Synthesis and Mesomorphic Behaviour of 5α-Cholest-8(14)-en-3β-yl Alkanoates

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Summary A homologous series of 5α-cholest-8(14)-en-3β-yl alkanoates has been synthesized *via* transacylation of 5α-cholest-8(14)-en-3β-ol with the imidazolides of alkanoic acids. All alkanoates of this series exhibit mesomorphic behaviour in the pure state except the formate and acetate. The mesomorphic transition temperatures are considerably lower than those of the corresponding cholesteryl derivatives.

THE unusual optical properties of cholesteric liquid crystals have made these compounds very attractive for use in device applications. For practical applications,[1] cholesteric mesophases which exist at or near room temperature are desirable. The majority of compounds which exhibit cholesteric mesophases are derivatives of cholesterol[2] and they have relatively high mesomorphic transition temperatures.[3] A number of studies on the modification of the structures of cholesterol derivatives have been reported.[4] Modifications of the 17β-side chain have led to impairment or complete loss of the mesomorphic properties [4c–4e] and Wiegand [4a–4b] found that movement of the double bond within ring B of cholesteryl benzoate has a small effect, but when the double bond is between C(8) and C(14) [5α-cholest-8(14)-en-3β-yl benzoate], the cholesteric–isotropic liquid transition temperature is 38° lower than that of cholesteryl benzoate. Recently, Leder[5] synthesized several derivatives of 5α-cholest-8(14)-en-3β-ol (**1**) which formed right-handed cholesteric liquid crystals having transition temperatures *ca.* 30° lower than the cholesteryl equivalents. We have now synthesized a homologous series of saturated aliphatic esters of (**1**) in an attempt to obtain new stable cholesteric liquid crystals with low mesomorphic transition temperatures.

Purity of material is important in the physical behaviour of liquid crystals[3a,b] so we prepared the compounds to a high degree of purity. Catalytic hydrogenation of purified 7-dehydrocholesterol in a mixture of ether–acetic acid (95:5) gave (**1**) (95%) m.p. 119—119·5° (lit.[7] 119°). The esters were prepared *via* transacylation of (**1**) with the imidazolides of alkanoic acids. This Staab[8] esterification procedure differs from conventional methods in using mild reaction conditions and producing a high yield of esters with very few side products. Purification of the esters by recrystallization alone was unsatisfactory so we purified the crude products first by column chromatography on silica gel, eluting with hexane–benzene (80/20). The fractions were monitored by t.l.c. and gave good yields of very pure compounds. Spot checks performed with a special gas-chromatographic method[6b] showed a minimum ester purity of 98%. Eighteen homologous esters were prepared (Table).

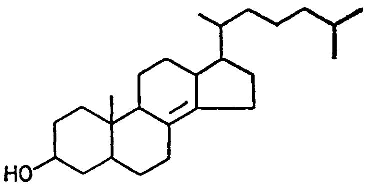
TABLE

The yields and mesomorphic transition temperatures of 5α-cholest-8(14)-en-3β-yl alkanoates

Alkanoate[a]	Yield (%)	Transition temperature (°C)[b] T_s	T_{ch}	T_i
Formate	90	—	—	106·4
Acetate	93	—	—	78·2
Propionate	72	—	82·3	85·2
Butyrate	73	—	(77·3)	85·3
Pentanoate	70	—	(67·4)	84·2
Hexanoate	75	—	(68·0)	85·9
Heptanoate	86	—	63·4	66·8
Octanoate	88	—	48·7	68·4
Nonanoate	91	(40·1)[c]	43·7	70·9
Decanoate	85	44·4	58·9	71·8
Undecanoate	81	57·4	63·9	70·7
Dodecanoate	82	57·0	67·0	71·2
Tridecanoate	80	54·3	68·1	70·0
Tetradecanoate	62	64·4	66·1	67·2
Pentadecanoate	64	63·9	68·1	68·5
Hexadecanoate	65	(67·8)	—	73·1
Heptadecanoate	63	(66·9)	—	69·4
Octadecanoate	61	(66·7)	—	77·5

[a] All compounds had acceptable elemental analyses. [b] T_s, T_{ch}, and T_i are temperatures of transition to smectic, cholesteric, and isotropic liquid, respectively. [c] Values in parentheses were obtained on cooling only.

The mesophases of the homologous esters were identified using a Leitz Ortholux polarizing microscope equipped with a Mettler Model FP-2 heating stage. The phase transition temperatures (Table) were determined by differential scanning calorimetry. Mesomorphic behaviour is shown by all esters except the formate and acetate. Smectic phases are observed for nonanoate and higher members. Monotropic cholesteric mesophases are found in butyrate, pentanoate and hexanoate. The next nine members, heptanoate—pentadecanoate, are enantiotropic cholesteric. The highest three members in the series exhibit only monotropic smectic mesophases; this extinction of cholesteric properties has apparently not been observed for any other series of cholesterogens of the steryl type. In nearly all cases, the mesomorphic transition temperatures of 5α-cholest-8(14)-en-3β-yl alkanoates (Table) are lower, by 10—40°, than those of the corresponding cholesteryl derivatives.[3a,9] When the temperatures T_{s-ch} and T_{ch-i} are plotted against the number of carbons in the ester chain, a close approximation to a regular distribution of the points with alternation of the T_{ch-i} values is found. The nonanoate has low transition temperatures and a reasonably broad cholesteric range. These properties appear to be desirable for practical applications.



(1)

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