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SYNTHESIS OF ACRYLIC ESTERS BY LIPASE

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Summary: Various acrylic esters were synthesized by the transesterification of vinyl acrylate with various alcohols. The yield of acrylic esters was about 40 and 66% with n-hexyl and β-phenethyl alcohol, respectively.

In the synthesis of esters by lipase in organic solvents, not only acids and esters but also acid anhydrides and vinyl compounds are used as the acylating agents. For example, Bianchi et al. used acid anhydrides on the synthesis of optically active esters catalyzed by lipase absorbed on celite[1]. Degueil-Castaing et al. used vinyl esters to synthesize the various esters[2]. These methods have an advantage that the reverse reaction, the hydrolysis of esters, hardly occurs because water or alcohols are not produced unlike the esterification with acids or esters.

Recently, we reported the synthesis of lauric esters by lipase immobilized on poly(vinyl alcohol)-poly(ethyleneimine) copolymers in organic solvents[3]. Acids of small carbon number such as acetic acid and propionic acid, however, did not prepare the corresponding esters on the same conditions due to their strong acidity. Then, we synthesized these esters using acid anhydrides or vinyl compounds as the acylating agents[4]. In these experiments we found that acrylic esters could be prepared with the use of vinyl acrylate.

Acrylic esters are generally synthesized by many chemical methods such as the acidic reaction of acrylic acid and alcohols at high temperature[5], but they have not been synthesized biochemically as far as we know. In this work, we will describe the synthesis of acrylic esters using the immobilized lipase in an organic solvent.

In a typical experiment the immobilized lipase[3] from *Candida cylindracea* was added to a solution of an alcohol and vinyl acrylate in isooctane, and the suspension was stirred at 37°C and 200rpm in a conical flask. Aliquots were withdrawn periodically and the determination of acrylic esters was carried out by gas chromatography.

The rate curves of the transesterification of vinyl acrylate with various alcohols were shown in Figure 1. The ease of transesterification was in the order of n-hexyl > n-octyl > n-butyl alcohol with paraffin alcohol and β-phenethyl >> benzyl alcohol with alcohol containing a phenyl group. The yield of acrylic esters was about 40 and 66% with n-hexyl and β-phenethyl alcohol,

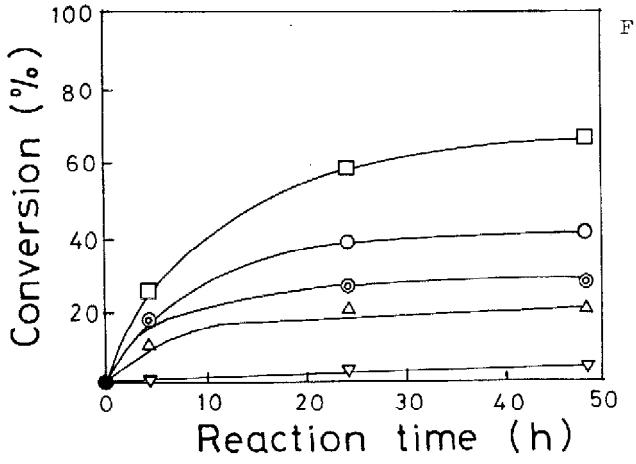

Figure 1. Transesterification of vinyl acrylate with various alcohols in isooctane: vinyl acrylate, 1mol/l; alcohol, 1mol/l; lipase, 50units; 37°C; 200rpm.
Alcohol: △, n-butyl; ○, n-hexyl; ◎, n-octyl; ▽, benzyl; □, β-phenethyl.

respectively. ^{1}H NMR spectrum of β-phenethyl acrylate showed the following signals: triplet at 2.98ppm corresponding to the α-methylene protons adjacent to a phenyl; triplet at 4.38ppm corresponding to the β-methylene protons; signals at 7.2-7.3ppm corresponding to the phenyl protons; signals at 5.8-6.4 ppm corresponding to the vinyl protons.

The mechanism of the synthesis of these acrylic esters is considered to be as follows[6].

$$CH_2=CHCOOCH=CH_2 + \text{lipase} \rightleftarrows [CH_2=CHCO\text{-lipase}] + CH_3CHO$$

$$[CH_2=CHCO\text{-lipase}] + ROH \rightleftarrows CH_2=CHCOOR + \text{lipase}$$

n-Hexyl acrylate was hardly prepared by the esterification of n-hexyl alcohol with acrylic acid or ethyl acrylate. These results show that the acyl-enzyme intermediate is liable to be formed with vinyl acrylate due to the activation of ester bond by vinyl group. However, released acetaldehyde might decrease the lipase activity[2].

n-Hexyl methacrylate was also synthesized in 21% yield using vinyl methacrylate.

β-phenethyl acrylate synthesized was polymerized to give a polymer with molecular weight of about 200000 on the suspension polymerization.

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