

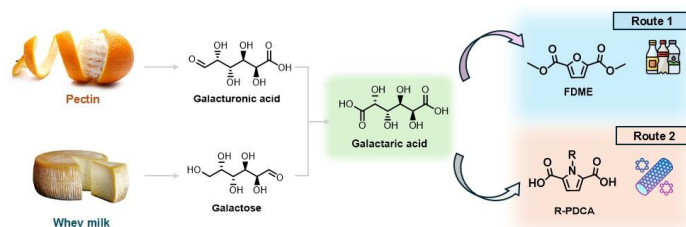
## Galactaric acid: an interesting molecule for the synthesis of furan and N-substituted pyrrole 2,5-dicarboxylic acids

<sup>1</sup> Davide Dalla Torre, <sup>1</sup> Giacomo Trapasso, <sup>1</sup> Marco Artuso, <sup>1</sup> Fabio Aricò

<sup>1</sup>Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Scientific Campus Via Torino 155, 30170 Venezia Mestre, Italy.  
Davide Dalla Torre: [davide.dallatorre@unive.it](mailto:davide.dallatorre@unive.it)

Within the biorefinery framework, the so-called bio-based platform chemicals play an important role and among them, aldaric acids are of particular interest.<sup>1</sup> A prominent member of this family is galactaric acid, first isolated from whey in 1826. Galactaric acid can be produced on a large scale through the oxidation of galacturonic acid, which is abundantly present in hemicellulosic polysaccharides such as fruit peel pectins.<sup>2</sup> Nowadays, galactaric acid is attracting increasing attention as a value-added biomass-derived chemical, as it represents a promising starting material for the synthesis of several platform molecules, including muconic acid, 2,5-furandicarboxylic acid (FDCA), and pyrones.<sup>3</sup> More recently, it has also been investigated as a precursor of nitrogen-containing heterocycles, such as pyrrole-2,5-dicarboxylic acids (PDCAs).<sup>4,5</sup>

From this premises, the present work focuses on two different procedures for the synthesis of 2,5-furandicarboxylic acid dimethyl ester (FDME) and a library of N-substituted PDCA derivatives starting from galactaric acid. In the first approach, a one-pot synthesis of FDME was developed using a commercial catalyst (Amberlyst-36) via dimethylcarbonate (DMC) chemistry. The reaction was carried out in an autoclave at 200 °C for 2 hours, affording FDME as a pure crystalline solid in 70% yield after a simple purification procedure. In the second approach, a fully optimized three-step procedure was established, enabling the high-yield synthesis of a library of PDCA derivatives from a 2-pyrone salt intermediate. A wide range of amines—including aliphatic amines, benzylamines, amino alcohols, and diamines—was successfully employed. All products were isolated without chromatographic purification and fully characterized. Compared to previously reported methods, this synthesis allowed a significant reduction in reaction times, improved yields at each step, and a successful scale-up of the process up to 100.0 g of galactaric acid.



**Figure 1.** Two different approaches for the application of galactaric acid

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