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Liquid Crystalline Cholestanyl and Cholesteryl Ether Lipids

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A homologous series of 3β-alkyl cholestanyl ethers was prepared and their liquid crystalline properties were studied. The compounds with alkyl groups consisting of $n = 3$ to $n = 20$ carbon atoms exhibit a cholesteric phase. In addition, the ethers with alkyl groups consisting of $n = 9$ to $n = 18$ carbon atoms show a S_A phase. Ordered or tilted smectic phases or blue phases are not observed. The S_A phase shows unusual textures several tenths of a degree below the transition to the cholesteric phase. The results obtained are compared with those of 3β-alkyl cholesteryl ethers and other homologous series of cholestanyl derivatives such as cholestanyl esters and cholestanyl carbonates.

*Keywords: liquid crystals, cholestanyl ethers, steroidal ether lipids, smectic A**

INTRODUCTION

Steroids are important materials for the synthesis of both chiral and aliphatic liquid crystals. Their derivatives occupy an extraordinary position among aliphatic liquid crystals showing chiral-nematic and blue phases as well as non-ordered smectic A phases. In contrast, other lipids such as paraffins show highly ordered phases, e.g. α phase, and other aliphatic liquid crystals such as cyclohexane derivatives show nematic and ordered smectic phases. We have studied liquid crystalline properties of new homologous series of sterol derivatives containing long alkyl chains.[1,2] Here we report the liquid crystalline properties of homologous series of 3β-alkyl cholestanyl ethers and 3β-alkyl cholesteryl ethers.

Alkyl Cholestanyl Ethers

The mesomorphic properties of alkyl cholestanyl ethers are given in Table I and Figure 1. The compounds with alkyl groups consisting of $n = 3$ to $n = 20$ carbon

TABLE I

Transition temperatures of 3β-alkyl cholestanyl ethers

n	Cr	S_A	Ch	recryst.
1	86.2			47
2[a]	82.8			63
3	65		46.4	20
4	74.2		52.6	50
5	74.8		42.8	40
6	67.9		51.5	40
7[b]	51.7		47.1	
8	41.2		53.1	
9	53.3	24.2	53.9	24
10	51.6	38.5	57.7	30
12	60.8	45.5	57.8	
13	69.4	46.6	56.0	
14	58.2	47.1	56.7	
15[c]	75.4	47.7	55.8	
16	73.2	48.5	56.4	
18	78.3	49	56.5	48
20[d]	82.1		>53	58
22	85.1			58
24	87.6			65

a) DSC : ΔH(Cr-I) = 17.3 kJ/mol, t=82.6°C.
b) DSC : ΔH(Cr-I) = 23.0 kJ/mol, t=52.9°C; DH(I-Ch) = -3.14 KJ/mol, t=47.1°C.
c) DSC : ΔH(Cr-I) = 56.4 kJ/mol, t=76.9°C.
d) DSC : ΔH(Cr-I) = 75.3 kJ/mol, t=83.3°C.

atoms exhibit cholesteric phases. Additionally, the compounds with alkyl groups consisting of $n = 9$ to $n = 18$ carbon atoms show smectic A phases. No other smectic phase or blue phase were observed. The octyl, nonyl and decyl derivatives show enantiotropic behavior, although the melting points are rather high and the clearing points low. All long-chain compounds have nearly the same transition temperatures for Ch and S_A. Thus, the low ordered cholesteric phase persists with a constant temperature range. Normally, in homologous series the smectic phases displace the nematic or cholesteric phase for long alkyl chains.

Similar to cholesteryl ethers or esters undercooling of the clearing points (Ch → I) by a few degrees has been also detected for alkyl cholestanol ether.

In addition, a strong even-odd effect was observed for the clearing points of the molecules with short carbon chains.

The smectic A phase shows changes in the texture several tenths of a degree below the transition temperature leading to the cholesteric phase. The fan-like texture changed to a texture with rods. These rods exist in a range of 0.3 to 0.7°C. The photographs 1 to 3 display the different textures of an uncovered droplet in the heating period, photographs 4 to 6 the corresponding textures in the cooling

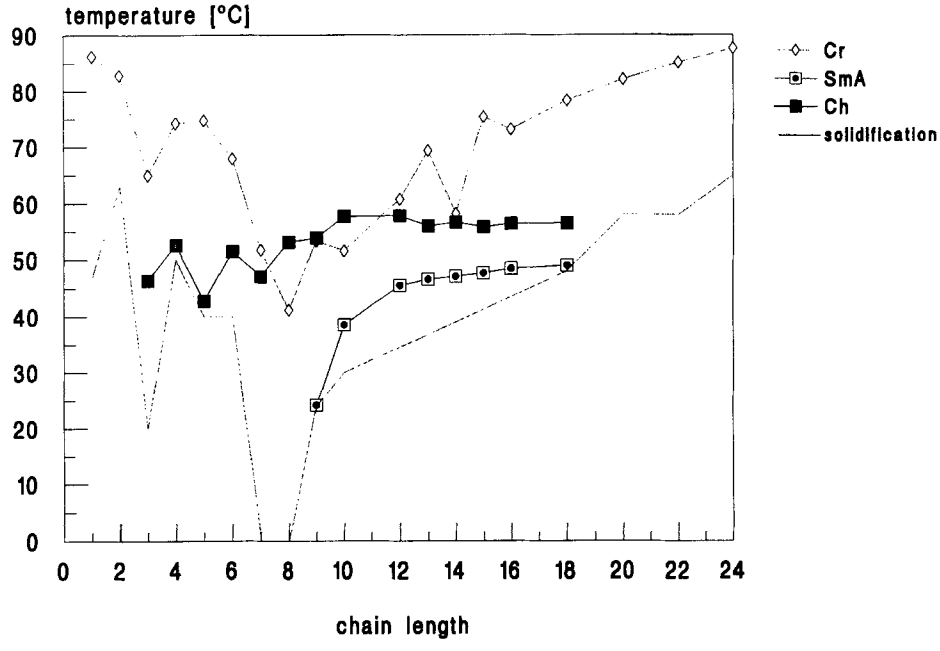
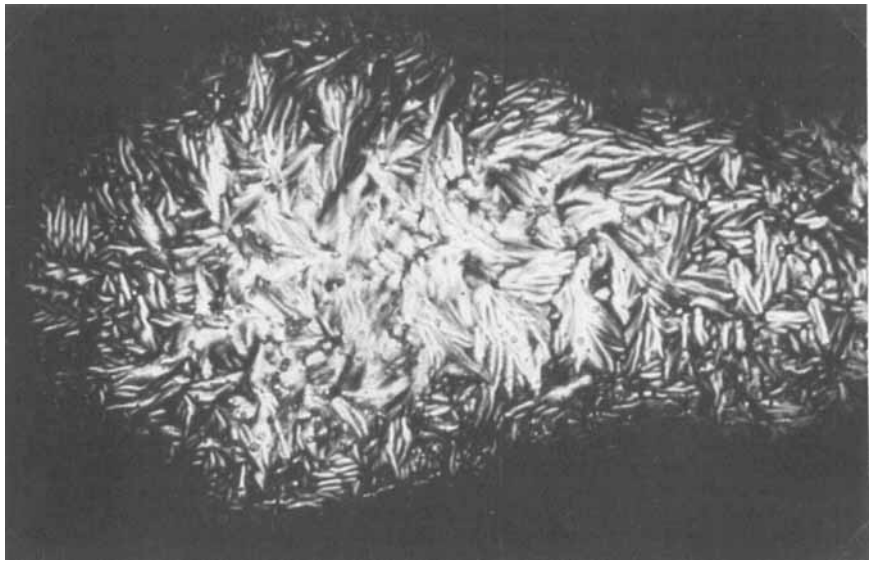
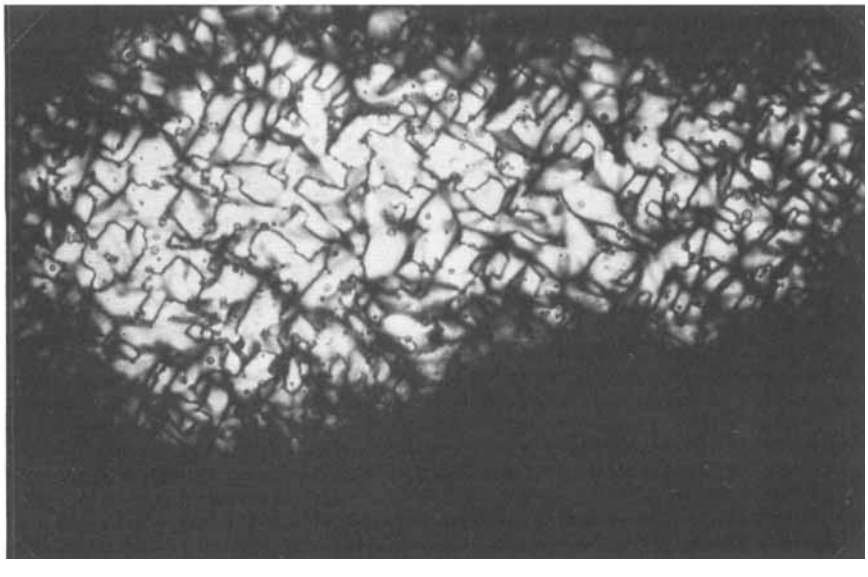


FIGURE 1 Transition temperatures of 3β-alkyl choestanyl ethers.



PHOTOGRAPHS Tridecyl cholestanyl ether (uncovered drop, crossed nicols, area 0.7 to 1.0 mm²: PHOTOGRAPH 1: 46.4°C, S_A, ↑

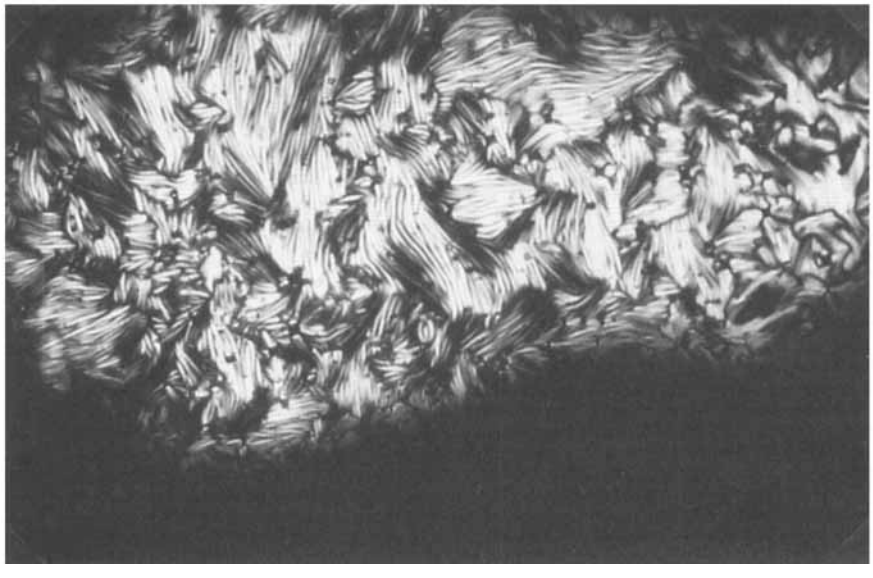
PHOTOGRAPH 2: 46.5°C, S_A, ↑



PHOTOGRAPH 3: 46.6°C, Ch, ↑

period. Probably these textures are formed by a twist grain boundary phase TGB_A^* ("smectic A*").[3–5] Because of the monotropic behaviour of the smectic A phase, it was possible to study this phenomenon in small drops only; in DSC the recrystallisation occurs before the formation of the smectic phase.

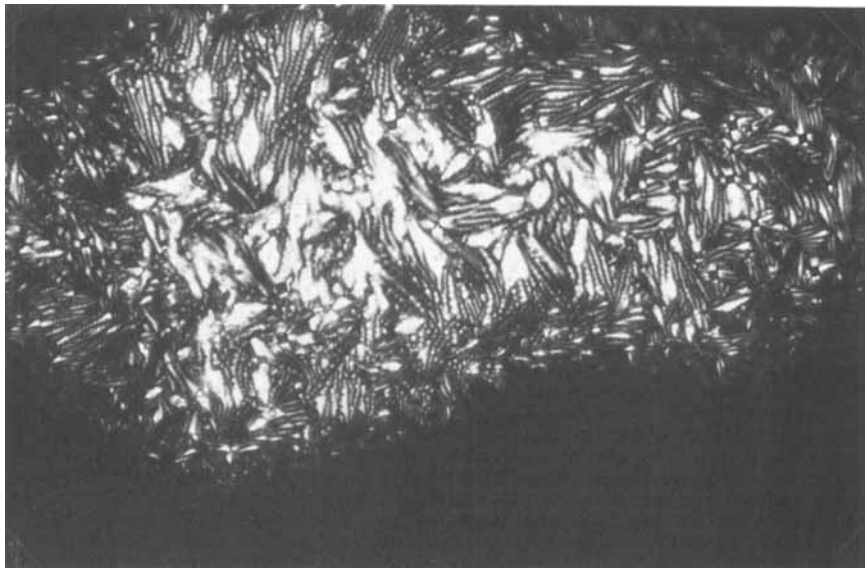
PHOTOGRAPH 4: 46.4°C. S_A. ↓



PHOTOGRAPH 5: 46.4°C, S_A, -

COMPARISION OF ALKYL CHOLESTANYL ETHERS WITH ALKYL CHOLESTERYL ETHERS

Figure 2 shows the mesomorphic properties of the alkyl cholesteryl ethers.[2] The structures of these compounds differ from those of the corresponding cholestanyl



PHOTOGRAPH 6: 45.9°C, S_A, ↓.

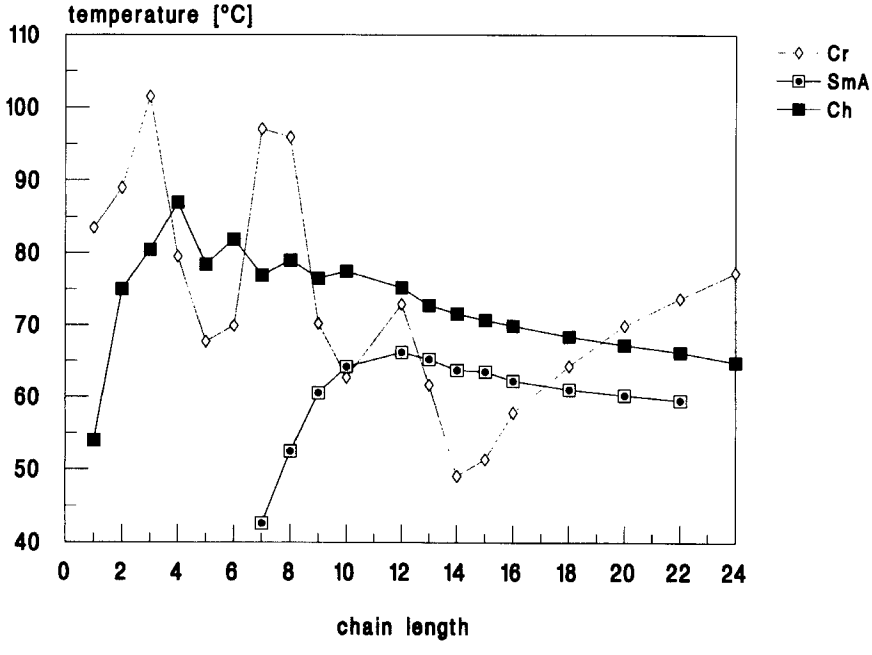


FIGURE 2 Transition temperatures of 3β-alkyl cholesteryl ethers.

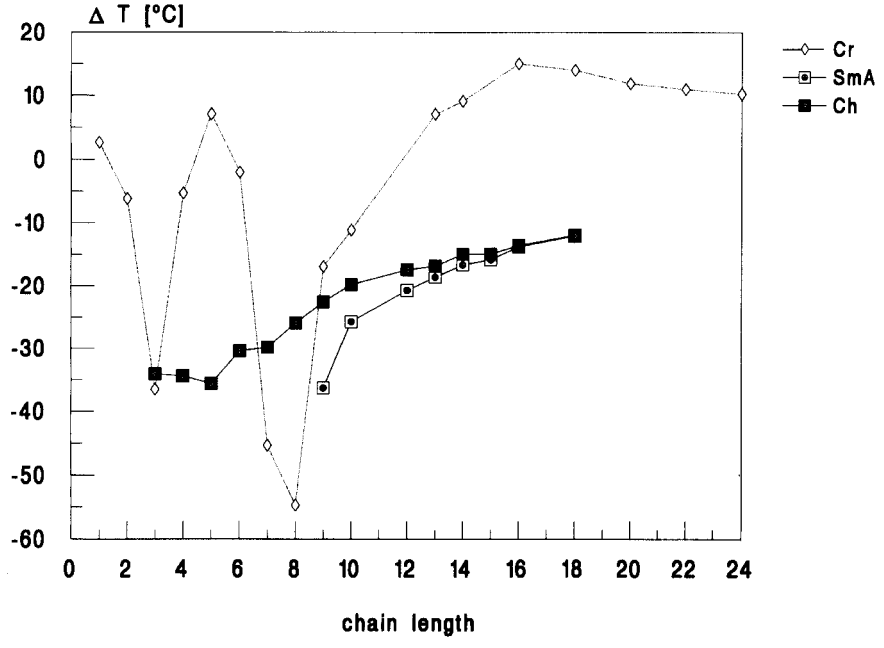


FIGURE 3 Differences of transition temperatures of alkyl cholestanyl ethers and cholesteryl ethers.

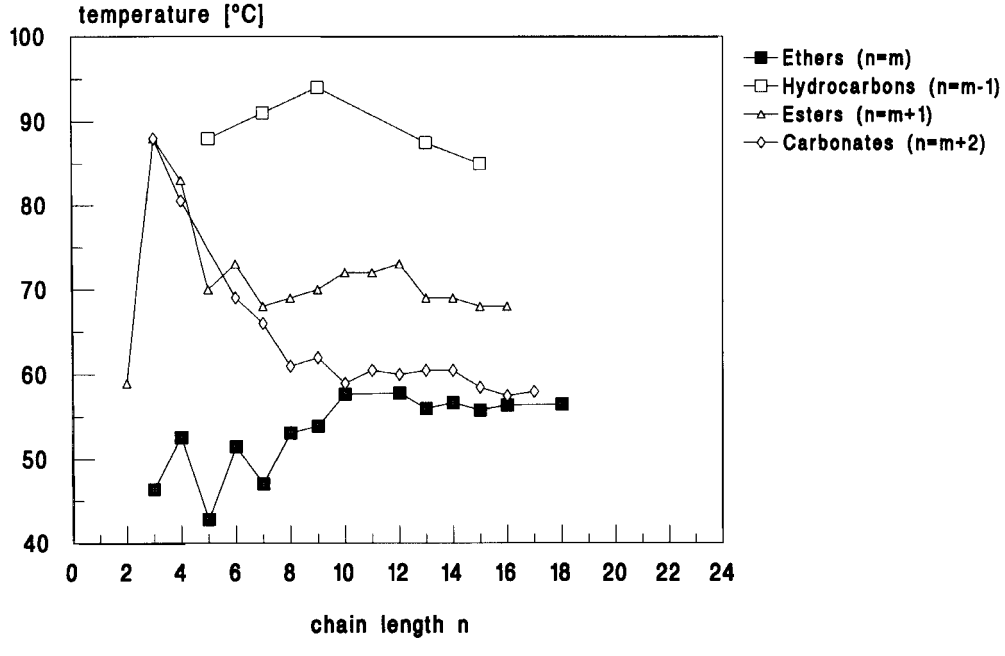


FIGURE 4 Clearing points (Ch → I) of homologous series of cholestanol derivatives.

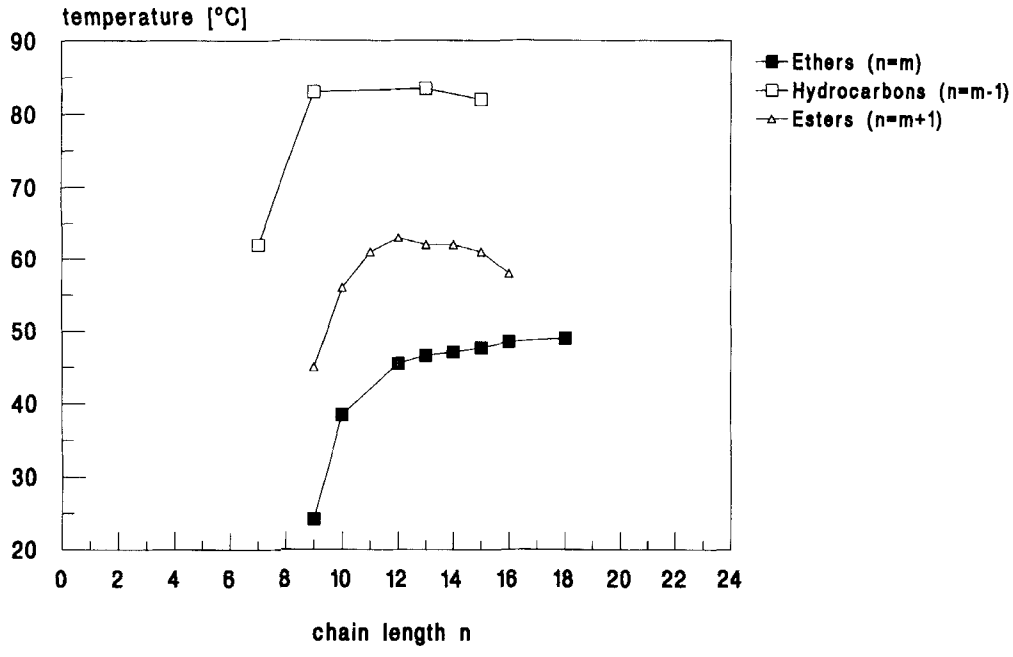


FIGURE 5 Transition points ($S_A \rightarrow$ Ch) of homologous series of cholestanol derivatives.

ether series only in the presence of a double bond in the ring B of the steroid moiety. Alkyl cholestanyl ethers show the same mesophases (cholesteric, S_A, no BP) as alkyl cholesteryl ethers but a different temperature dependence. Figure 3 shows the differences of the phase transition temperatures between the two homologous series. No simple or linear behavior was observed. Alkyl cholestanyl ethers have both lower clearing points and $S_A \rightarrow$ Ch transition temperatures than the corresponding alkyl cholesteryl ethers. This effect is higher for short-chain molecules than long-chain molecules. No simple relationship between phase transition temperatures of the two homologous series was observed.

Alkyl cholesteryl ethers show the same textures with rod like structures as the corresponding cholestanyl derivatives, however, this phase can be observed only in a very narrow range of less than 0.1°C.

COMPARISION OF ALKYL CHOLESTANYL ETHERS WITH OTHER HOMOLOGOUS SERIES OF CHOLESTANYL DERIVATIVES

Mesomorphic properties for some homologous series of cholestanyl derivatives have been reported, e.g. 3β-alkyl-cholestanes (hydrocarbons),[6] 3β-acyloxy-cholestanes (esters),[7] 3β-alkyloxycarboxy-cholestanes (carbonates)[8] and corresponding thiocarbonates[9]:

Series	Formula	Chain length for comparison
Hydrocarbons	C_mH_{2m+1}-Cholestane	$n = m - 1$
Ethers	C_mH_{2m+1}-O-Cholestane	$n = m$
Esters	C_mH_{2m+1}-COO-Cholestane	$n = m + 1$
Carbonates	C_mH_{2m+1}-OCOO-Cholestane	$n = m + 2$

m = number of carbon atoms of the alkyl chains; n = 'effective' chain length.

Figure 4 demonstrates the clearing points of hydrocarbons, ethers, esters and carbonates of the cholestanyl series. Of all the series of compounds the alkyl cholestanyl ethers have the lowest clearing points. In the corresponding ester and carbonate series the short-chain molecules have the highest clearing points, whereas in the alkyl cholestanyl ether series the short-chain molecules have the lowest clearing points. These findings may be explained by polar and/or stereochemical properties of the difference cholestanyl derivatives as discussed below.

For example, the nonpolar alkylcholestanes and the relatively polar alkyl cholestanyl esters have higher clearing points than the medium polar alkyl cholestanyl ethers. Thus, the different clearing points are not explained by the varying polarities of the cholestanyl derivatives. The bridging groups (-, O, COO, or OCOO) are responsible for the distinct angles between steroid moiety and alkyl chain. These angles could determine the liquid crystalline properties. The alkyl cholestanyl ethers show a strong even-odd effect demonstrating a more linear arrangement of steriod moiety and alkyl chain. Therefore, the contribution of the static conformational effect[10] to the different clearing points observed may be negligible. Another reason for the unusual behavior may be the difference in chain flexibility[11] of the various cholestanyl derivatives. It is known that alicyclic ring systems, e.g. cyclohexane derivatives with alkoxy groups as substituents normally show lower clearing points than those compounds with alkyl substituents. Tschierske *et al.*[11] explain these effects by difference in chain flexibilities. (So far, no data are available for acyloxy and alkyloxycarboxy wing groups.) It seems, that different chain flexibility may be the best explanation for the varying clearing temperatures of steroid derivatives.

Figure 5 shows the S_A to Ch transition temperatures of cholestanyl hydrocarbons, ethers and esters; again the alkyl cholestanyl ethers have the lowest transition temperatures. Skoulios *et al.*[12] found that a generalized amphiphilic character is present for nearly all columnar discotic and smectic liquid crystals. In this case, the hydrocarbons without any amphiphilic character have the highest clearing points.

PREPARATION

3β-Alkyl cholestanyl ethers were prepared by reaction of the corresponding alkyl methanesulfonates with cholestan-3β-ol (E. Merck) in the presence of KOH.[13,14] The compounds were purified by column chromatography (Silica Gel 60, E. Merck), eluted with hexane/diethyl ether (95:5), followed by preparative thin-layer chromatography (Silica Gel H, E. Merck) and repeated crystallization from acetone (n = 1 to 13) or hexane (n = 14 to 20).

Optical rotations (c = 1, hexane) were measured on a Perkin-Elmer Polarimeter 241 MC. ^{1}H-NMR and ^{13}C-NMR-APT spectra were obtained on a Varian Gemini 200 spectrometer in deuterochloroform using tetramethylsilane as internal standard. Mass spectra (EI mode; 70 eV) were recorded on a Hewlett Packard 5989 A instrument using Direct Insertion Probe (DIP).

Physical data of 3β-cholestanylpentadecylether are given as an example; values of other homologous compounds are similar:

$[\alpha]_D^{20}$ + 15.2°.

MS: m/e (rel%) 598 (0.1; M^+); 387 (8, cholestane−H); 372 (41; cholestane backbone); 357 (13, cholestane−CH_3); 257 (9; cholestane−side chain); 99 (21); 85 (33); 71 (52); 57 (100).

^{1}H-NMR: δ (ppm) 0.67 (s; 3H, Ch_3-18); 0.79 (s, 3H, CH_3-15′); 0.84 (d, 3H, CH_3-23); 0.88 (s, 6H, CH_3-26 and CH_3-27); 1.59 (s, 3H, CH_3-19); 3.1−3.3 (m, 1H, 3α-H); 3.43 (t, 2H, —CH_2—O).

^{13}C-NMR: δ (ppm) 68.1 (—CH_2—O); 78.5 (C-3).

CONCLUSION

In general, alkyl cholestanyl ethers show the same principle phase transition behavior as it is known for other cholesterol and cholestanol derivatives, i.e. less ordered cholesteric and smectic A phases. In contrast to various other lipids no highly ordered phases are observed.

3β-Alkyl cholestanyl derivatives have lower clearing points than the corresponding cholesterol derivatives.

Alkyl cholestanyl ethers have lower clearing points than the corresponding esters and carbonates which may be explained by a dynamic conformational effect.

Special textures of the smectic A phase of alkyl cholestanyl ethers still have to be explained.

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