Process Biochemistry 47 (2012) 1439–1451

Contents lists available at SciVerse ScienceDirect

Process Biochemistry

journal homepage: www.elsevier.com/locate/procbio

Review

Emerging sustainable technology for epoxidation directed toward plant oil-based plasticizers

Seong-Chea Chua, Xuebing Xu, Zheng Guo*

Department of Engineering, Department of Molecular Biology, Aarhus University, 8000 Aarhus, Denmark

ARTICLE INFO

Article history:
Received 13 October 2011
Received in revised form 29 April 2012
Accepted 31 May 2012
Available online 9 June 2012

Keywords:
Sustainable plasticizer
Green technology
Epoxidation
Ionic liquids
Biocatalyst
Reaction specificity

ABSTRACT

The chemical industry is increasingly looking toward sustainable technology to reduce the environmental impact and minimize the footprint of a chemical process. This work, which presents emerging technologies in academia and industry, discusses the development of advanced processes for the production of epoxidized plant oil-based plasticizers. The effects of the substrate structure, oxygen-donor properties, catalysts and biocatalysts on the specificity of the epoxidation reaction are intensively discussed. The progress in enzymatic epoxidation and the application of neoteric media, such as ionic liquids, are also highlighted. Particular attention is given to understanding how the emerging processes, including the new catalysts and novel reaction systems, work to dictate the reaction efficiency and selectivity. Hence, this review will be of value for developing further improved processes.

Contents

* Corresponding author at: Department of Engineering, Aarhus University, Gustav Wieds Vej 10, DK-8000 Aarhus C, Denmark. Tel.: +45 8715 5285; fax: +45 8612 3178.
E-mail address: guo@mb.au.dk (Z. Guo).

1359-5113/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.procbio.2012.05.025

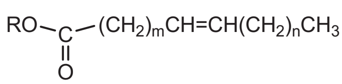
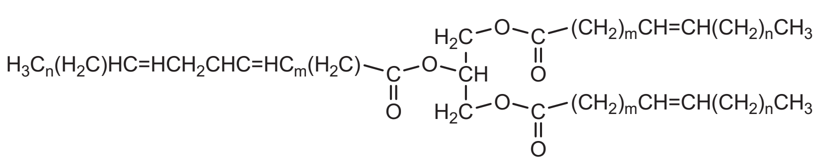
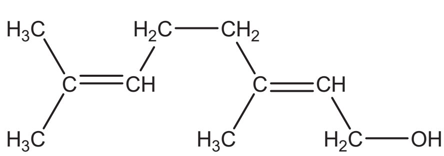
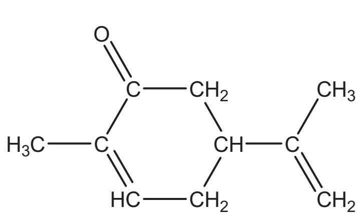
1. Introduction

Epoxidation reactions, which add an oxygen atom to a carbon–carbon double bond (olefin), have been established as an important method for the formation of carbon–oxygen bonds [1]. Epoxides are highly reactive, versatile, polyfunctional intermediates that are used for the production of chiral compounds [2]. Epoxides are also the precursors for alcohols, glycols, carbonyls, alkanolamines, substituted olefins, polyesters polyurethanes and epoxy resins [3–5]. Epoxides can be derived from synthetic compounds or natural resources like plant oils. Increasing environmental concerns have made plant oils an attractive alternative for the production of epoxy-based materials, as plants are biorenewable resources that can be used to reduce the stress from synthetic chemical industries on the environment.

The rapid development of the plastics industry has made the demand for plasticizer rise tremendously, as was demonstrated by a world annual industrial production of epoxidized soybean oils (ESO) of greater than 200,000 tons [6,7]. Notably, some natural seed oils, including the oil from *Vernonia galamensis* [8] and *Euphorbia lagascae* [9,10], contain epoxy groups in their fatty acids. However, the application of these seed oils in industry at a large scale is impossible due to limited sources. Therefore, current commercial epoxidized oils are chemically produced from unsaturated plant oil through Prilezhaev epoxidation. In Prilezhaev epoxidation, a short-chain peroxy acid, preferably peracetic acid is prepared by an in situ reaction of acetic acid with hydrogen peroxide (H_2O_2) and is used as a catalyst [11]. However, Prilezhaev epoxidation produces highly corrosive waste, and chemical epoxidation also leads to undesirable epoxy-ring opening as well as the polymerization of the product under acidic conditions [5].

In addition to the increasing global market demand, the ban on phthalates in plastic materials, which were shown to lead to endocrine disruption and other negative effects, serves as another reason for the attention toward plant oils as a renewable source for plasticizer manufacturing. Therefore, considerable efforts have

Table 1
Representative olefins widely investigated in epoxidation reactions.

Chemical structure	Common name	Reaction kinetics	Ref.
$R_1CH{=}CHR_2$	Alkene	Chemical catalysts; 90–100% conversion; oxidants O_2, H_2O_2, t-BuOOH, etc.; faster and higher selectivity in general	[13–15]
	Unsaturated carboxylic acid ester	Chemical catalysts/biocatalyst; 60–95% conversion; oxidants H_2O_2, t-BuOOH, etc.; medium reaction rate and selectivity; side reactions: polymerization and dihydroxylation, etc.	[5,16–25]
	Unsaturated triglycerides	Chemical catalysts/biocatalyst; 50–80% conversion; oxidants H_2O_2, t-BuOOH, etc.; slower reaction rate and lower selectivity; side reactions: hydrolysis, polymerization and dihydroxylation, etc.	[10,26–31]
	Geraniol	Dimethyldioxirane/metal catalyst, oxidants: H_2O_2 or O_2 transfer agents; faster reaction and positional selectivity;	[13,32]
C_nH_{2n-2}	Cycloalkene	Metal catalysts; oxidants: O_2 or O_2 transfer agents; high selectivity and low conversion	[33–36]
	Carvone	Metal catalyst; Oxidants: peroxy acids and alkaline H_2O_2; reaction kinetics and selectivity controlled by temperature and catalysts, etc.	[37–39]