linear notation is described in Ref. 13.

[d] Ref. 11 reports only m.p. 126–127° for this compound crystallized from acetone. We observed the compound to melt at this temperature and to then resolidify. Recrystallization from ethyl acetate-methanol gives material melting at 140–140.5°.

TABLE II

Transition temperature data for *para*-substituted-3-phenyl-cholest-3,5-dienes[a]



Compound No.	R^b	Phase transitions and temperatures,[c] °C	Cholesteric range, Δt
11	H	K 149 C 170 I	21
12	CH_3	K 175 C 198 I	23
17	C_4H_9	K 138 C 168 I	30
14	CH_3O	K 160 C 239 I	79
15	C_4H_9O	K 132 C 198 I	66

[a] All compounds gave satisfactory elemental analyses.
[b] Alkyl groups are normal.
[c] The linear notation is described in Ref. 13.

DISCUSSION

For the monosaturated steroids in Table I, assignment of the double bond to the 2-position was based in part on the work of Barton, Campos-Neves, and Cookson,[10] in which the two epimeric tertiary alcohols obtained from 5α-cholestan-3-one by treatment with methyl magnesium iodide were dehydrated with acetic acid containing a small amount of perchloric acid to give 3-methyl-cholest-2-ene, which was oxidized to the known *seco*-cholestan-2,3-dioic acid.

Independent substantiation of the 2-position of the double bond was obtained from the epoxidation of 3-phenylcholest-2-ene, **1**, with monoperphthalic acid to the known 2,3α-oxido-3β-phenylcholestane reported by Zderic *et al.*,[11] and by Cookson and Hudec.[12]

The double bond positions in the steroidal 3,5-dienes in Table II were confirmed by the presence of two vinyl olefin resonances in the NMR spectra, integrating for a single proton each; one a multiplet near 5.3 ppm assigned to H-6, and an unsplit peak as expected, near 6.5 ppm, assigned to H-4. In addition, the conjugated nature of the diene system was reflected by the large ultraviolet absorption coefficients, ε_{max}, ca. 30,000 in the 280–320 nm spectral region.

Inspection of Dreiding molecular models for the 3-*para*-substituted phenyl steroids in both series indicates the molecules to possess a long molecular axis essentially parallel to the C–3 bond axis. For maximum orbital overlap, the plane of the aromatic substituent would be expected to be parallel to the C–2 double bond in the first series and to the 3,5-diene system in the second series. This conformation causes the aromatic ring and the steroid A-ring to be almost coplanar (A-ring in half-chair conformation) and would allow the molecules in the liquid to approach close enough to maximize intermolecular attractive forces.

The cholesteric temperature range in the cholest-3,5-diene series is not very susceptible to changes in the nature of the *para*-substituent, changing from a range of 21° for the parent compound, **11**, to 30° for the *para*-butyl derivative, **13**, and from 79° for the *para*-methoxy compound **14** to 66° for the *para*-butoxyphenylcholest-3,5-diene, **15**. However, the cholest-2-ene system is found to be sensitive to small molecular changes, Table I. Introduction of a *para*-methyl group increases the mesophase range from 6° in **1** to 49° in **2**. Addition of another CH_2 group to give the *para*-ethyl derivative **3**, must result in an unfavorable packing arrangement since the mesophase range is now only 16° broad. The *para*-butyl derivative **4**, has the broadest cholesteric mesophase range, 53°, in the series of *para*-alkylphenylcholest-2-enes examined.

Introduction of a *para*-alkoxy group produces a relatively strong dipole at the *para* position. The *para*-methoxy derivative **5**, is cholesteric between 120 and 210°. This is the broadest mesophase range found for any of the compounds in our series.

It is interesting that the clearing point, the temperature at which the mesophase is destroyed by thermal forces, is almost the same for **5** and for the *para*-methyl derivative **2**. The highest clearing point found in our study is for the *para*-methoxyphenylcholest-3,5-diene, **14**, indicating the significant contribution of the 3,5-conjugated double bonds to mesophase stability.

EXPERIMENTAL

Mesophases were identified using a 100-power AO Spencer polarizing microscope equipped with a variable temperature stage designed in these laboratories.[14] The temperatures reported are those at which the solid or mesophase has just disappeared. Temperatures are corrected.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

The 3-(*para*-substituted-phenyl)-cholest-2-enes were prepared by Grignard addition of the appropriate *para*-substituted bromobenzene to 5αcholestan-3-one, followed by perchloric acid-catalyzed dehydration. The diene series was prepared from cholest-5-ene-3-one and the appropriate Grignard reagent, followed by perchloric acid-catalyzed dehydration to give the 3-(*para*-substituted phenyl)-cholest-3,5-dienes. The intermediate 3-aryl-3-hydroxysteroids were not isolated but were dehydrated directly to the corresponding monoene or diene. Representative procedures are given below.

3 - para - Anisylcholest - 2 - ene (**5**). An anhydrous ether solution of 5α-cholestan-3-one (Sigma Chemical Col., St. Louis, Mo., 5.00 g, 12.95 mmol) was added slowly to a well-stirred solution of excess *para*-anisyl magnesium bromide [prepared from *para*-bromoanisole (7.50 g, 40 mmol) and magnesium turnings in dry ether]. The reaction mixt. was refluxed for 3 hr., then poured into aq. ammonium chloride solution, followed by extraction into benzene. The benzene soln. was dried over anhyd. sodium sulfate, filtered, and the residue, after rotary evaporation, was chromatographed on neutral alumina in carbon tetrachloride. The alcohol fraction was eluted with 50:50 (v:v) carbon tetrachloride and benzene.

The crude alcohol mixt. was dissolved in 96% acetic acid, a drop of 60% perchloric acid was added, and the mixt. heated for 25 min. on a steam bath. The mixt. was extracted into benzene as described above and chromatographed on neutral alumina in carbon tetrachloride. Elution with carbon tetrachloride gave 3-*para*-anisylcholest-2-ene, **5**, K 120 C 210 I (from ethyl acetate/petroleum ether), $[\alpha]_D$ +66.5° (c 1.23, methanol); λ_{max}254, 18,000 (methanol).
Anal. Calc. for $C_{34}H_{52}O$: C, 85.65; H, 10.99; Found: C, 85.52; H, 11.07.

3 - (para - Tolyl) - cholest - 3,5 - diene (**12**). A solution of cholest - 5 - ene -3 - one[15] (7.50 g, 19.5 mmol) in anhyd. ether was added slowly to a well-stirred solution of excess *para*-tolyl magnesium bromide [prepared from *para*-bromotoluene (10.35 g, 60.5 mmol) and magnesium turnings]. The reaction mixt. was refluxed for 8 hr., then poured into aq. ammonium chloride solution and extracted with benzene. The benzene solution was dried over anhyd. sodium sulfate, filtered, the solvent stripped under reduced pressure, and the residue chromatographed on neutral alumina in carbon tetrachloride. The alcohol-containing fraction was eluted with 50:50 (v:v) carbon tetrachloride and benzene.

The crude mixture was dehydrated by dissolving it in 96% acetic acid, adding a drop of 60% perchloric acid, and heating the mixt. on a steam bath for 1 hr. The mixt. was extracted into benzene, washed twice with 5% sodium carbonate solution, dried over anhyd. sodium sulfate, filtered and evaporated under reduced pressure, and the residue purified by chromatography on neutral alumina in carbon tetrachloride. Elution with CCl_4/ether (98:2 v:v) gave *3-para*-tolyl-cholest-3,5-diene, **12**, K 175 C 198 I (from ethylacetate/petroleum ether), $[\alpha]_D$-99.1° (c 0.94, methanol), λ_{max} 282, 26,000 (methanol. Anal. Calc. for $C_{34}H_{50}$: C, 89.01; H, 10.99; Found: C, 88.98; H, 11.06.

Acknowledgement

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