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Iron Homogenous Catalysis for Upgrade of local Agricultural waste: Selective Oxidation of unprotected Monosaccharides from Sugar Beet Pulp.

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PURPOSE OF THE ABSTRACT

The Région Normandie Ranks as one of the leading providers on the French sugar beet market, mostly used for saccharose and bioethanol production,[1] with 29 000 hectares of crop and 7.5% of the total national surface production.[2] The process of saccharose extraction produce sugar beet pulp as waste mainly used for animal feed, biogas production through methanisation or as insulation material for building construction.[3] However, this waste is still underexploited for high added value compounds production such as bioactive molecules.[2]

After hydrolysis, Sugar beet pulp is a carbohydrate-enriched biomass containing a large number of unexploited monosaccharides such as glucose, arabinose, galacturonic acid. The aim of this project is the valorisation of these monosaccharides into a variety of chiral and poly-functional molecules such as iminosugars using a hybrid catalysis cascade using transfer hydrogenation (organometallic) and transaminase (biocatalysis). The main challenge of this strategy is to start from unprotected carbohydrates in order to avoid the tedious and wasteful use of protecting group.

Our first step was the development of a new catalytic and eco-friendly method for the oxidation of unprotected carbohydrates using iron as earth abundant inexpensive metal, in contrast to the classical strategies employing toxic stoichiometric reagents[4], precious metals, halogens derivatives[5] or bases[6] with conditions incompatibles with green chemistry principles or sensitives substrates. Even though, transition metal catalysed oxidation of unprotected carbohydrates have already been reported, they were only relying on the use of rare and precious metals, such as Palladium, Rhodium or Ruthenium.[7],[8],[9]

We have developed a base free iron-catalysed methodology for the oxidation of unprotected sugars employing mild conditions using a Knölker type iron catalyst which was either reported for the oxidation of secondary alcohols to form ketones or primary diols to form lactones.
Our conditions allow an efficient and selective anomeric oxidation of various unprotected carbohydrates leading to the corresponding lactones (5- and 6 ring membered lactones) using green solvents such as tert-butanol or acetone. All main components of sugar beet pulp were converted in high/quantitative yields in 5 to 24 hours and in the presence of 2.5 to 5%mol catalyst and were recovered without wasteful chromatographic methods.

Moreover, we were able to take advantage of the kinetic differences in the oxidation of hexoses and pentoses, to adjust the procedure and allow the selective oxidation of pentoses from a mixture of sugars. Thus, one

monosaccharide was selectively upgraded into a lactone while the others remain mostly untouched, allowing an easy ?separation? even from ternary mixtures.

In summary, we have developed an efficient, selective and green oxidative method for the conversion of unprotected monosaccharides into valuable lactones. Our approach is compatible with a wide range of monosaccharides, can be performed in solvents such as acetone or tert-butanol and in the latter simple acceptors like acetophenone, cyclohexanone, methyl pyruvate or methyl levulinate can be used.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

Iron catalysis | Unprotected carbohydrates | Transfer hydrogenation | Biomass conversion

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