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<AT>Enzymatic incorporation of caffeoyl into castor oil to prepare the novel castor oil-based caffeoyl structured lipids

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<ABS-Head><ABS-HEAD>Graphical abstract

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<ABS-HEAD>Highlights ► A novel castor oil-based caffeoyl structured lipids was successfully prepared. ► Two competitive reactions hydrolysis and transesterification took place in parallel. ► The highest lipophilic CMAG+CDAG yield of $78.1 \pm 1.35\%$ was obtained using RSM. ► Ea of CMAG+CDAG and CG+DCG formations were 58.86 and 60.53 kJ/mol, respectively. ► High reaction temperature can favor selective formation of lipophilic CMAG + CDAG.

□ <ABS-HEAD>Abstract

<ABS-P>In this work, a novel castor oil-based caffeoyl structured lipids was successfully prepared by the enzymatic transesterification using castor oil (CO) as caffeoyl acceptor. During the structured lipids preparation, two competitive reactions, the hydrolysis of CO to form hydrophilic caffeoyl glycerols (CG) + dicaffeoyl glycerols (DCG) and the transesterification of CO with ethyl caffeate (EC) to form lipophilic caffeoyl mono- and di-acylglycerols (CMAG and CDAG), were found. Reaction progress was monitored using HPLC-ESI-MS and HPLC-UV. The effects of by-product ethanol removal and reaction variables on the transesterification and reaction selectivity were evaluated.

<ABS-P><ST>Results</ST> showed that, the activation energies for the transesterification and for the selective formations of CMAG+CDAG and CG+DCG were 57.60 kJ/mol, 58.86 kJ/mol, and 60.53 kJ/mol, respectively. Under the optimal reaction conditions (enzyme load 23%, 90°C, 1:3 molar ratio of EC to CO, and 46.5h), EC conversion and the yield of CMAG+CDAG were $93.68 \pm 2.52\%$ and $78.11 \pm 1.35\%$, respectively.

<KWD>Abbreviations:CA: Caffeic Acid, CG: Caffeoyl Glycerols, CO: Castor Oil, CDAG: Caffeoyl Di-acylglycerols, CMAG: Caffeoyl Mono-acylglycerols, DCG: Dicaffeoyl Glycerols, Ea: Activation Energies, EC: Ethyl Caffeate, HPLC-ESI-MS: High Performance Liquid Chromatography-Electro Spray Ionization-Mass Spectroscopy, RSM: Response Surface Methodology.

<KWD>Keywords: Castor oil-based caffeoyl structured lipids; Lipase; Transesterification; Castor oil; Caffeic acid; Reaction selectivity

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