Extracts & Distillates

Long-chain fatty acid determination

You, J., X. Zhao, Y. Suo, Y. Li, H. Wang, and G. Chen, Determination of Long-Chain Fatty Acids in Bryophyte Plant Extracts by HPLC with Fluorescence Detection and Identification with MS, *J. Chromatogr. B 848*:283–291, 2007.

A sensitive method has been developed for the determination of long-chain fatty acids (LCFAs) (>C20) using 1-[2-(*p*-toluenesulfonate)-ethyl]-2-phenylimidazole-[4,5-f]-9,10-phenanthrene (TSPP) as tagging agent with fluorescence detection, separation by high-performance liquid chromatography (HPLC) on a reversed-phase column and identification with post-column atmospheric pressure chemical ionization (APCI) coupled with mass spectrometry (MS). TSPP could easily and quickly label LCFAs at 90°C with high efficiency. Separation of the derivatized LCFAs showed good resolution. Detection limits from 1.0 pmol injection were 26.19-76.67 fmol obtained from 0.2 g of plant sample. Eleven free LCFAs were determined in extracts of bryophyte plants.

Determination of hydroxyl-fatty acids

Jenske, R., and W. Vetter, Highly Selective and Sensitive Gas Chromatography-Electron-Capture Negative-Ion Mass Spectrometry Method for the Indirect Enantioselective Identification of 2- and 3-Hydroxy Fatty Acids in Food and Biological Samples, *J. Chromatogr. A 1146*:225–231, 2007.

Derivatization of 2- and 3-hydroxy acids (OH-FA) was made using (*R*)-(–)-α-methoxy-α-trifluoromethylphenylacetyl chloride (MPTA-Cl) to yield a diastereomeric (*S*)-MTPA derivative. The enantiomers of each derivatized OH-FA were well separated on three nonchiral gas chromatography (GC) columns and detected with electron-capture detection (ED) and electron-capture negative-ion mass spectrometry (ECNI-MS). The method allowed for a highly selective identification without influence from the sample matrix. The high sensitivity and selectivity of the method is considered useful for the analysis of complex samples such as wool wax, where 16 enantiopure 2-OH-FAs were detected.

Palm kernel oil isolation

Zaidul, I.S.M., N.A. Nik Norulaini, A.K. Mohd Omar, Y. Sato, and R.L. Smith, Jr., Separation of Palm Kernel Oil from Palm Kernel with Supercritical Carbon Dioxide Using Pressure Swing Technique, *J. Food Eng. 81*:419–428, 2007.

Application of supercritical carbon dioxide using initial pressurization–depressurization treatments was examined for the separation of palm kernel oil (PKO) from undehulled ground palm kernel. Extractions were performed at 80°C and at pressures ranging from 10 to 25 MPa. These pressure swing (PS) extractions allowed some intact or bound oil to be extracted from the third PS step at 15 MPa , while for continuous extractions using a packed bed system a pressure of 20 MPa was required to obtain a comparable oil extraction. Essentially complete extraction of PKO could be achieved using combined PS and continuous extraction at 25 MPa. A model for the estimation of the minimum amount of carbon dioxide to provide a given yield is available. Application of the methodology is considered for the separation and fractionation of PKO for cocoa butter replacers.

Slow CPO crystallization

Chong, C.L., Z. Kamarudin, P. Lesieur, A. Marangoni, C. Bourgaux, and M. Ollivon, Thermal and Structural Behaviour of Crude Palm Oil: Crystallisation at Very Slow Cooling Rate, *Eur. J. Lipid Sci. Technol. 109*:410–421, 2007.

The crystallization behavior of crude palm oil (CPO) has been studied using time-resolved synchrotron X-ray diffraction coupled to high-sensitivity differential scanning calorimetry at cooling rates of 0.1 and 0.4°C/min from melt temperature to –20°C. The triacylglycerol (TAG) organizations formed as a function of temperature and thermal treatments were determined. At slow cooling rate, CPO TAG sequentially crystallized in apparently two different lamellar structures. A time-dependent slow $\beta' \rightarrow \beta$ irreversible transition was observed at low temperatures but only affected a few percent of the TAG population. Crystallization at 0.4°C showed the formation of many additional structures, including some that were evanescent. The coexistence of β and β′ forms even at high temperature demonstrated that the whole system was not in a two-phase domain but rather in a three-phase one (β + β′ + liquid) in which all TAG molecules did not fit into a single β′ structure, which was considered to be related to the granular separations observed in margarine.

Biosurfactant characterization

Monteiro, S.A., G.L. Sassaki, L.M. de Souza, J.A. Meira, J.M. de Araújo, D.A. Mitchell, L.P. Ramos, and N. Krieger, Molecular and Structural Characterization of the Biosurfactant Produced by *Pseudomonas aeruginosa* DAUPE 614, *Chem. Phys. Lipids 147*:1–13, 2007.

Pseudomonas aeruginosa DAUPE 614 produced rhamnolipids at 3.9 g/L when cultivated on a medium containing glycerol and ammonium nitrate. These rhamnolipids were capable of reducing the surface tension of water to 27.3 mN m^{-1}, with a critical micelle concentration of 13.9 mg L^{-1}. The maximum emulsification index against toluene was found to be 86.4%. The structure of the carbohydrate moiety of the glycolipid was determined by gas chromatography-mass spectrometry (GC-MS) coupled to electrospray ionization mass spectrometry and nuclear magnetic resonance spectroscopy. Analysis of the hydroxyl-fatty acid components was

made by GC-MS as hydroxyl-acetylated fatty acid methyl ester derivatives. The positions of the fatty acids in the lipid moiety were found to be variable with six monorhamnolipid homologs being detected. The methodology allowed isomeric pairs to be distinguished. For each isomeric pair, the congener with the shorter chain adjacent to the sugar was always more abundant than the congener with longer chain.

n-3 Fatty acid delivery into food systems

Shaw, L.A., D.J. McClements, and E.A. Decker, Spray-Dried Multilayered Emulsions as a Delivery Method for ω-3 Fatty Acids into Food Systems, *J. Agric. Food Chem. 55*:3112–3119, 2007.

The stability of spray-dried multilayer emulsions containing n-3 fatty acids was examined upon reconstitution into an aqueous system. The primary (lecithin: PL) and multilayered secondary emulsions (lecithin + chitosan: SLC) were sprayed-dried with corn syrup solids. The SLC multilayer interfacial membrane remained intact on the emulsion droplets upon reconstitution. Reconstituted SLC emulsions were more oxidatively stable than reconstituted PL emulsions. A minimum of 5 wt% corn syrup was needed to microencapsulate SLC droplets. Addition of EDTA inhibited oxidation of reconstituted PL and SLC systems. The suggestion was made that a microencapsulated multilayered emulsion system could be used for the delivery of n-3 fatty acids in functional foods.

DAG, TAG chylomicron clearance

Yasunaga, K., S. Saito, Y.-L. Zhang, A. Hernandez-Ono, and H.N. Ginsberg, Effects of Triacylglycerol and Diacylglycerol Oils on Blood Clearance, Tissue Uptake, and Hepatic Apolipoprotein B Secretion in Mice, *J. Lipid Res. 48*:1108–1121, 2007.

Oral ingestion of either diacylglycerol (DAG) oil or triacylglycerol (TAG) oil resulted in secreted chylomicrons primarily composed of monoacyl-glycerol and DAG with similar total acylglycerol composition. Clearance of DAG-chylomicrons was found to be more rapid than that of TAG-chylomicrons. Intravenously infused DAG was also cleared faster than TAG, although infused TAG increased plasma TAG levels. Apolipoprotein B secretion was similar after DAG and TAG infusions, indicating the assembly of larger very low density lipoproteins after DAG.

Oral or infused DAG gave reduced plasma TAG levels due to more efficient clearance of DAG. It was concluded that DAG emulsions may be useful for intravenous nutrition in people with preexisting hypertriglyceridemia.

n-3 PUFA and metabolic syndrome

Lombardo, Y.B., G. Hein, and A. Chicco, Metabolic Syndrome: Effects of n-3 PUFAs on a Model of Dyslipidemia, Insulin Resistance and Adiposity, *Lipids 42*:427–437, 2007.

A study has been made of the effectiveness of fish oil (FO) and its n-3 polyunsaturated fatty acid (PUFA) component in reversing or improving the dyslipidemia, insulin resistance and adiposity induced in rats by long-term feeding of a high-sucrose diet. Dietary FO was found to have positive effects.

FO reduced adipocytes' cell size, yielding greater insulin sensitivity and reduced release of fatty acids. FO also normalized both the oxidative and nonoxidative glucose metabolic pathways in muscle. A response with modification of fatty acid composition of membrane phospholipids was observed. It was concluded that these various effects resulting from dietary FO could be attributed to the normalization of glucose-stimulated insulin secretion and muscle insulin insensitivity.

Increased oilseed rape oil content engineered

Vigeolas, H., P. Waldeck, T. Zank, and P. Geigenberger, Increasing Seed Oil Content in Oil-seed Rape (*Brassica napus* L.) by Over-expression of a Yeast Glycerol-3-phosphate Dehydrogenase Under the Control of a Seed-Specific Promoter, *Plant Biotechnol. J. 5*:431–441, 2007.

A yeast gene (gpd1) coding for cytosolic glycerol-3-phosphate dehydrogenase (GPD) was expressed in genetically modified (GM) oilseed rape under the control of the seed-specific napin promoter. A twofold increase in GPD activity was found to result in a three- to fourfold increase in the level of GPD in developing seeds that resulted in a 40% increase in the final seed lipid content and substantially unchanged protein content. An accompanying decrease occurred in the glycolytic intermediate dihyroxyacetone phosphate, the direct precursor of glyceraldehyde-3-phosphate. The levels of the various metabolites involved in the biosynthesis of fatty acids remained unaltered. Findings indicate that glyceraldehyde-3-phosphate supply co-limits oil accumulation in developing oilseeds and provides a target for the strategic increase of oilseed oil.

Drying oils for low-VOC applications

Booth, G., D.E. Delatte, and S.F. Thames, Incorporation of Drying Oils into Emulsion Polymers for Use in Low-VOC Architectural Coatings, *Ind. Crops Prod. 25*: 257–265, 2007.

Use of vegetable oil macromers (VOM) as co-monomers in emulsion polymerization allows good film production without the use of traditional coalescing solvents and formation of volatile organic compounds (VOC). Various vegetable oils were derivatized to yield VOMs, which were subsequently polymerized into latexes with conventional (meth)acrylate monomers. The degree of ambient crosslinking was related to the extent of chain transfer provided by the several oils. Retention of VOM unsaturation was influenced by reaction temperature with linseed oil showing the greatest variability. Lower reaction temperatures yielded latexes with higher molecular weight and retention of unsaturation, which was also favored by single-step polymerizations. It was concluded that drying oils can be incorporated into emulsions in limited quantities as effective reactive monomers for internal plasticization and auto-oxidative crosslinking after application. ■