LIQUID CRYSTAL BEHAVIOR OF AN ETHYL HEXANOYL GLUCOFURANOSE DERIVATIVE

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Introduction

Amphiphilic carbohydrate derivatives exhibit liquid crystalline behavior as the carbohydrates can be substituted relatively easily with non polar alkyl chains. The alkyl chain can be linked directly to the carbohydrate via an ether, ester, amine or glyceryl linkage. In the present study, a carbohydrate liquid crystal was synthesized by the selective acylation of the 1,2 : 5,6-di-O-isopropylidene-D-glucofuranose with an acylating agent 2-ethylhexanoyl chloride to yield a product which formed thermotropic hexagonal columnar phase liquid crystals. The structure was characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and GC-MS. The mesomorphic behavior was studied using polarized optical microscopy, differential scanning calorimetry and X-ray diffraction technique.

Materials and Methods

All the reagents used were commercially available and the solvents were purified by distillation and dried with anhydrous magnesium sulphate before use. IR spectra were recorded on a FTIR spectrophotometer using KBr pellets. The structures of all the products were confirmed by NMR spectroscopy (300 MHz Varian VTR-300 spectroscopy. GC-MS values were recorded by Varian VA-5MS (Varian 3800 Gas chromatograph-detector-Varian Saturn GC/MS/MS 2000). Identification of optical texture was carried out using a polarizing optical microscope. Thermo microscopy was performed by connecting the polarizing microscope to a temperature control unit (CHINO). X ray diffractometer D-500 (SIEMENS) was used to determine the layer spacing; 2θ range from 2.0^0 to 7.0^0 at 1.5406 A^0 wavelength. Quantitative thermal analysis was performed using a Perkin Elmer PC Series DSC 7.

Synthesis of 1,2 : 5,6-di-O-isopropylidene-D-glucofuranoside (diacetone glucose)

1,2:5,6-di-O-isopropylidene-D-glucofuranoside (diacetone glucose) was synthesized according to a previous study carried out by Widanapathirana, *et al.*,(2007). Yield; 3.07 %. mp; 103-107 ^{0}C. (*Lit.* mp; 106-110 ^{0}C). IR (KBr): ν_{max} 3433 cm^{-1} (-OH).

Synthesis of 3-O-2-ethyl-hexanoyl-1,2:5,6-di-O-iso propylidene -D-glucofuranoside (EHIG)(Figure 1(c))

Diacetone glucose (200.2 mg) was dissolved in dry pyridine (6 mL) and was cooled to 0 ^{0}C. This was reacted with 2-ethylhexanoyl chloride (0.20 mL) at 0 ^{0}C for 4 h and allowed to stand at room temperature overnight. A few pieces of ice were added and

stirred well. The contents were extracted with chloroform (3 x 15 mL). The combined chloroform layers were washed with dilute hydrochloric acid, followed by saturated aqueous sodium hydrogen carbonate and finally with distilled water and was dried over anhydrous magnesium sulphate and evaporated to give the crude extract. This was then purified by column chromatography using hexane and ethyl acetate as the solvent system and further purified by recrystalizing with hexane to give the desired product. Yield; 85.92 %, mp; 80-100 ^{0}C. IR(KBr); ν_{max} 2933 cm^{-1}, 1707 cm^{-1}, 1008-1376 cm^{-1}, 794 cm^{-1} . 1H-NMR; δ_H ppm 5.93 (1H, d), 4.53 (1H, dd), 4.35 (1H, dd), 4.32 (1H, dd), 4.15 (1H, dd), 4.05 (1H,dd), 3.98 (1H,dd), 2.27 (1H, m), 1.62 (2H, m), 1.56 (2H, m), 1.51, 1.49, 1.46, 1.43 (4 x 3H:4 x s), 1.36 (2H, m), 1.31 (2H, m), 0.95 (3H, t), 0.88(3H, t). GC-MS ; m/z - 346, 239, 125, 96, 69.

Synthesis of 3-O-2-ethyl-hexanoyl-D-glucopyranose by the deprotection of EHIG

EHIG (80.0 mg) was heated with trifluoroacetic acid (1.10 mL) in a mixture of isopropanol/water (95/5 v/v) in a round bottomed flask immersed in a hot water bath maintained at 40-50 ^{0}C for one hour with intermittent shaking. Solvent isopropanol was evaporated under reduced pressure. Hot water (2.50 mL) was added to the obtained syrup and neutralized with solid sodium hydrogen carbonate. The solution was filtered and heptane (5.00 mL) was added and heated until two clear layers were obtained. The aqueous layer was separated and concentrated under reduced pressure. The colorless semi solid obtained at low temperature turned into liquid at ambient temperature.

Results and Discussion

Liquid crystals can be studied with a polarizing light microscope where characteristic textures and birefringence colors are displayed. The textures displayed by liquid crystals are often used for a preliminary characterization of the mesophase type.

In both diacetone glucose and EHIG, the well defined extinction brushes appeared between crossed polarizes. The white color brushes were seen in diacetone glucose, EHIG was observed as brushes with various colors.

These extinction brushes are characteristic of the hexagonal columnar phase as well as smectic phase. Here two types of defects can be observed. In both smectic and hexagonal columnar phases, the ends of all four brushes point to the center of flower like domain. The second type of defect is significant for hexagonal columnar phases, where the two pairs of brushes do not contact at the central point. Both defects were observed in, diacetone glucose and EHIG.

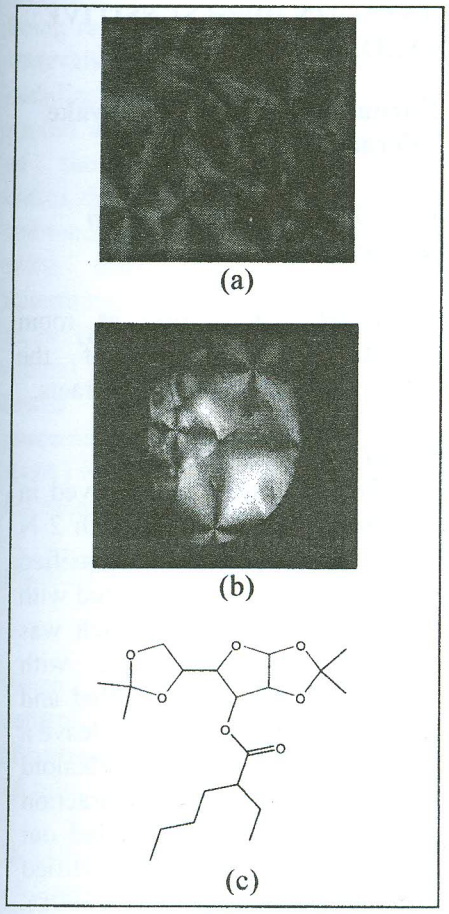

Figure 1. Texture of thermotropic hexagonal columnar phase of a) diacetone glucose b) EHIG at ambient temperature under crossed polarizing microscope. c) Chemical structure of 3-O-2-ethylhexanoyl-D-glucopyranose

For EHIG, X-ray analysis in the small angle region, one sharp reflection peak corresponding to the d spacing of 41.2804 A^0 was observed at 2θ = 2.138, from X-ray analysis which suggests the layered structure. DSC heating scan for EHIG showed melting point range at 80-100 ^{0}C. The clearing point was observed at 100 ^{0}C. Phase transitions were observed at 60-65 ^{0}C. Upon cooling from the isotropic state fan like textures were formed in between 45-65 ^{0}C.

Conclusion

Textures of both diacetone glucose and EHIG belong to hexagonal columnar liquid crystal phase.

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References

Widanapathirana, L. S., Liyanage, G. L. A. D., Karunaratne, D. N., Perera, A. D. L. C. (2007). Synthesis and characterization of two carbo-hydrate derived liquid crystals. p.48. In: National Conference on Advanced Materials for Emerging Technologies, Peradeniya, Sri Lanka.