LIQUID CRYSTALLINE BEHAVIOR OF BIOLOGICALLY IMPORTANT LIPIDS

POLYUNSATURATED CHOLESTEROL ESTERS AND PHOSPHOLIPIDS

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Lipids are biologically important molecules. They give structure to plasma membranes and intracellular organelles, provide a source of metabolic energy and play a role in many essential biological processes such as transmission of information across membranes, transmission of nerve impulses, antigen-antibody reactions and thrombogenesis. Lipids have also been implicated in pathological processes, for instance the lipid storage diseases (1) gallstones and (2) atherosclerosis (3).

The physical properties of some individual lipid classes (e.g. phospholipids, fatty acids, bile acids, triglycerides, sterols) have been extensively studied (4–9) and the interactions between certain lipid classes, for example phospholipid-cholesterol, have been examined both in bulk aqueous phases and at various interfaces (8,10,11). However biologically important cholesterol esters have received less attention considering the early demonstration of their behavior as liquid crystals (12). Recently the phase behavior of the biologically-important, long-chain, saturated and unsaturated esters have been studied by microscopy, calorimetric and x-ray diffraction methods (7,13). Of interest is the demonstration that the melting and liquid-crystal transitions of the cholesterol esters of the C18 fatty acids are dependent upon the chain unsaturation (stearate > oleate > linoleate > linolenate). (7,14) Furthermore the thermodynamic stability of the different liquid-crystal phases may be important in terms of their structural role in biological environments.
In this paper we summarize the behavior of 2 biologically important polyunsaturated esters of cholesterol, cholesteryl linoleate and cholesteryl linolenate with the phospholipid lecithin.

METHODS

a) Chemicals

Egg lecithin (Grade 1: Lipid Products, Surrey, England), cholesteryl linoleate and cholesteryl linolenate (Hormel Institute, Austin, Minn.) were judged to be greater than 99% pure by a number of chromatographic methods (15,16). The fatty acid composition of the egg lecithin was determined by gas liquid chromatography. The major fatty acids were: C16:0 41.8%, C16:1 0.4%, C18:0 2.0%, C18:1 52.1%, C18:2 2.2%, others 1.2%. The molecular weight calculated from this fatty acid composition was 765.

b) Preparation of Mixtures.

Appropriate proportions of chemicals were taken up in organic solvent (chloroform-methanol), mixed and the solvent removed under vacuum. In some mixtures an appropriate amount of water was added. All tubes were flushed with nitrogen, sealed, and equilibrated at an appropriate temperature.

Equilibration was facilitated by centrifuging the sample back and forth through a constriction in the tube during the incubation period. A sample which appeared homogeneous by microscopy and gave reproducible transitions on repeated heating and cooling was determined to be equilibrated. Each sample was then observed with respect to fluidity and homogeneity. The tube was opened and samples taken for polarizing light microscopy, differential scanning calorimetry (DSC), x-ray diffraction and in some cases proton magnetic resonance.

c) Techniques

Polarizing microscopy on a heating-cooling stage was carried out as described previously (7,15,17). DSC was carried out in a Dupont 900 Differential Thermal Analyser fitted with a scanning calorimeter (7). x-ray diffraction studies were performed on sealed samples in a special heating chamber utilizing nickel-filtered Cu Kα radiation from an Elliot GX-6 rotating anode generator. Two x-ray focusing cameras were used: toroidal mirror optics (18) or double mirror optics (19). Proton magnetic reson-