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Unusual Temperature-Dependence of the Cholesteric Pitch of Pure Methyl 3β-Nonanoyloxychol-5-en-24-oate

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Unusual Temperature-Dependence of the Cholesteric Pitch of Pure Methyl 3β-Nonanoyloxychol-5-en-24-oate

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New derivatives of 3β-hydroxychol-5-enoic acid have been prepared. Their purities were checked by TLC, IR, PMR and DSC. It was found that the cholesteric pitch of methyl 3β-nonanoyloxychol-5-en-24-oate (I) exhibits a non-typical increase with increasing temperature. Since this phenomenon occurs in the visible light range, it may eventually be of great practical importance.

INTRODUCTION

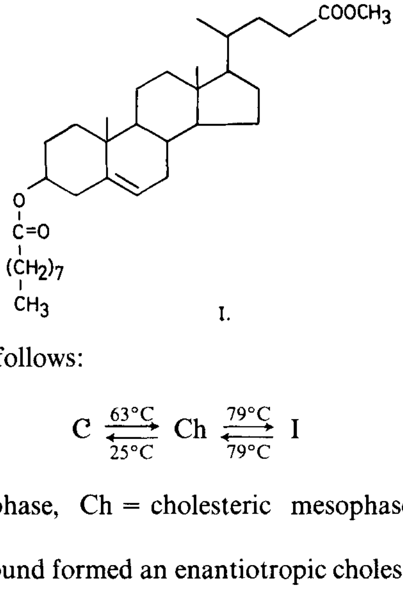
Several research teams have prepared sterane derivatives bearing a carboxyl group[1-6] and studied their mesomorphic properties. Since previous investigations were concerned, with the exception of one compound, only with methyl esters, and only a small number of substituents were replaced in position 3β, we considered it necessary to synthesize further compounds[7-8] and to study their mesomorphic behaviour.

MATERIALS

The compounds prepared were purified by means of column chromatography with subsequent repeated crystallization from pure solvents. The purities of the products were checked by thin-layer chromatography, melting point control, IR and PMR spectroscopy and absolute purity control using DSC.

RESULTS AND DISCUSSION

Of our new compounds, methyl 3β-nonanoyloxychol-5-en-24-oate (I) displays a characteristic phenomenon. The phase transition scheme for this material is an follows:



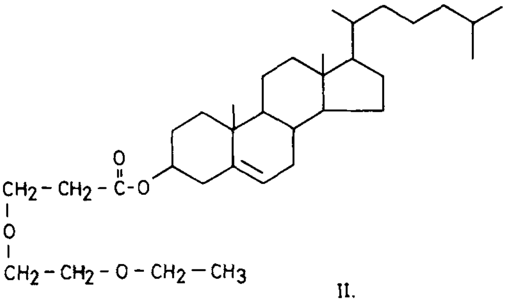
I.

$$\mathrm{C} \underset{25^\circ\mathrm{C}}{\overset{63^\circ\mathrm{C}}{\rightleftarrows}} \mathrm{Ch} \underset{79^\circ\mathrm{C}}{\overset{79^\circ\mathrm{C}}{\rightleftarrows}} \mathrm{I}$$

(C = crystalline phase, Ch = cholesteric mesophase, I = isotropic liquid)

Thus, the compound formed an enantiotropic cholesteric mesophase. On melting the crystals, the liquid crystalline state was blue when observed under a polarising microscope and the visible light reflected changed to light of *longer* wavelength with increasing temperature of the sample. This demonstrated that the helical pitch of the cholesteric structure increases with increasing temperature. On cooling the isotropic liquid, a yellowish-green cholesteric mesophase developed; this became blue on further cooling, and later crystallized.

The most customary feature of single-component cholesteric liquid crystals is that the pitch of the helix decreases with increasing temperature[9-11] and remains finite at all temperatures. To the best of our knowledge, only one pure single-component material has so far been reported and studied in which the cholesteric pitch increases with increasing temperature. This compound is cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate (CEEC) (II), synthesized by Durand.[12]



II.

Harada and Crooker[13] verified that its cholesteric pitch varies in the abnormal direction. Lin-Liu and co workers[14,15] have proved theoretically that this could arise for other compounds and there does not appear to be any fundamental reason why these should not occur in nature. However, in most cases the phenomenon is probably prevented by the relatively narrow temperature range spanned by the cholesteric phase.

In the absence of smectic phases, cholesteric phases do *normally* follow the qualitative rule that k_{22}/P is a constant, i.e., as resistance to twist decreases, so the pitch (P) decreases. No liquid crystals that have been studied show an increase in k_{22} with increasing temperature, and therefore if things were as simple as the constancy of k_{22}/P implies, P should decrease with increasing temperature. However, it is well known from studies[16] of many commercial nematic hosts such as the cyanobiphenyls, the PCH's and the CCH's that when these are doped to around 40–50 wt % with the chiral dopant CB15 (4-(2-methylbuthyl)-4′-cyanobiphenyl), the mixtures show an increase in P with temperature of between 1 and 2 nm/°C. There is no explanation of this, but it is interesting that the mixtures which behave in this way are cyano-substituted systems involving strong local ordering (dipole-dipole correlations). Now, however, we have observed the same behaviour in a pure compound of the cholesteryl ester class which does not contain a terminal function with a strong dipole, as in the cyano-systems.

In the case of our compound the colour changes were followed spectrometrically. The wavelength of the transmitted light was mea-

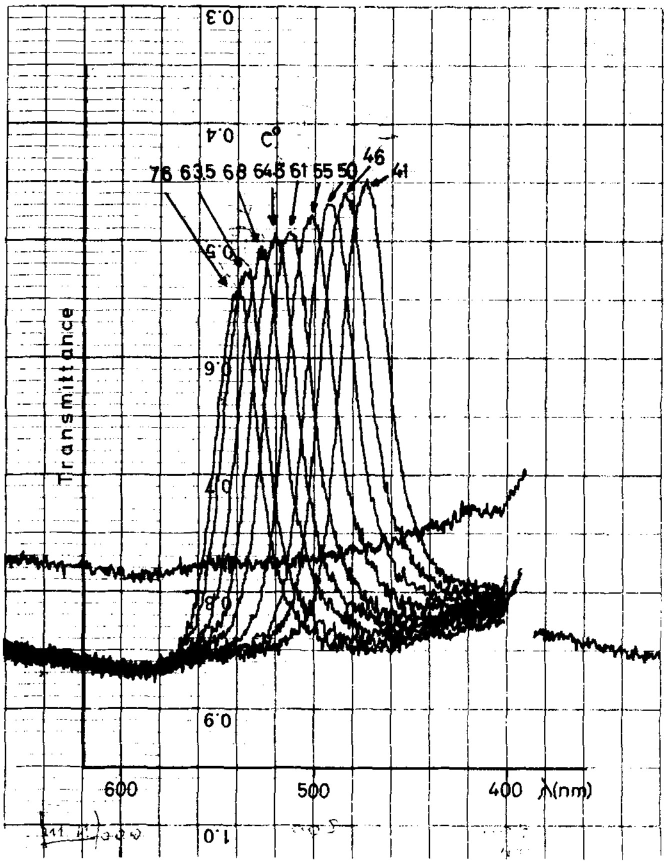


FIGURE 1 Transmitted light spectra at different temperatures.

sured as a function of temperature. The spectrum is shown in Figure 1. The temperature dependence is strikingly demonstrated if the reciprocal wavelength at the peak maximum for the transmitted light is plotted against temperature Figure 2.

Since this new compound scatters visible light, its practical applications are of great promise.

MEASUREMENTS

For our investigations an AMPLIVAL POL-U (Carl Zeiss, Jena) polarizing microscope, UNICAM SP 200, JEOL 60 HL, and VARIAN

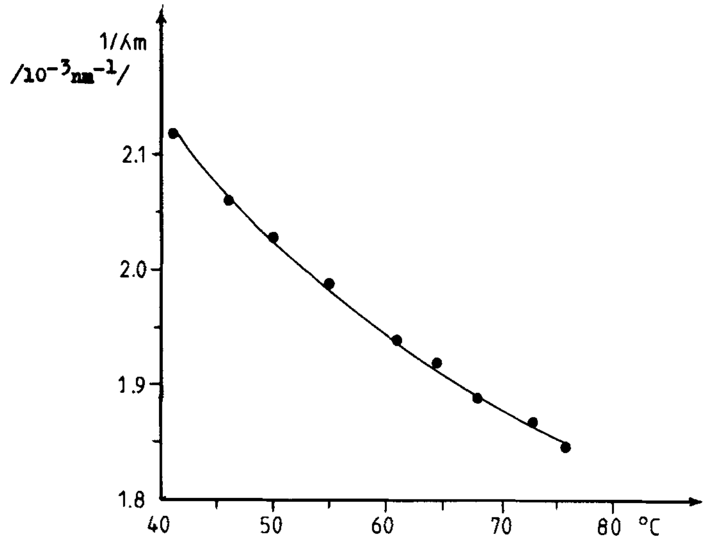


FIGURE 2 Temperature-dependence of reciprocal wavelength at peak maximum for the transmitted light.

CARY 17D spectrometers, and a PERKIN-ELMER DSC-2 calorimeter were used.

Acknowledgments

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