

ESOC 2019

21st European Symposium on Organic Chemistry







KINETIC QUANTIFICATION OF ALDOSE OPEN-CHAIN CONTENT

Hubert Kalaus, Alexander Reichetseder, Christian Stanetty* and Marko D. Mihovilovic

Institute of Applied Synthetic Chemistry, TU Wien, 1060 Vienna, Austria

Within our research we aim to translate the ever-expanding repertoire of aldehydemethodology chemistry to Nature's most prominent, yet, in most studies scorned representatives: aldoses. In most sugars, the cyclic lactol form dominates with only minute amounts being present as open-chain (aldehyde) species. Consequently reactions of sugars acting as aldehydes occur significantly slower than usual and sidereactions can become favored, thus in the case of unstable reagents incomplete or complete lack of conversion can be observed.

So far, an efficient tool for the quantification of aldoses' open chain-contents (OCC) was missing, with previously established methods relying on NMR-analysis of [1-¹³C]-enriched sugars [1] or long-time (up to years) kinetic measurements [2].

Herein, we now demonstrate a photometric kinetic assay for the quantification of OCCs exploiting the fast and irreversible adduct-formation of aldehydes and 2-aminobenzoamidoxime [3]. The kinetic curves of the adduct formation of all parent C4-C6 aldoses were determined, which suggested two separate families depending on the relative 2,3-configuration (*erythro* and *threo*). The derived OCCs proved to be in consistence with literature data with our approach significantly outperforming aforementioned methods in respect to reduced measurement times (hours) and ease of operation. Furthermore, a first real case example will be presented; that of 2,3-isopropylidene protected L-erythrose which did by no means undergo indium mediated acyloxyallylation in vast contrast to its unprotected very reactive counterpart. Utilizing our assay, relative OCC and respective aldehyde reactivity could be deduced for the unreactive species in a few straight-forward measurements [4].

The developed assay will prove a valuable tool in future projects, where the availability and reactivity of the aldehyde moiety in sugar molecules has to be addressed.

SYNTHESIS OF

Guillaume Erb

^aCEMES, U
^bDivision of Ma

In a context of ultimastering their control

Following a bottom-udesigned and symmolecular motors, to single molecule scal Microscopy (STM) [1] based organometallidissymmetric rotating undergo unidirection excitation, with a direby the location of the

Our next aim is to transfer of rotary mo molecules, so as to pr molecular gears. W penta(aryl)cyclopenta carbazole, BODIPY o

The multi-step synthetic focus on the method synthesis of the thioet

One-pot
N-deprotection / reductive so

^[1] Y. Zhu, J. Zajicek and A. S. Serianni, J. Org. Chem., 2001, 66, 6244-6251.

^[2] J. P. Dworkin and S. L. Miller, Carbohydr. Res., 2000, 329, 359-365.

^[3] P. I. Kitov, D. F. Vinals, et al., J. Am. Chem. Soc., 2014, 136, 8149-8152.

^[4] M. Draskovits, C. Stanetty, et al., J. Org. Chem., 2018, 83, 2647-2659.

^[1] Kammerer, C.; Rapen

^[2] Rapenne, G.; Joachim

^[3] Erbland, G.; Gisbert,