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Synthesis of Glycosides Bearing Chalcone Derivatives *via* Ferrier Rearrangement

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Abstract : A series of glycoside derivatives bearing chalcones moieties has been synthesized. A convenient synthetic method was performed from the reaction of 3,4,6-tri-O-acetyl-D-glucal with *(E)*-1-(4-alkyloxyphenyl)-3-(4-hydroxy-phenyl)prop-2-en-1-one **(2a-2c)** employing O→C rearrangement to afford *C*-glycoside **4a-c** over prolonged reaction times, in the presence of $BF_3.OEt_2$ as a catalyst. The compounds differ in the length of alkyl groups, $C_nH_{2n+1,}$ where n= 7, 8 and 9.

Keywords: glycosylation, chalcones, glycosides, O→C rearrangement

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Introduction

Glycosides are found abundantly in nature and serve many important roles in living organisms.[1,2] Plants usually store chemicals in the form of inactive glycosides which are activated by enzyme hydrolysis. Naturally occurring glycosides commonly show high potential as antibiotics. There are a wide range of glycoside antibiotics isolated from natural products.[3]. For many years, numerous research have been devoted to the total synthesis of *C*- and *O*-glycoside antibiotics, such as erythromycin A, amphotericin B, olivomycin A, urdamycinone B, vancomycin and digitoxin.[4] Besides, glycosides are also increasingly utilized in the synthesis of non-carbohydrate compounds and carbohydrate mimetics.[5] Glycosides have also been synthesized for liquid crystalline materials. Over the past years, tremendous attention has been dedicated to research on the synthesis of glycoside derivatives and studies on the application for liquid crystal properties.[6-8]

Ferrier rearrangement, on the other hand, is an attractive methodology for the synthesis of glycoside derivatives with various alcohols. It is an efficient reaction for the substitution at the anomeric position with allylic rearrangement.[9,10] The Ferrier rearrangement involves the addition of nucleophile onto the intermediate allylic oxycarbenium ion, preferentially in a quasi-axial orientation.[9] This rearrangement leads to the formation of alkyl and aryl 2,3-unsaturated-*O*-glycosides, which are versatile chiral intermediates in the synthesis of several biologically active natural products.[9,10] 2,3-unsaturated-*O*-glycosides are also important building blocks in the synthesis of some antibiotics.[9]

Recently, we reported on the preparation of Lewis acid-promoted allylic rearrangement of 3,4,6-tri-O-acetyl-D-glucal with 4-hydroxybenzaldehyde and aliphatic alcohols with different type of catalysts in different solvents.[11] This prompted us to study the reaction of glycoside bearing chalcone derivatives *via* Claisen-Schmidt condensation of aldehyde and acetophenone. Chalcone derivatives were reported to have outstanding non linear optic properties for optical electronics and communications[12], liquid crystal displays[13,14] and alignment film[15]. Chalcones were also reported to promote excellent blue light transmittance and good crystallability,[16,17] high photosensitivity and thermal stability for various crystalline electro-optical devices.

We herein report the synthesis of new glycosides bearing hydroxylated chalcone **(2a-c)** which differ in the length of the alkyl groups ranging from C7 to C9. This study could be used as a reaction model for potential liquid crystals compounds.

Results and Discussion

The series of chalcone derivatives (*E)*-1-[4-(alkyloxy)phenyl]-3-[4-hydroxyphenyl] prop-2-en-1-one **(2a-2c)** were prepared *via* Claisen-Schmidt condensation of **1a-1c** and 4-hydroxybenzaldehyde by the route depicted in Scheme 1.