KINETIC QUANTIFICATION OF ALDOSE OPEN-CHAIN CONTENT

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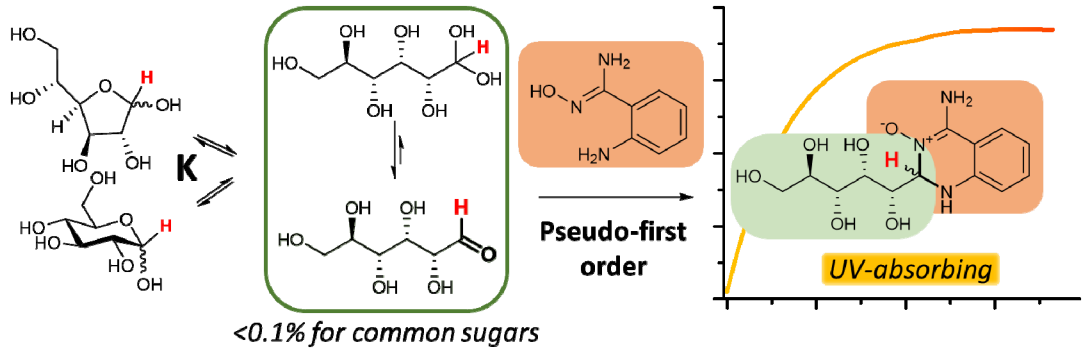
Within our research we aim to translate the ever-expanding repertoire of aldehyde-methodology chemistry to Nature's most prominent, yet, in most studies scorned, representatives: aldoses. In most sugars, the cyclic lactol form dominates with only minute amounts being present as open-chain (aldehyde) species. Consequently, reactions of sugars acting as aldehydes occur significantly slower than usual and side-reactions 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-^{13}C]-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.

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[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.