Preliminary Investigation of the Liquid Crystal Behaviour of β-sitosteryl-β-D-glucopyranoside

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Introduction

Glycolipids are a very important class of molecules having liquid crystal properties which are abundantly found in biological membranes. Although most glycolipids seem to show liquid crystal properties, their liquid crystalline behaviour is not well understood. Liquid crystals are a state of matter that has properties between those of a conventional liquid and those of a solid crystal. For instance, a liquid crystal may flow like a liquid, but the molecules in the liquid are arranged and /or oriented in a crystal like way (Wikipedia). Carbohydrates are a new, but a very important source for liquid crystals (Vill *et al.*, 1998). Normally, mono-, di- and oligosaccharides substituted with an alkyl chain having more than six carbon atoms show liquid crystal properties. Their amphiphilic nature leads to the formation of liquid crystals via microphase separation (Smits, 1969). β-sitosteryl-β-D-glucopyranoside is found to occur naturally in some plants (Vill *et al.*, 1998). The commercial potential of the use of this compound as a liquid crystal has not been investigated. In this study, we attempted the synthesis of β-sitosteryl-β-D-glucopyranoside starting from glucose and β-sitosterol via Koenigs-Knorr synthesis. Its thermotropic liquid crystalline properties were investigated using polarizing microscopy. It was found that, this glycolipid has hexagonal columnar phase.

Materials and methods

D-glucose was purchased from Seelze-Hannover Ltd. and β-sitosterol was purchased from Koch-Light Laboratories Ltd. All reagents used were of Analar grade. Identification of the optical texture was done using a polarizing light microscope and the determination of phase transitions was done using a temperature controller.

Synthesis of β-D-glucose pentaacetate

A mixture of D-glucose (10 mmol, 1.8 g) and acetic anhydride (60 mmol, 5.75 cm^3) was stirred at 0 °C while adding one drop of sulphuric acid in 5 cm^3 of acetic anhydride. Dichloromethane (50 cm^3) was added, stirred for three hours and the dichloromethane layer was removed using a separating funnel. The crude product (2.170 g, 55.69%) was obtained after washing, drying and evaporating the organic extract. Finally, the residue obtained was recrystallized from ethanol (1.675 g, 42.95% , m.p. 85-105 °C).

Synthesis of Tetra-O-acetyl-β-D-glucopyranosyl chloride

β-D-glucopyranose pentaacetate (5 g) was reacted with crushed anhydrous aluminium chloride (1.8 g) in chloroform. Dry benzene (50 cm^3) and dry silicic acid (1.25 g) were added, filtered and the precipitate was washed with benzene (6.25 cm^3). The product was recrystallized using a 1:1 mixture of ether and pet ether. (1.200 g. 25.44%, m.p. 93-95 °C).

Synthesis of β-sitosteryl-2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside

β-sitosterol (2.180 g), tetra-O-acetyl-β-D-glucopyranosyl chloride (1.105 g), finely powdered silver oxide (0.75 g) and powdered anhydrous calcium sulphate (1.25 g) in ether were stirred for 24 hrs at room temperatrue. The solids were removed by filtration and ether was evaporated. Washing with cold methanol yielded pure β-sitosteryl-2,3,4, 6-tetra-O-acetyl-β-D-glucopyranoside in the crystalline form (0.766 g, 33.6%, 131.7 °C). The product was checked for mesogenic properties.

Synthesis of β-sitosteryl-β-D-gluco-pyranoside

β-sitosteryl-β-D-glucopyranoside was synthesized by the deacetylation of β-sitosteryl-2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside using excess sodium methoxide in methanol and dichloromethane (1:1, 2.5 cm^3). The product (0.056 g, 72.72%) was checked for mesogenic properties.

Results and discussion

In a thin liquid crystal sample placed between two crossed polarizers under an optical microscope, a variety of textures and

birefringence colors can be observed. A thermotropic hexagonal columnar phase was observed on cooling β-sitosteryl-2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside, after it was heated to melt (Figure 1).

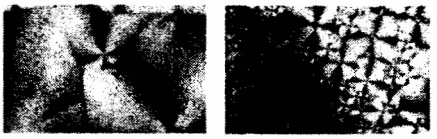

Figure 1. Texture of β-sitosteryl-2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside in the thermotropic hexagonal columnar mesophase under crossed polarizer and analyzer

The compound β-sitosteryl-2, 3, 4, 6-tetra-O-acetyl-β-D-glucopyranoside started to melt at 131.7 °C. When cooling, it started to solidify at 127 °C forming the hexagonal columnar phase. This texture was clearly observed when the temperature was around 28 °C.

Although the compound appears to be solid at room temperature, it can exist in the liquid crystalline phase due to super cooling on the cooling cycle, and the transition from the anisotropic liquid crystalline phase to crystalline solid may occur below ambient temperature.

This molecule consists of a rigid moiety which is also called as mesogenic core (sugar group) to which several flexible alkyl chains are connected. Such kind of molecules have the ability to form discotic liquid crystals which can be stacked into columns (Figure 2). According to the texture obtained under polarizing light microscopy, the compound synthesized in this study seems to arrange in a hexagonal array forming hexagonal columnar phase.

Figure 2. Schematic diagram of side view of the 2D array of hexagonal columnar mesophase

Conclusions

The glycolipid synthesized via Koenigs-Knorr synthesis has thermotropic liquid crystalline properties.

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