SUGAR ESTERS LIPASE-MEDIATED SYNTHESIS FROM VEGETABLE OILS

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1. Introduction

Sugar esters are biodegradable surfactants which are largely used in the food industry, cosmetics, detergents, pharmaceuticals, pesticides... They can be synthesized by chemical or enzymatic way [4]. Their chemical synthesis is industrially performed at high temperature with basic catalysts. This procedure is poorly selective and produces coloured side-products. However, numerous works have reported that enzyme-catalysed processes are milder and more selective [1,2,3]. The originality of the present work is to investigate the entire production process of sugar esters from cheap and renewable resources: carbohydrates and vegetable oils. In the prospect of a process as natural as possible, two enzymatic steps were integrated: hydrolysis of olive and rapeseed oils by the *Yarrowia lipolytica* lipase and synthesis of fatty acids glucose esters catalysed by the lipase B from *Candida antarctica*.

2. Hydrolysis of olive and rapeseed oils by *Yarrowia lipolytica* lipase

Oil hydrolyses were optimised by varying some parameters: emulsifier, oil / aqueous phase ratio, lipase quantity (Table 1) and reaction time (Figure 1). The monitoring of reactions and the quantification of the different species were performed by HPLC-ELSD. For both oils, optimal conditions were: 37°C, gum arabic as emulsifier, oil / water ratio of 1:3, 100 units of lipase per ml of oil, 24h of reaction. The final percentage of free fatty acids expressed as oleic acid was 60% for both oils. Fatty acids are recovered by centrifugation followed by solvent extraction.

Table 1: Effect of the emulsifier, of the oil / water phase ratio and of the lipase quantity on the hydrolysis of olive oil by the crude lipase from *Yarrowia lipolytica*.

Factor Investigated	Hydrolysis yield (%)		
Emulsifier	PVA	Gum arabic	No emulsifier
	33.6 ± 0.5	45.7 ± 1.3	13.7 ± 2.8
Oil / water phase ratio	1:7 (v/v)	1:3 (v/v)	
	45.7 ± 1.3	60.7 ± 1.9	
Enzyme activity	50 U/ml_{oil}	100 U/ml_{oil}	200 U/ml_{oil}
	50.0 ± 0.7	60.7 ± 1.9	66.8 ± 1.3

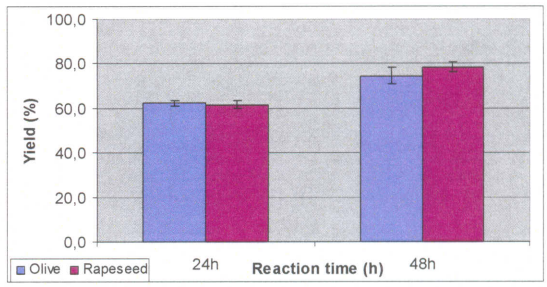

Figure 1 : Hydrolysis yields of olive and rapeseed oils by the *Yarrowia lipolytica* lipase after 24h and 48h of reaction.

3. Synthesis of glucose sugar esters by the lipase B from *Candida antarctica*

The optimal conditions for the glucose esters synthesis were [3]: 60°C, sugar / fatty acid molar ratio of 1:3, 2.5 g of lipase, 25 g of molecular sieve, 48h of reaction. The reaction was performed on a 2l–scale and the determination of ester quantities was performed by HPLC-ELSD. The best synthesis yield, namely 50% (expressed as glucose oleate), was obtained with olive oil. Yields of 25 % were obtained with rapeseed oil. The HPLC chromatograms of the synthesis products show that glucose oleate is the major reaction product for olive and rapeseed oils (Table 2) and that another glucose ester was produced by the lipase B from *Candida antarctica* in the case of both oils (Figures 2 and 3). A third ester was also synthesised with the fatty acids issued of rapeseed oil. Each ester is detected as a pair of peaks which are the esters derived from the α and β anomers of the glucose.

Table 2: Relative composition of the sugar esters mixture obtained after synthesis with both oils. (*) Not detected.

Fatty acids origin	Ester 1	Ester 2	Ester 3 (Glucose Oleate)
Rapeseed	6.64 %	17.22 %	76.14 %
Olive	n.d. (*)	2.86 %	97.14 %

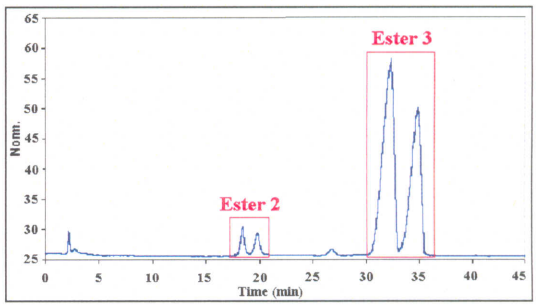

Figure 2 : Glucose esters synthesised with the fatty acids issued of the olive oil enzymatic hydrolysis.

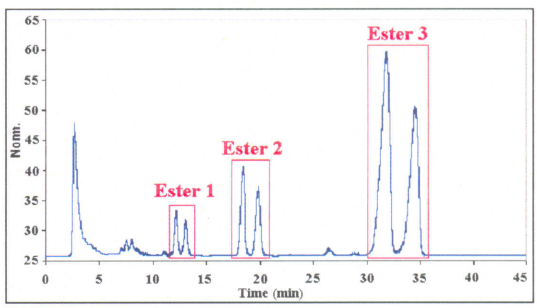

Figure 3 : Glucose esters synthesised with the fatty acids issued of the rapeseed oil enzymatic hydrolysis.

4. Conclusions

The aim of this work was to study the production of fatty acid sugar esters in two enzymatic steps, starting from two vegetable oils. The influence of several parameters on the oil hydrolysis (emulsifier, oil / aqueous phase ratio, lipase quantity and reaction time) has been investigated. Both oils were hydrolysed at 60 % by the *Yarrowia lipolytica* lipase. HPLC analyses of the synthesis products showed that two glucose esters were obtained with olive oil and three with rapeseed oil. The identification of the different glucose esters is in progress. The best synthesis yields were obtained with the fatty acids issued of olive oil (50 %). These results obtained with olive oil are promising for the prospect of a synthesis of glucose oleate from renewable resources.

Acknoledgments

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