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Mesomorphic Properties of Some Sitosteryl Esters

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The mesomorphic properties of some esters formed by aromatic acids with β-sitosterol are reported. It is shown that para-substituted benzoates are compounds exhibiting enantiotropic cholesteric and some smectic mesophases. Connections between the clearing points of sitosteryl esters and their homologous cholesteryl derivatives are discussed.

1 INTRODUCTION

The interdependence of the molecular structure and mesogenic properties of 3β-sterol derivatives has been recently the subject of many investigations.[1–4]

To elucidate some aspects refering to the mesogenicity of sitosterol (24 R-stigmast-5-en-3β-ol) compounds, Pohlmann *et al.*[1] synthesised the following derivatives: β-sitosteryl acetate, octanoate, *n*-heptyl carbonate, *n*-octyl carbonate and *n*-nonyl carbonate. All of them were found to be monotropic exhibiting smectic properties.

These results were in agreement with those obtained by G. W. Gray;[5] it was shown that the sitosteryl dodecanoate and sitosteryl tetradecanoate have liquid crystal properties and the mesophases exhibited by cooling are smectic.

Recently, Galanov *et al.*[6] examined several sitosteryl esters such as: acetate, hexaonate, octanoate, nonanoate and octadecanoate. They pointed out that the compounds were all monotropic without mentioning the nature of the mesophase.

If these are the only data examined, one may conclude that derivatives of β-sitosterol are only smectogenic. It may be assumed that the ethyl group in the 17β-side chain and its corresponding spacing requirement is responsible for the smectogenic character.

All the same, there is still experimental evidence on cholesterogenic properties in some sitosteryl compounds.

Verbit and Lorenzo[7] have discovered that the *N*-*p*-methoxyphenylcarbamate of sitosterol exhibits a cholesteric enantiotropic mesophase within a narrow temperature range (141–143°C).

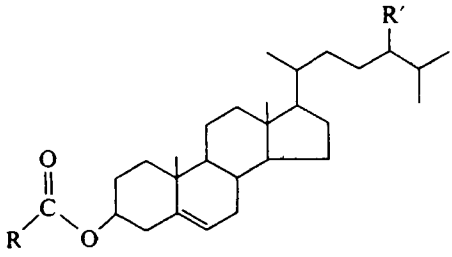
Tanaka *et al.*[8] have described cholesteric β-sitosteryl 3-methoxy-4-acyloxycinnamates.

This is an indication that different 3β-substituents are of importance for changes in molecular structure. These substituents may induce mesophases or may destroy the mesomorphic properties of the steroid compounds. It may be suggested that the supplementary dipole moment of the substituent is responsible for the mesomorphic properties.

It is the aim of this paper to investigate the ability of some 3β-substituents to induce cholesteric mesophases in sitosteryl esters.

2 RESULTS AND DISCUSSION

The compounds were obtained as a result of esterification of the 3β-hydroxyl groups of sitosterol and cholesterol:



R′ = H (cholesteryl esters)
R′ = C_2H_5 (sitosteryl esters)

2.1 Esters of benzoic acids

As shown in Table IA, the sitosteryl benzoates with different substituted groups in para-position of the benzenic ring exhibit mesomorphic properties as their homologous cholesteryl derivatives.

The cholesteric mesophases are revealed by extremely brilliant colours ranging from red to violet when the sample temperature is raised starting from the crystalline phase up to the isotropic one.

In most compounds the cholesteric mesophase is enantiotropic. An unexpected behaviour is displayed by the compound nr. 1 (sitosteryl benzoate):

the cholesteric mesophase was found only after cooling from the isotropic phase. Moreover, these compounds exhibit smectogenic properties. For the esters nr. 2–5, the smectic mesophases are monotropic; for the esters nr. 6, 7, 8 they are enantiotropic.

Two types of smectic mesophases were identified: smectic A and smectic C. The corresponding transition temperatures are also indicated in Table IA.

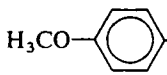
It is immediately obvious (Table IA) that the cholesteric–isotropic transition temperatures are dependent on the para-substituent groups. We may place the terminal groups in order of their decreasing effect upon the thermal stability of cholesteric mesophases as follows:

$$\phi > NO_2 > OCH_3 > Cl(Br) > CH_3 > n\text{-}C_4H_9 > H$$

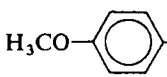
The efficiency order is similar to that reported by G. W. Gray[9] for cholesteryl benzoates.

As for the *n*-alkyl esters synthesised up to date, the clearing points of sitosteryl benzoates are lower than those of their homologous cholesteryl benzoates. The difference between the corresponding clearing points are within the range of 40–50°C.

The same holds true for the two carbamates synthesised by Verbit and Lorenzo:[7]



(K155C194I)



(K141C143I)

where Ch is the cholesteryl moiety and Sit the sitosteryl moiety.

A rather high difference in the clearing points of sitosteryl and cholesteryl esters respectively, was found for the para-iodobenzoate (80°C).

We note that when the cholesteryl and sitosteryl derivatives are examined there are no connections between the temperatures of the solid–cholesteric and smectic–cholesteric transitions. All the same, the sitosteryl derivatives have lower transition temperatures.

The highest thermal stability is displayed by the phenyl substituent; it is followed by the nitro and methoxy substituent.

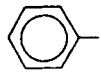
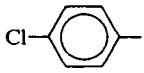
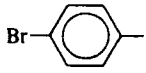
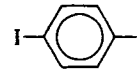
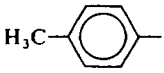
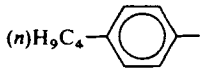
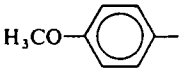
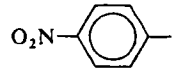
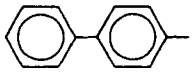
The existence of smectic mesophases in sitosteryl benzoates is easily understandable, as the first publications have shown that sitosteryl alkyl esters and sitosteryl carbonates were smectogenic. When the substituent is a halogen or methyl, the smectic mesophase is obtained only by cooling.

For substituents with higher electronegativity, such as nitro, phenyl or, unexpectedly, *n*-butyl, the smectic mesophase is enantiotropic.

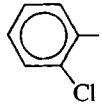
TABLE I

Transition temperature data for some esters of sitosterol and cholesterol[a]

A. *Para-substituted compounds*

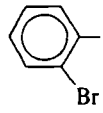
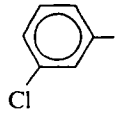
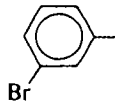
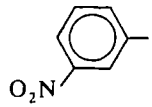
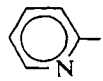
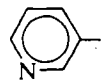
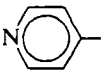
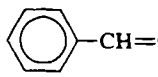
Compound number	R—	Phase transitions and temperatures		Ref.
		R′ = C_2H_5	R′ = H	
1		K 141 I (108 C)	K 154 C 180 I	10
			K 149 C 178 I	11
2		K 136 C 207 I(108 S)	K 170 C 253 I	10
			K 170 C 257 I	11
3		K 145 C 206 I	K 178 C 252 I	10
		(132 S_A 126 S_C)	K 170 C 257 I	11
4		K 158 C 196 I (−S)	K 187 C 268 I	10
5		K 145 C 203 I	K 184 C 243 I	10
		(132 S_A 118 S_C 98 S)	K 179 C 246 I	11
6		K 94 S_A 158 C 175 I	K 127 C 215 I	
7		K 146 C 226 I	K 181 C 267 I	10
			K 180 C 268 I	11
8		K 185 S_A 192 C 232 I	K 185 C 265 I	10
			K 191 C 260 I	11
9		K 162 S_A 181 C 255 I	K 180 C 287 I	11

B. *Ortho and meta substituted benzoates*

10		K 125 I (57 C − S)	K 106 C 146 I	11

[a] The linear notation is the same as in Ref. 7.
The sitosteryl esters are new compounds. (−S) means undercooled smectic.

TABLE I (*Continued*)

11		K 123 I (80 C − S)	K 105 C 137 I	11
12		K 131 I (98 C − S)	K 146 C 147 I	11
13		K 131 I (70 C − S)	K 135 C 142 I	11
14		K 159 I (−S)	K 140 C 174 I	11
	C. *Esters of some heteroaromatic acids*			
15		K 167 I ($-S_B$)	K 178 I (162 S)	
16		K 126 C 146 I	K 152 C 205 I	
17		K 156 I ($-S_B$)	K 173 I (136 C − S)	
	D. *Esters of some unsaturated acids*			
18	$H_2C{=}CH-$	K 138 I (−S)	K 118 C 126 I	12
19	$H_3C{-}CH{=}CH-$	K 137 I (−S)	K 113 C 162 I	13
20	$H_2C{=}CH{-}(CH_2)_8-$	K 70 I (62 S)	K 78 C 86 I (48 S)	
21		K 154 C 157 I	K 163 C 215 I K 156 C 197 I	13 11

We found mesogenic properties for some ortho- and meta-substituted sitosteryl benzoates. The corresponding transition temperatures are shown in Table IB. Data obtained by Tischenko *et al.*[11] for their homologous cholesteryl benzoates are also indicated for purposes of comparison.

Although the data included in Table IB are not sufficient to allow generalization, it may be assumed that the monotropic cholesteric and smectic polymorphism is specific to ortho- and meta-substituted sitosteryl benzoates.

2.2 Heteroaromatic derivatives

Cholesteryl and sitosteryl esters synthesised with monocarboxylic acids of pyridine are mesomorphic compounds as shown in Table IC.

The lowering of electron density in the 2,4,6-positions of the pyridinic ring by the carbonyl groups induces different aromaticity degrees for the synthesised compounds. It may be assumed that this is the reason why their sitosteryl and cholesteryl esters exhibit different mesomorphic behaviors.

The nicotinic acid with a higher aromaticity yields enantiotropic cholesteric mesogens, similar to those obtained for the para-substituted benzoates. The differences in the clearing points of sitosteryl and cholesteryl nicotinate are of the same order of magnitude as those of the benzoate series.

The isonicotinic acid yields monotropic mesogens. The cholesteryl derivative is cholesteric and smectic while the undercooled sitosteryl derivative is only smectic.

The picolinic acid, exhibiting the lowest aromaticity, yields no cholesteric mesophases. Both cholesteryl and sitosteryl derivatives are smectogenic.

2.3 Derivatives of unsaturated acids

Table ID contains data which make it possible to compare the mesomorphic properties of cholesteryl and sitosteryl esters formed with acrylic, crotonic and undecylenic acids.

These acids have a double bond differently positioned with respect to the carboxylic group. With cholesterol they yield enantiotropic cholesteric mesogens. The homologous mesogens of sitosterol are smectogenic. They have the same mesogenic character as their derivatives with saturated acids.

We may conclude that the double bond is not essential in ascertaining cholesterogenic properties in these esters.

As expected, the pronounced aromatic character of the cinamic acid determines cholesterogenic properties for its corresponding sitosteryl ester.

3 CONCLUSION

As a result of esterification with aromatic acids of the 3β-OH group of sitosterol, cholesteric mesogens are obtained.

As the ethyl group in the 17β-side chain has no significant influence on the over-all polarity of the sitosteryl derivatives, we may conclude that a high dipole moment in the 3β-side chain is important for changes in polarizability along the principal molecular axis. It may be suggested that these high dipole moments and their associated spacing requirements are responsible for helical arrangements typical for cholesteric mesophases.

The dipole moments induced by aromatic acids are more effective than those induced by aliphatic acids in promoting cholesteric properties.

The double bond introduced as a result of unsaturated acid esterification enhances the smectic mesophase formation.

4 EXPERIMENTAL PART

We used as starting compounds: β-sitosterol (Merck, 98%, m.p. 137–139°C) and cholesterol (Fluka AG, m.p. 145–148°C). Both were purified by successive recrystallizations from ethanol.

The sitosteryl and cholesteryl esters were obtained by reactions of the corresponding sterol with acidic chlorides.[14]

In some cases, as for example in the esterification reaction with pyridine carboxylic, the reaction via carbonyldiimidazole was used.[15]

The compounds were purified by successive recrystallizations from amyl alcohol and then from methyl ethyl ketone. Sometimes column chromatography has been used. The purity was checked by thin layer chromatography on silica gel (Merck G-Type 60) using 75 mL of hexane and 20 mL of benzene or benzene-hexane-ethyl acetate (9 : 6 : 2) as eluents.

Satisfactory elementary analysis were obtained from the newly described compounds.

The structure of the new compounds was confirmed by nuclear magnetic resonance and infra-red spectroscopy.

Transition temperatures and their associated texture changes were determined with a polarizing microscope equipped with a heating stage. The identification of mesophases was made by examining texture changes, according to the method of Sackmann and Demus.[16,17]

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