Enzymatic synthesis of fatty acid derivatives in organic solvents and oil-water emulsions

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Naturally sourced fatty acids provide an important feedstock of renewable, biobased carbon for the chemical industry. In addition to the fatty acids that are the major constituents of common plant and animal fats and oils (e.g. stearic, palmitic, oleic and linoleic acids), a number of more uncommon fatty acid (derivatives) with interesting chemical structures can be obtained from natural sources. Examples include the hydroxy fatty acids ricinoleic acid (12-hydroxy-*cis*-Δ^9-octadecenoic acid), found in castor oil, and 16-hydroxypalmitic acid, which is a constituent of the plant cell wall polymer cutin. Monounsaturated fatty acids with their double bonds in an unusual position, such as gondoic acid (*cis*-Δ^{11}-eicosenoic acid), a major constituent of the seed oil of the plant *Camelina sativa*, are also of interest for selective functionalisation at the double bond. Enzymatic conversion presents an interesting method by which such unusual fatty acid derivatives can be converted into value-added products. The poor solubility of fatty acids in aqueous reaction systems may necessitate the use of non-conventional reaction media for such a conversion.

Here, we present enzymatic methods to derivatize or isolate unusual fatty acid (derivatives) making use of non-conventional reaction media. Naturally occuring hydroxy fatty acids were esterified using lipases in organic solvents to yield macrolactones or estolides with interesting applications as e.g. biolubricants, cosmetics ingredients or fragrances.[1] Hydroxy fatty acids were also co-polymerised with ε-caprolactone, yielding polyester co-oligomers.[2] We also report a novel bienzymatic cascade for the reactive separation of fatty acids from the seed oil of *Camelina sativa*. The cascade relies on lipase-catalysed oil hydrolysis followed by oleate hydratase-catalysed conversion of oleic acid to 10-hydroxystearic acid and enables the facile separation of oleic acid and gondoic acid present in oil hydrolysates. The seed oil is treated directly with both enzymes in an oil-water emulsion reaction system. Our results demonstrate how biocatalysts can be applied in organic solvents or oil-water emulsions to convert fatty acids or plant oils into value-added biobased chemicals.

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References

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