Cholesteryl and Diosgenyl Glycosteroids: Synthesis and Characterization of New Smectic Liquid Crystals

Rémi Beaulieu, Sébastien Gottis, Claire Meyer, Eric Grand, Virginie Deveaux, José Kovensky, Imane Stasik

PII: S0008-6215(14)00436-4
DOI: http://dx.doi.org/10.1016/j.carres.2014.11.020
Reference: CAR 6902

To appear in: *Carbohydrate Research*

Received Date: 16 July 2014
Revised Date: 18 November 2014
Accepted Date: 22 November 2014

Please cite this article as: Beaulieu, R., Gottis, S., Meyer, C., Grand, E., Deveaux, V., Kovensky, J., Stasik, I., Cholesteryl and Diosgenyl Glycosteroids: Synthesis and Characterization of New Smectic Liquid Crystals, *Carbohydrate Research* (2014), doi: http://dx.doi.org/10.1016/j.carres.2014.11.020

Cholesteryl and Diosgenyl Glycosteroids: Synthesis and Characterization of New Smectic Liquid Crystals

Rémi Beaulieu[a,b,d], Sébastien Gottis[a], Claire Meyer[c], Eric Grand[a,b], Virginie Deveaux[d], José Kovensky[a,b] and Imane Stasik*[a,b]

[a]Laboratoire de Glycochimie, des Antimicrobiens et des Agro-ressources (LG2A), CNRS FRE 3517, 33 rue Saint-Leu, 80039 Amiens, France
[b]Institut de Chimie de Picardie FR 3085, Université de Picardie-Jules Verne, 33 rue Saint-Leu, 80039 Amiens, France
[c]Laboratoire de Physique des systèmes complexes EA 4663, Université de Picardie-Jules Verne, 33 rue St Leu, 80039 Amiens, France
[d]Semences, Innovation, Protection, Recherche et Environnement (SIPRE), rue des Champs Potez, 62217 Achicourt, France

Abstract

While present in large numbers in nature, studies on the physical chemical aspects of glycosteroids are quite rare and focused on cholesterol, and all compounds studied thus far have shown liquid crystalline properties in a narrow temperature range. New glycosteroids composed by cholesterol or diosgenin and different glycosidic moieties have synthesized here in order to analyze the influence of the structure on the formation of mesophases. These compounds have been studied by crossed polarized optical microscopy. These studies have revealed that these new glycosteroids form Smetic A liquid crystals in a broad temperature range. © 2014 Elsevier

Keywords: Glycolipids; Cholesteryl glycosteroids; Diosgenyl glycosteroids; Synthesis; Characterization; Liquid crystals; Smectic A phase.

In the last two decades, much attention has been devoted to the liquid-crystalline properties of glycoamphiphiles.[1-9] Liquid-crystalline carbohydrates substituted with alkyl chains attached by ester, ether or thioether linkages have been previously reported,[8-14] however thermal data for complete homologous series are rare.[7, 8, 15-17]

The chemical structures able to form mesophases are quite numerous, and glycolipids are a class of amphiphilic compounds extensively studied for their mesomorphic properties in recent years by different researchers,[18] including our laboratory.[19] On the other hand, it is well known that some steroid derivatives (such as cholesteryl esters) also possess liquid-crystalline properties.[20, 21]

Glycosteroids also show mesomorphic properties. Among them, solanine (one of the two glycoalkaloids of potato) has a Smectic A (SmA) phase between 260 and 295 °C.[22] Goodby and Queneau have reported the synthesis of cholesteryl derivatives on which mono or disaccharides were grafted through an amide bond. In this work, the formation of liquid-crystalline phases reveals to be allowed with both configurations, either R or S, on the asymmetric carbon in position 3 of the steroid.[23, 24] They also examined two compounds with a longer spacer arm: a glucose derivative and a cellobiose derivative (a disaccharide), which possess a short aliphatic chain between the saccharide unit and the steroidal moiety. A second non-bridging aliphatic chain, of a defined length, was attached to the sugar unit. The obtained results allowed the authors to conclude that this derivative with a long spacer arm exhibits a lamellar phase.[23] Finally, they emphasized the importance of the spacer arm between the aglycone and the saccharide counterparts. When the sugar was directly grafted to the aglycone, no liquid-crystalline properties were observed.[25, 26] The insertion of a short spacer arm (one to four atoms) resulted in glycosteroid mesophases around 200 °C and a temperature range of about 40 °C. However, the products tend to decompose at these temperatures.

We synthesized twelve new glycosteroids by coupling D-glucose, D-galactose or L-rhamnose to cholesterol or diosgenin, as candidates for liquid-crystalline studies. First, the 3-OH of the steroid was substituted by a three carbon-atom spacer bearing an azido group (compounds **1** and **2**). Then, they were coupled to propargyl or 1-*S*-propargyl glycosides by click chemistry (copper catalyzed azide-alkyne cycloaddition, CuAAC), to afford the glycosteroids **3**-**14** (Scheme 1).[27]

Corresponding author. Tel.: +33 322827566; fax: +33 322827560. E-mail address: imane.stasik@u-picardie.fr (I. Stasik).