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Review

Enzyme catalyzed synthesis of cosmetic esters and its intensification: A review

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ABSTRACT

The cosmetic industry is constantly trying to develop alternatives to chemical routes for synthesis because of an increased focus on environmental safety, sustainability, and increased awareness in the society regarding natural and chemical-free products. Biocatalysis shows a distinct advantage over the chemical route in terms of process simplification, quality of product, and reduction in waste formation. Lipases are the most commonly used enzymes for enzyme-catalyzed synthesis in the cosmetic industry because they have the ability to recognize a wide variety of substrates and catalyze a large number of reactions. The first half of the present article gives a brief overview of the role of biocatalysts in the synthesis of various cosmetic esters. The second half of the review points out the limitations of conventional biocatalytic synthesis of cosmetic esters and discusses the application of novel green techniques such as ultrasonication and microwave irradiation to address the drawbacks of the conventional enzymatic technique.

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1. Introduction

1.1. World cosmetic market

The global beauty market is generally divided into five major segments: skincare, hair care, color (makeup), fragrances, and toiletries. The products falling under these segments are needed on an everyday basis by the consumers irrespective of their age group and economic status [1]. The composition of these cosmetic products mainly depends on various factors such as product application, manufacturer's choice, and product target segment. Among all the classes of organic compounds used in cosmetics, esters have a wide range of applications in the cosmetic industry, such as emollients in creams, surfactants in shampoos, antioxidants in anti-aging creams, fragrances in perfumes, and flavors in lip cosmetics, depending on their specific properties. Of all the esters, emollient esters are the major class of esters manufactured commercially using biocatalysis. Evonik Industries AG, earlier known as Degussa, was the first to launch lipase-catalyzed emollient esters in the market. The company also commercialized many other emollient esters such as isoamyl cocoate, cetyl ricinoleate, decyl cocoate, and myristyl myristate [2,3]. They now manufacture these products on a multiton scale. Eastman Company was the first to commercially synthesize 2-ethylhexyl palmitate using their GEM technology. According to Eastman Company, application of biocatalysis to synthesize 2-ethylhexyl palmitate leads to significant reduction in CO_2 emission, waste generation, and energy consumption [4]. Thus, it is worthwhile presenting an overview and discussing different aspects of biocatalysis in the synthesis of esters with cosmetic value. This review also explores the application of techniques such as ultrasound and microwave irradiation in enzymatic synthesis with an intention of addressing the biggest drawback of enzymatic process, that is, slow rate of reaction.

2. Biocatalysis in synthesis of cosmetic esters

2.1. Biocatalytic process and sustainability

Cosmetic esters can be synthesized by direct esterification (Fig. 1) or by transesterification (Fig. 2). The current industrial synthesis of cosmetic esters is carried out at a high temperature using an acid or a base catalyst, which requires temperatures as high as 150–240 °C. Such high temperature conditions generate poor quality product (non-desirable for skin application) and require additional treatment and cost. The application of enzyme is one of best alternatives to overcome these drawbacks as the enzymatic methods operate at low temperatures, 30–70 °C, and low pressure, which results in the formation of ultrapure, colorless, and odorless products. Esters produced through biocatalysis can be considered close to 'green' and can satisfy recent consumer demand of green products [4]. For the production of some cosmetic esters, biocatalysis provides a good mean to obtain the quality mandatory for cosmetic use. For example, the traditional chemical route for synthesis of isopropyl ricinoleate (ricinoleic acid ester) at elevated temperatures leads to oxidation of double bonds and polymerization through intermolecular esterification, which leads to the formation of the by-product estolides [5]. Enzymatic synthesis of isopropyl ricinoleate using *Candida antarctica* lipase has been reported to give a yield of more than 90% at a low temperature of 40 °C without estolide formation. The plants used for enzymatic reactions can be set up and operated at much lower capital and energy cost as compared with the plants used for chemical reactions, which require huge investment in equipment and machinery. Enzymatic reactions also tend to have lower waste treatment costs, as enzymes are biodegradable and usually are dosed at a concentration of 0.1–5.0% of the substrate. The contribution of the enzyme to the biological oxygen demand (BOD) in the waste water is also very low [6,7].

A large number of enzymes such as lipases, esterases, proteases, and cellulases obtained from animals, plants, and microorganisms can be used as biocatalysts for regioselective reactions in different solvent systems [7]. Among all the classes of enzymes, lipases are currently attracting a great deal of attention. They are a very important class of biocatalysts for biotechnological reactions. Many species of yeasts, bacteria, and molds produce lipases. Their stereoselectivity, chemoselectivity, and regioselectivity have made them tremendously interesting to scientists and industrialists [7,8].

2.2. Overview of biocatalysis in the synthesis of esters with cosmetic value

2.2.1. Biosurfactant esters

Biosurfactants are enzymatically or microbially produced surface active compounds, which are amphipathic molecules comprising both hydrophobic and hydrophilic parts. The enzymatic method is an in vitro bioorganic method of synthesis using enzymes, which is an alternative to chemical route. Microbial method is a biosynthetic process catalyzed by enzymes present in metabolically active cells (fermentation). Microbial surfactants are generally produced using agro-based raw materials. The major classes of biosurfactants include glycolipids, lipoproteins, phospholipids, and polymeric surfactants. Most industrially known biosurfactants are glycolipids [4,9]. They are carbohydrate fatty acid esters and are the most widely used biosurfactant esters in the food, beverage, cosmetic, and drug industry today [9]. Surfactants are very important ingredients in cosmetic formulations as emulsifiers and foaming agents. Sorbitan esters and sucrose esters are the most developed esters in this category, with a market size of approximately 20,000 and 4000 tons/year, respectively [10]. The chemical synthesis of biosurfactants requires protection and de-protection

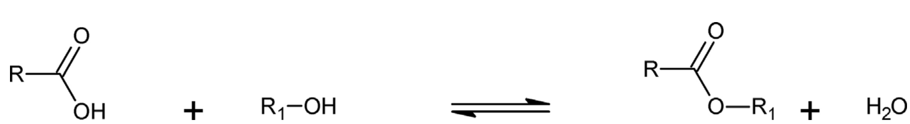

Fig. 1. Direct esterification reaction.

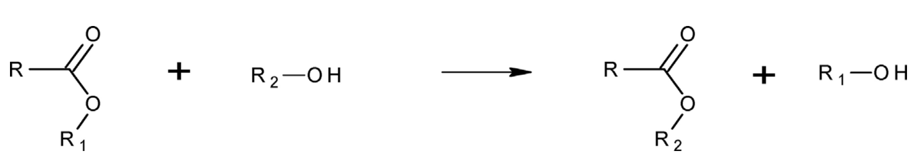

Fig. 2. Transesterification reaction.