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Optimization of a multi-step enzymatic synthesis of lauryl(3-hydroxypropyl)-succinate, precursor for the synthesis of extended carbohydrate-based surfactants

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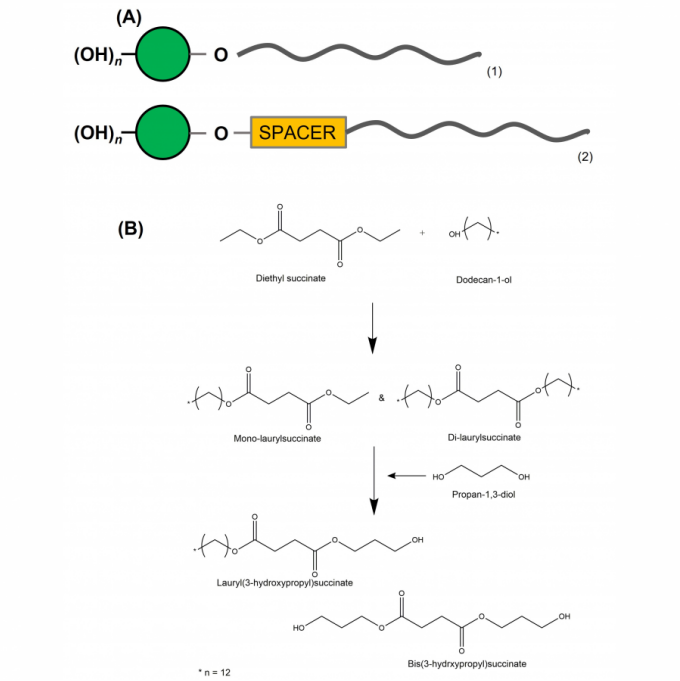
PURPOSE OF THE ABSTRACT

The actual worldwide need for a more sustainable and renewable consumption leads conventional chemistry to undergo profound changes to meet nowadays and future challenges, especially processes decarbonization. Biocatalyzed processes can fit with this purpose of more sustainable industrial processes [1], as in surfactant-producing industry. As example of “green” surfactants, non-ionic biobased fatty acid carbohydrate esters are used in multiple fields, such as cosmetics, food industry, and pharmacology and biocontrol [2]. These multi-applications have created a worldwide market for such bioproducts and consequently expectations for their production. As a reminder, a surfactant is generally composed of a polar part, a carbohydrate for example, a lipophilic moiety with in-between, but rarely, a spacer/linker conferring an additional property to the surfactant, such as improved amphiphilic properties and a lower CMC (critical micellar concentration) value (Figure 1) [3]. Beyond the surfactant aspects, add a spacer would allow to integrate molecular patterns to classical surfactants and thus create a molecule-application relationship, with for example Pathogen-Associated Molecular Patterns (PAMP). The present work, as a part of biocatalyzed synthesis of carbohydrate-based surfactants, deals with the selective conception of a spacer-lipophilic synthon in two steps. In a first phase, the purpose is to condense a fatty alcohol, dodecan-1-ol, onto succinic acid using a lipase as catalyst. Then, propan-1,3-diol is added to the reaction medium to react with the products obtained in the first step to obtain lauryl(3-hydroxypropyl)succinate (Figure 1). The reference synthesis is performed in 2-methylbutan-2-ol, at 56°C, under stirring (240 rpm) and using 1% (w/v) supported Aspergillus Niger lipase. The first step provides mono-laurylsuccinate and di-laurylsuccinate, with molar yields of 49% and 25%, respectively. A kinetic study shows that a maximum yield is obtained after only 2h reacting. Then, the addition of propan-1,3-diol allows to obtain the lauryl(3-hydroxypropyl)succinate. The decrease of monolaurylsuccinate ratio shows its conversion to the product, lauryl(3-hydroxypropyl)succinate, and thus the interest to favor its synthesis at the expense of dilaurylsuccinate (Figure 2). An optimization based-on reagent ratios variation, solvent and co-solvent ratios, reaction media water content, as well as enzymatic cocktails has been performed and reaction kinetics were controlled using liquid and gas chromatography. To summarize few results, different ratios were tested, with diethylsuccinate/dodecan-1-ol molar ratio ranging from 3/1 to 1/3. To maximize the formation of mono-laurylsuccinate and minimize di-laurylsuccinate, the ratio that gave the best yield is 1/2. A temperature effect study highlighted an optimal temperature of 56°C for supported Aspergillus Niger lipase and supported CalB (Novozym 435). Various solvents were tested. For example, 2-methyltetrahydrofuran-3-one, a biobased solvent, reduced the amount of di-laurylsuccinate produced but the yield of mono-laurylsuccinate decreased from 49% to 30%. The addition of water to the reaction medium also limits the formation to di-laurylsuccinate (Figure 2). For instance, with CalB, the addition of 0.5% (V/V) water increased the mono-laurylsuccinate/di-laurylsuccinate ratio from 2 to 4. We have therefore mapped various parameters and so we can propose a multi-step one-pot synthesis of lauryl(3-hydroxypropyl)-succinate in 4h, without treatment. We are now working on the grafting

lauryl(3-hydroxypropyl)-succinate onto carbohydrate using a β glucosidase, to implement an enzymatic cascade. Other parameters, such as the effect of bioprinting on monodispersity, are currently evaluated. At least, the impact of these optimizations on the recycling and reuse of enzymes will also be studied.

FIGURES



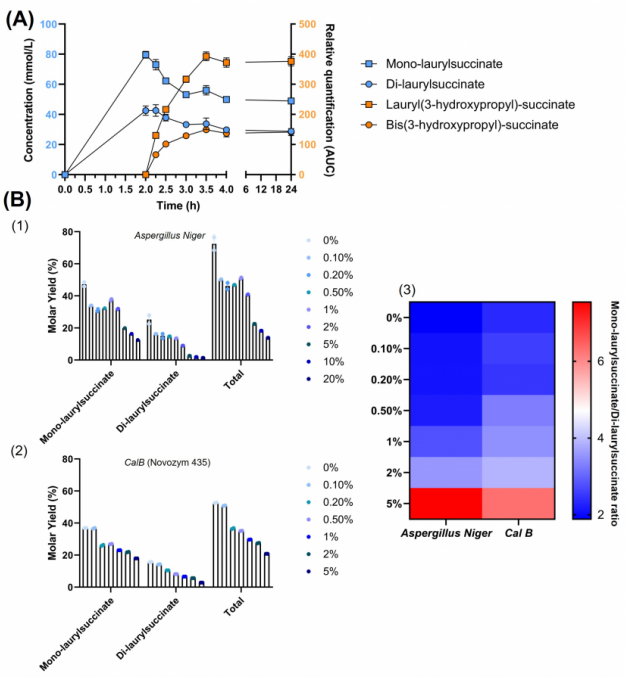


FIGURE 1

Synthesis pathway

(A) Classical structure of a surfactant (1), surfactant with spacer (2), with polar part in green, and lipophilic part in grey. (B) Synthesis pathway for lipase-catalyzed synthesis of lauryl(3-hydroxypropyl) succinate.

FIGURE 2

Kinetics study of formation and conversion of mono-laurylsuccinate and di-laurylsuccinate

(A) Kinetics study of formation and conversion of mono-laurylsuccinate and di-laurylsuccinate in mmol/L to lauryl(3-hydroxypropyl) in AUC.

(B) Evolution of yields obtained for the synthesis of mono-laurylsuccinate and di-laurylsuccinate according to varia

KEYWORDS

enzymatic cascade | multi-step | surfactant | spacer

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