Structure-reactivity study of electroactive alkyl *S*-glycoside glycosyl donors

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Introduction

The sophisticated biological functions of glycans have stimulated the development of novel synthetic methods to efficiently access complex saccharide architectures. Transition metal and enzyme catalysis have widely been exploited to develop novel synthetic strategies. However, little attention has been given to electrosynthetic methods in carbohydrate chemistry. We have centered our attention to the electrochemical activation of alkyl *S*-glycoside glycosyl donors as a strategy to construct glycosidic bonds. Herein, we present our preliminary results of the structure-reactivity study of a series of protected alkyl-S-glycosides.

Study Objective

To understand the molecular features modulating the reactivity of alkyl S-glycosides to electrochemical activation.

Main Finding.

We have synthesized a series of five alkyl glycosides substituted with aglycone alkyl groups of varied volume. Compounds were prepared by direct glucosylation of the respective mercaptans using glucose *per*-acetate (**1**) as donor activated by a Lewis acid. The oxidation potentials of each substrate were determined from the half-peak potential ($E_{p/2}$) in the respective cyclic voltammogram. We observed a dependency of $E_{p/2}$ with the degree of substitution of the aglycone alkyl group where $E_{p/2}$ progressively moves to more positive potentials as the size of the aglycone increases. Compounds with small alkyl groups exhibit lower $E_{p/2}$, meaning that these types of substrates are more reactive (armed) to electrochemical activation compared with the bulky (disarmed) counterparts. The correlation of $E_{p/2}$ with the Taft steric parameter of the aglycone substituent suggests the contribution of steric effects to the electrochemical reactivity in these substrates.

Figure 1: CV of alkyl *S*-glycosides

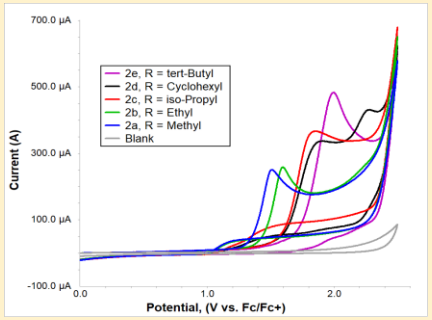
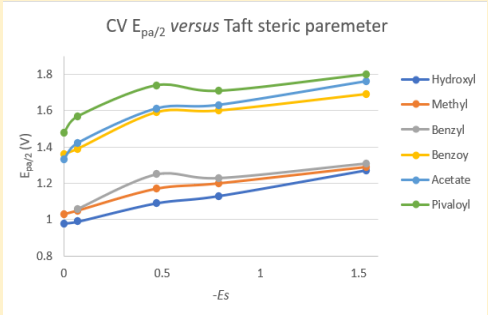


Figure 2: Correlation of $E_{p/2}$ with aglycone volume



Conclusions

The voltametric study of a series of alkyl *S*-glycosides shows a dependency of the oxidation (activation) potential with the size of the aglycone substituent.

Acknowledgements

We thank the Department of Pharmaceutical Sciences and the Office of Sponsored Research for the continuous support of this work.