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Effect of the C-2 hydroxyl group on the mesomorphism of alkyl glycosides: synthesis and thermotropic behavior of alkyl 2-deoxy-D-*arabino*-hexopyranosides

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ABSTRACT

A homologous series of alkyl 2-deoxy-α-D-*arabino*-hexopyranosides and alkyl 2-deoxy-β-D-*arabino*-hexopyranosides were synthesized, upon glycosylation of 1-alkanols (from C_8 to C_{18} alkanols) with ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-D-*arabino*-hexopyranoside, followed by a deprotection. The thermotropic behavior of these new types of alkyl glycosides was investigated. It was observed that the β-anomers of these alkyl glycosides, bearing nonyl to tetradecyl alkyl chain are mesomorphic, exhibiting monotropic smectic A phase. In contrast, the α-anomers are all non-mesomorphic. An effort to identify the liquid crystalline behavior of binary mixtures of the α- and β-anomers was undertaken and it was found that mixtures containing equimolar amounts of the anomers exhibited mesomorphic behavior. A fine balance of the hydrophilic and hydrophobic components within the molecule is also found to be important for the alkyl 2-deoxy glycosides to form the mesophase.

1. Introduction

Amphiphilic sugars are known to exhibit liquid crystalline behavior owing to their amhiphilicity (van Doren et al., 2000; Vill and Hashim, 2002; Jeffrey, 1986; Paleos and Tsiourvas, 1995; Goodby et al., 1998, 2007; Tschierske, 1998). Cell membrane bound glycolipids are examples *par excellence* of the lyotropic behavior of the amphiphilic sugars and their importance in biological functions (Abraham and Pascher, 1997; Wolken and Brown, 1980). A driving force for the mesophase formation in these molecules is the phase segregation, leading to aggregates, possessing distinct lipophilic and hydrophilic regions (Boullanger, 1997; van Doren and Wingert, 1994). Amphiphilic sugars possess an abundance of chiral centers and their liquid crystalline phases are generally smectic or columnar and/or cubic phases (Molinier et al., 2003, 2006, 2007). The absence of macroscopic chirality in the amphiphilic sugars and glycolipids could be attributed to the strong hydrogen bonding network between the hydroxyl groups of the sugar moiety, which force a layering with head to head arrangement of the molecules. It was shown recently that features that affect hydrogen bonding network can lead to the formation of chiral mesophases in sugar-based bolaamphiphiles (Abraham et al., 2005; Das et al., 2008).

Hexdecyl β-D-glucopyranoside is an early example of the glycolipids exhibiting liquid crystalline properties (Fischer and Helferich, 1911; Noller and Rockwell, 1938). The homologous series of both alkyl α-D-glucopyranosides and alkyl β-D-glucopyranosides exhibit the smectic A (SmA) phase and the SmA to isotropic transition temperature increases with increasing alkyl chain length (Goodby, 1984; Pfeffer et al., 1976; Jeffrey and Bhattacharjee, 1983). With detailed information available currently on the mesomorphic behavior of only the normal alkyl glycosides, it is pertinent to investigate the mesomorphic behavior on alkyl glycosides that lack one or more hydroxyl group in their hydrophilic sugar component. This report presents the results of the studies on alkyl glycosides, wherein 2-deoxy sugar constitutes the hydrophilic segment. Several homologues of the alkyl α-D-*arabino*-hexopyranosides and alkyl β-D-*arabino*-hexopyranosides series are synthesized and the thermotropic behavior of these new alkyl glycosides is assessed with the aid of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

2. Results and discussion

2.1. Synthesis

The synthesis of alkyl 2-deoxyglucosides was initiated from ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-D-*arabino*-hexopyranoside (Paul and Jayaraman, 2004). The alkyl 2-deoxyglucosides were

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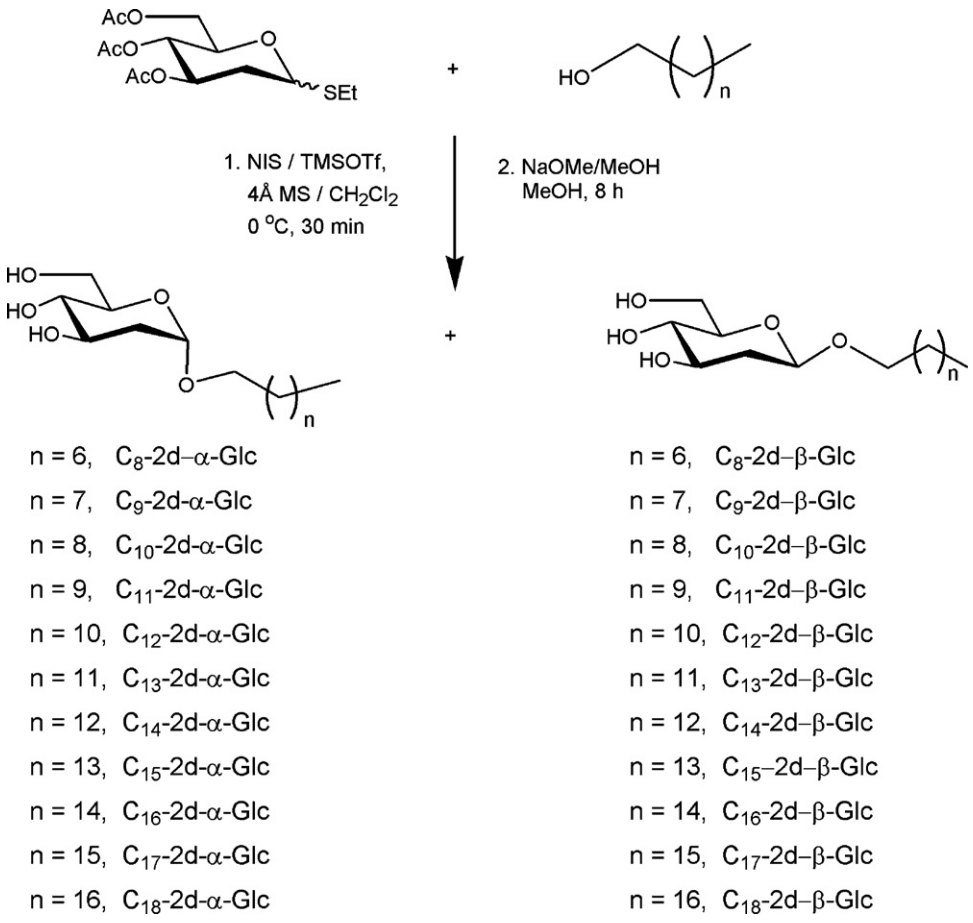

Scheme 1. Synthesis of alkyl 2-deoxy-D-*arabino*-hexopyranosides (C_n-2d-α/β-Glc).

prepared by the glycosylation of 1-alkanols with the above glycosyl donor in the presence of *N*-iodosuccinimide (NIS)/trimethylsilyl trifluoro-methanesulfonate (TMSOTf), followed by the deprotection of the acetate protecting groups (Scheme 1). The glycosylation led to almost equal amounts of both the α- and the β-anomers. The alkyl 2-deoxy-α- and β-D-*arabino*-hexopyranosides (C_n-2d-α-Glc and C_n-2d-β-Glc) were characterized by physical methods to confirm their constitutions.

2.2. Thermal behavior

The mesomorphic behavior of these new alkyl glycosides was investigated by POM and DSC techniques. Among the alkyl 2-deoxy-β-glucosides (C_n-2d-β-Glc), compounds C_9–C_{14} (n = 9–14) exhibited a monotropic SmA phase. Upon slow cooling from the isotropic state, a fan-shaped texture was observed (Fig. 1). When the sample exhibiting the undisturbed fan-shaped focal conic pattern was pressed, a near complete homeotropic alignment was observed, thereby suggesting the texture to be a SmA phase. The observed SmA texture is seen commonly for the sugar mesogens (Gray and Goodby, 1984; Zur et al., 1998; Jayaraman et al., 2007). The compounds C_9-2d-β-Glc, C_{11}-2d-β-Glc and C_{13}-2d-β-Glc exhibited an endothermic peak in the heating cycle and two exothermic peaks in the cooling cycle. The higher temperature peak corresponded to the I–SmA transition, whereas the low temperature peak in the cooling cycle was due to the SmA–Cr transition. A representative DSC thermogram is shown in Fig. 2. The even numbered compounds C_{10}-2d-β-Glc, C_{12}-2d-β-Glc and C_{14}-2d-β-

Fig. 1. The fan-shaped texture of the SmA phase obtained upon slow cooling of the isotropic liquid of C_{13}-2d-β-Glc (left) and binary mixture C_{12}-2d-α,β-Glc (1:1) (right).