



## New one-pot syntheses of ketals and acetals from oleic acid



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### ABSTRACT

Ketals derived from unsaturated fatty acids, such as oleic acid (OA), are widely used as intermediates in the synthesis of various polymers, biologically active compounds and other high-value derivatives. We propose the study of new conditions for one-pot syntheses of ketals and acetals from oleic acid, using acetone or different alcohols as both reactant and solvent. OA was oxidized in a batch reactor in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) as an oxidant and a peroxo-tungsten anion supported on resin as the catalyst. We investigated the influence of several parameters of this process, using 9,10-dihydroxyoctadecanoic acid as the target molecule. The best operating conditions resulted in an OA conversion above 80%, with a good yield (60%) obtained for the OA/H<sub>2</sub>O<sub>2</sub>/[PO<sub>4</sub>{WO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>}<sup>3-</sup> system supported on a resin, at 70 °C for 16 h in acetone. The hydroxyl moiety was oxidized, generating the corresponding aldehyde derivative, when alcohols were used as the solvent.

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### 1. Introduction

Fatty acids are very interesting renewable platform molecules because they are cheap and available worldwide. The double bonds present on their hydrocarbon chain display specific reactivity, making it possible to synthesize a wide range of derivatives. Fatty acid derivatives can then be used to functionalize other building blocks, to produce high-value molecules. These derivatives include ketals, potentially interesting molecules, the uses of which have been widely described (Fig. 1). For example, a ketal derived from 9,10-dihydroxyoctadecanoic acid has been used to synthesize sterol derivatives, such as ester **A** (Julien-David et al., 2008). The molecules produced were found to have antiproliferative and apoptotic properties against cancer cell lines.

Furthermore, protected dihydroxy fatty acids, such as **B**, may be relevant starting materials for the synthesis of dendrimers (Leonard et al., 2010). Making use of the orthogonal protection of fatty acid derivatives, Kurawaki's team was able to obtain dendron-stabilized gold nanoparticles of potential value as candidates for the construction of drug delivery devices.

Fatty acid chains are also useful for modification of the physical properties of compounds such as phosphocholine **C** (Jaeger et al., 1997). Jaeger's group demonstrated that these polar substituents affect the *T<sub>c</sub>* values of phosphocholine bilayers and the sizes and population distributions of the derived vesicles.

The dihydroxylated fatty acid-based building blocks used in previous syntheses require protection, to control their reactivity. They are generally synthesized from oleic acid in a multistep process involving esterification of the carboxylic acid, dihydroxylation or epoxidation of the double bond, followed by the acetalization of the obtained oxygenated moiety (Fig. 2). Finally, the carboxylic acid functional group is regenerated and the fatty acid derivatives obtained are then grafted onto the chosen molecule.

The dihydroxylation of oleic acid and other olefins (styrene, cyclohexene) has been described, with supported catalysis, based on the oxidant OsO<sub>4</sub> supported on resin or silica (Choudary et al., 2003), or with the use of hydrogen peroxide as an oxidant in the presence of resin-supported sulfonic acid (Usui et al., 2003) or silica-supported sulfonic acid (Maggi et al., 2012) as a catalyst and without organic solvent.

The diol moiety can be acetalized in acidic conditions (perchloric acid (Wood, 1967), sulfuric acid (Jaeger et al., 1994), *para*-toluenesulfonic acid (Rufino et al., 2009)), which can be problematic for acid-sensitive compounds. These problems can be overcome by using zeolites, such as montmorillonite K-10 (Leonard et al., 2010), or mild acid resins, such as Amberlyst (Chandrasekhar et al., 2000). Other protocols involving the use of CuSO<sub>4</sub> (McCloskey and McClelland, 1965) or ZnCl<sub>2</sub> (Overs et al., 2002) have been

Abbreviations: AA, azelaic acid; AL, aldehyde; DI, diol; EP, epoxide; FAME, fatty acid methyl esters; KE, ketal; OA, oleic acid; PA, pelargonic acid; TBME, *tert*-butyl methyl ether; TMSH, trimethylsulfonium hydroxide; TPA, tungstophosphoric acid.

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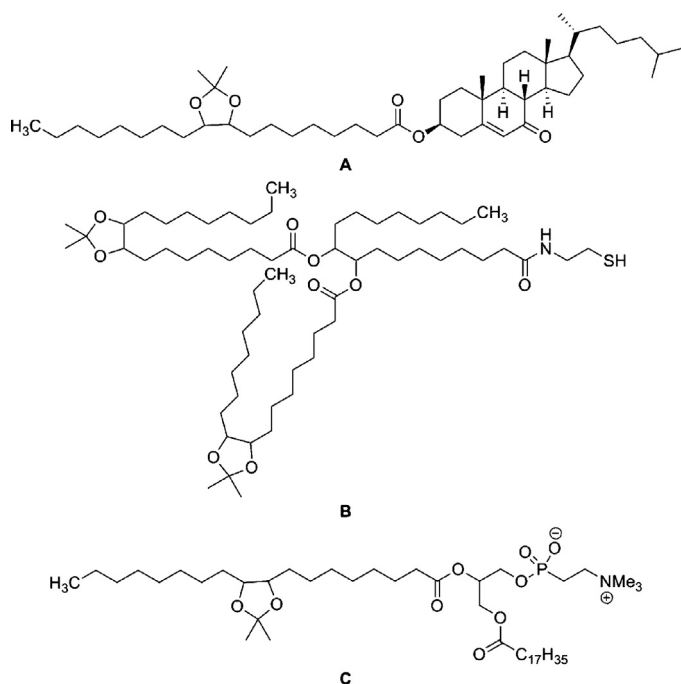


Fig. 1. Examples of molecules bearing protected diols derived from fatty acids.

described, but both these catalysts are highly toxic to aquatic organisms.

None of the published methods can really be described as “environmentally friendly”, as they use hazardous starting materials, in many reaction steps, involving low atom economy and the production of waste. We therefore aimed to develop a new one-pot process, generating the desired protected dihydroxy fatty acid directly from an unsaturated fatty acid, in a safer “greener” system. In the context of green chemistry, hydrogen peroxide is an ideal oxidant as it only produces water as waste. We therefore decided to develop new conditions combining the use of hydrogen peroxide as an oxidant and with a tungstophosphoric acid-based heterogeneous catalyst. In the resulting oxidative conditions, a diol would be formed, which would then react *in situ* with an appropriately chosen reactive solvent, to generate the desired ketal.

## 2. Materials and methods

### 2.1. Reagents

High oleic sunflower oil was purchased from Itegr (Pessac, France). Aqueous hydrogen peroxide (aqueous solution, 30%), tungstophosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ , TPA, reagent grade), tetrabutylammonium chloride ( $\geq 97\%$ ), ethyl acetate (technical grade), ethanol, propanol, benzyl alcohol, and *tert*-butyl methyl ether (TBME, reagent grade) were purchased from Sigma Aldrich

Co. *Candida cylindracea* lipase and trimethylsulfonium hydroxide (TMSH) were purchased from Lyven and Macherey-Nagel, respectively. Milli-Q water was obtained with a Milli-Q system (Millipore Corp.). Amberlite IRA 900 chloride-form resin and Lewatit K7367 chloride-form resin were purchased from Rohm & Haas and Lanxess, respectively.

### 2.2. Hydrolysis of high oleic sunflower oil

High-oleic sunflower oil (22.5 kg) was hydrolyzed with *Candida cylindracea* lipase in distilled water (20.1 kg) at 40 °C for 5 h, with stirring (Mouloungui and Melching, 2004). The fatty acid composition of the hydrolysate was determined by gas chromatography (GC), as described in Section 2.5 (w/w): 84.0% oleic acid, 4.3% linoleic acid, 3.2% palmitic acid, 2.1% stearic acid, and other fatty acids. This hydrolysate was used as the source material of oleic acid for all experiments.

### 2.3. Preparation of the heterogeneous catalyst

The commercial resin was dried in an oven at 60 °C for 24 h. The resin (10 g) was prepared in its  $\text{NO}_3^-$  form by incubation with  $\text{NaNO}_3$  (1 N, 50 mL), with stirring, for 3 h. The resin was filtered and washed with Milli-Q water (50 mL). It was then mixed with 50 mL of Milli-Q water and stirred for 30 min. The resin was washed twice in this way and then dried in an oven at 60 °C before immobilization of the catalyst.

We tested two catalyst immobilization methods:

- $\text{Q}_3$  fixing mode: Catalytic complexes  $[\text{n-Bu}_4\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$  were synthesized by a published procedure before the reaction (Pai et al., 2005). We dissolved 6 g of  $[\text{n-Bu}_4\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$  in 32 mL of acetone and 12.5 mL of 30%  $\text{H}_2\text{O}_2$  and 3.5 g of resin was added to the solution (Villa et al., 1999).
- TPA fixing mode: We prepared a solution of tungstophosphoric acid (TPA) in water (17.5 mL) and added the resin (3.5 g) to the solution.

In both cases, ion exchange was performed at room temperature for 16 h, with stirring. The solid was filtered, washed with Milli-Q water, Milli-Q water/acetone (50/50 vol%) and acetone. Finally, the resin was air-dried overnight at room temperature.

### 2.4. Synthesis and characterization of ketal (or acetal) from oleic acid

Typically, a 250-mL, three-necked, round-bottomed flask was loaded with 4.2 g (15.0 mmol) of OA (i.e. 5 g of the high oleic sunflower oil hydrolysate) and the heterogeneous catalyst. The solvent (ketone or alcohol, 25 mL) was added when the resin was fully impregnated. The reactor was equipped with a condenser, a mechanical stirrer and a thermocouple device. The reaction medium was heated at 60 °C and a 30% aqueous solution of  $\text{H}_2\text{O}_2$  (110.0 mmol) was added dropwise over the course of 1 min. The

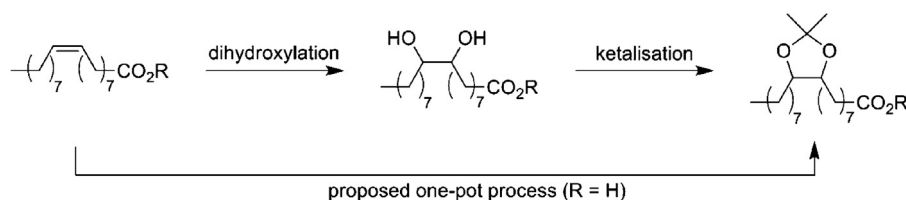


Fig. 2. Synthesis of ketal derived from oleic acid.

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