

INFORM

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NUTS & SHELF LIFE

ALSO INSIDE:

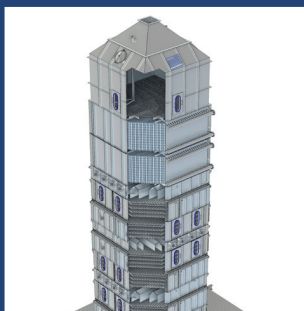
Phase-change materials

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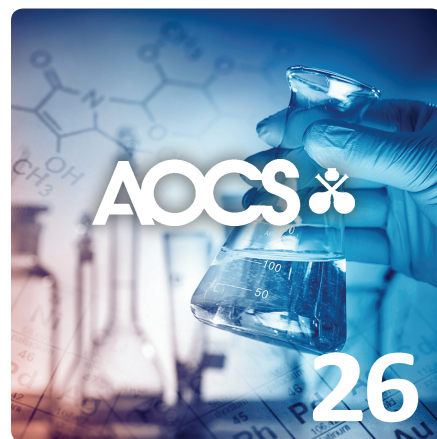
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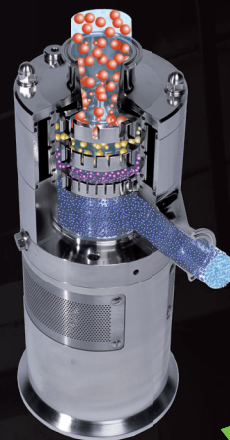
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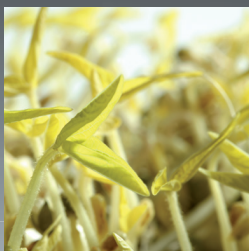
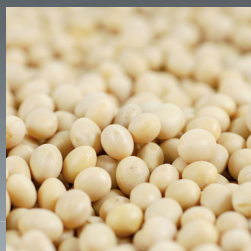
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James B.M. Rattray

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Scott Bloomer
Leslie Kleiner
Fiona Case

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ASSOCIATE EDITOR: Laura Cassiday
CONTENT DIRECTOR: Janet Brown
COPY EDITOR: Lori Weidert

PAGE LAYOUT: Moon Design

2710 South Boulder Drive
P.O. Box 17190
Urbana, IL 61803-7190 USA
Phone: +1 217-359-2344
Fax: +1 217-351-8091
Email: publications@aocs.org

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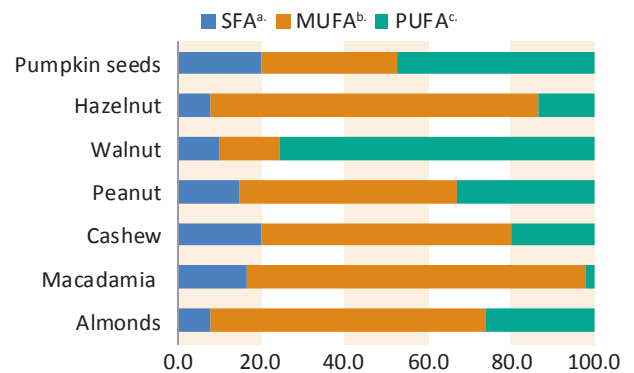
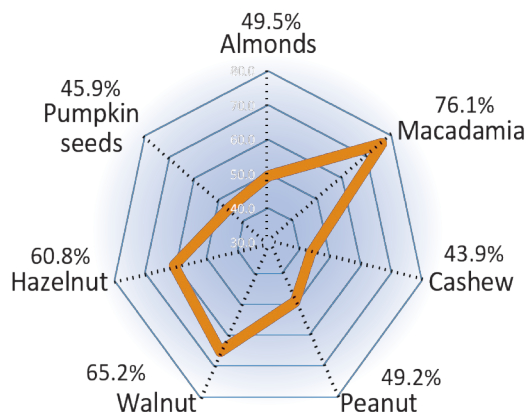
Storage Stability of Roasted Nuts and Stabilization Strategy Using Natural Antioxidants

Cindy Tian

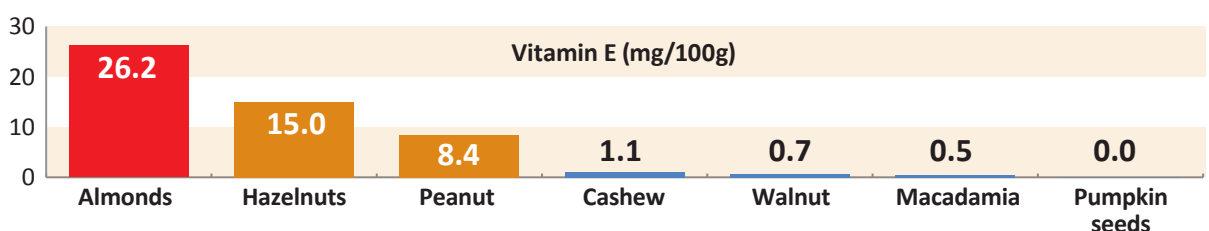
Nuts and seeds have been considered valuable food commodities since prehistoric times. However, they are susceptible to oxidation because of their high fat content and high percentage of polyunsaturated fatty acids (PUFAs). Improving the stability of nuts and products containing nuts has been a big challenge for the food industry. Nut stability is impacted by oil content, and especially by fatty acid composition. For example, a macadamia nut with a high fat content is more stable than the less oily walnut which has much higher PUFA in the oil. Micronutrients also affect stability. The high amount of tocopherol in an almond protects it from oxidation even though it has moderately high oil and PUFA content.



Fat percentage of nuts



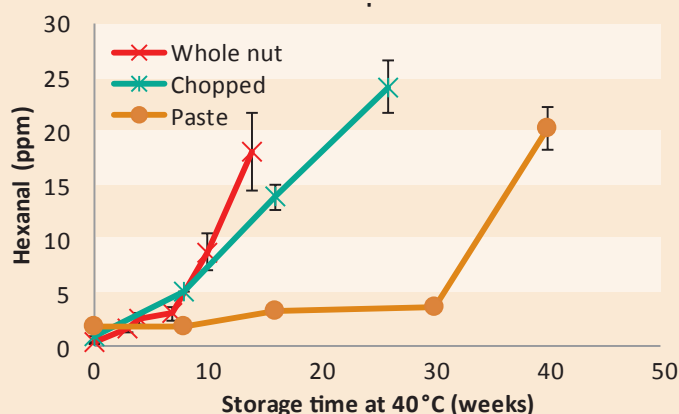
a: saturated fatty acid; b: monounsaturated fatty acid; c: polyunsaturated fatty acid



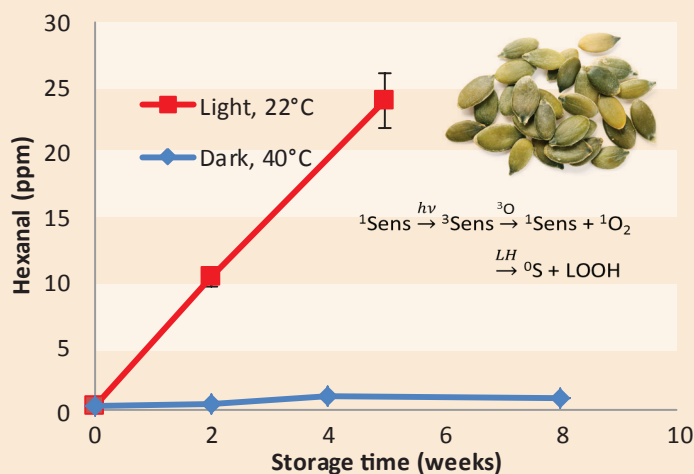


The forms of hazelnuts greatly affect their stability. Clear packaging introduces light as an oxidation catalyst and poses new challenges to the shelf life of nuts. This is especially true for nuts and seeds, such as pumpkin seeds, that contain photosensitizers.

Stability of whole hazelnut, chopped hazelnut, and hazelnut paste



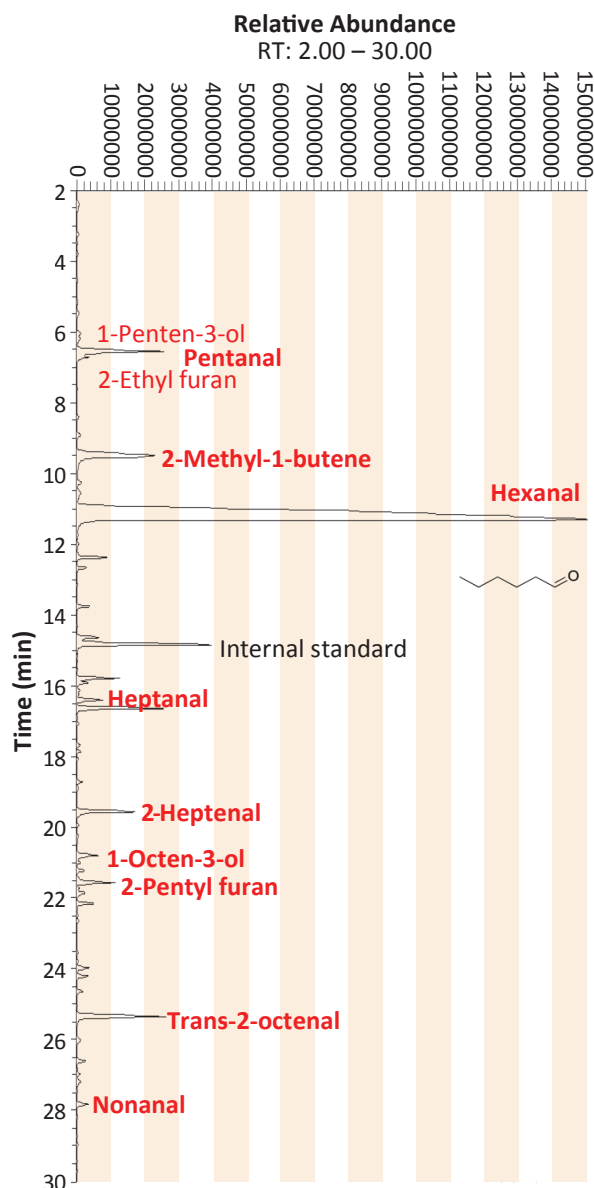
Pumpkin seed stability under dark vs. light conditions



Hexanal: a major marker

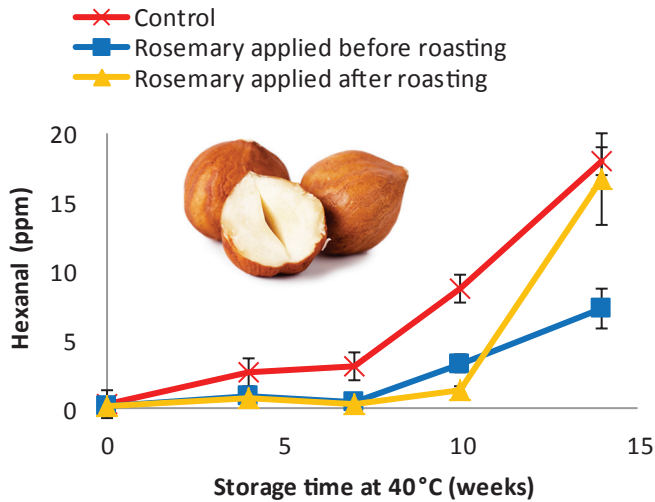
Among all oxidation products detected in rancid nuts, hexanal is the major marker. Natural extractive of rosemary proved to be an excellent antioxidant for stabilizing roasted nuts, either through topical application or through brine treatment.

Topical treatment	Storage time (40°C)	Hexanal reduction %
Peanuts	6 weeks	83%
Hazelnuts	14 weeks	60%
Sliced almonds	10 weeks	73%
Macadamia nuts	18 weeks	88%
Brine treatment		
Cashew	9 weeks	88%
Walnuts	1 week	62%

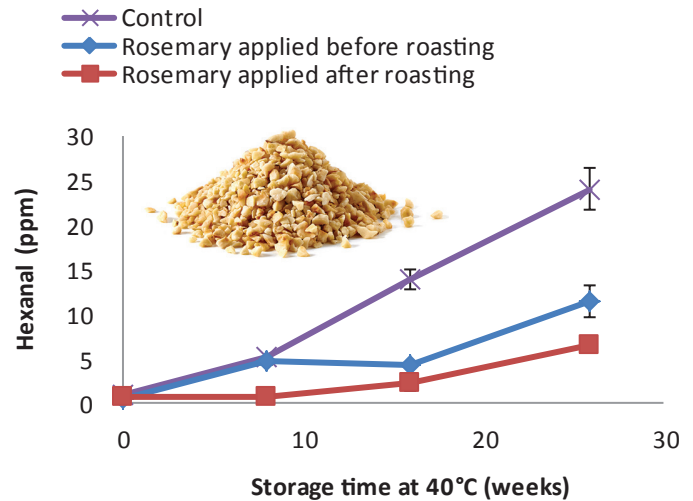


When and where antioxidants are added is important. Generally, the earlier they are applied, the better the protection. However, if the nuts are to be cut or chopped, adding antioxidants to the final product form is recommended to protect exposed surfaces.

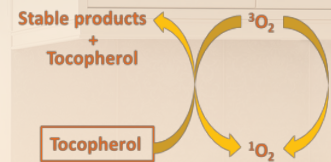
Whole hazelnut stability



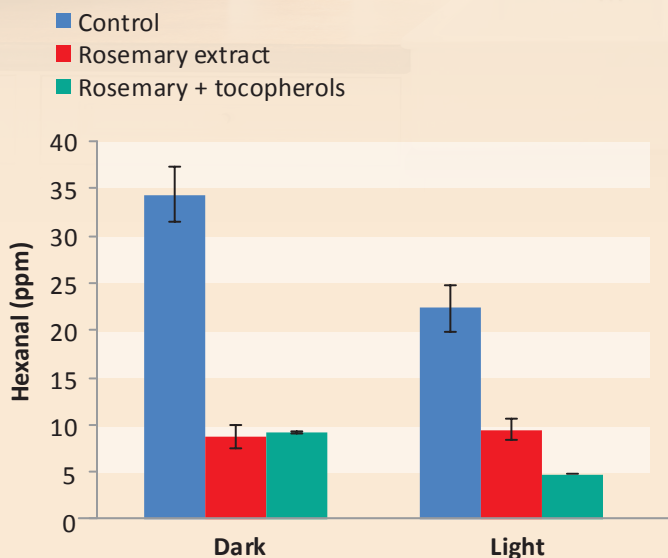
Chopped hazelnut stability



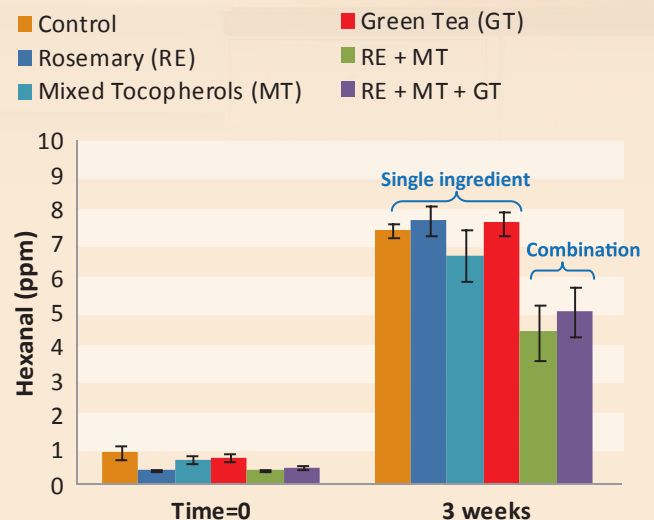
Light has great impact on the oxidation rate of nuts. When a single antioxidant fails to do the job, the use of antioxidant combinations is required for optimum protection.



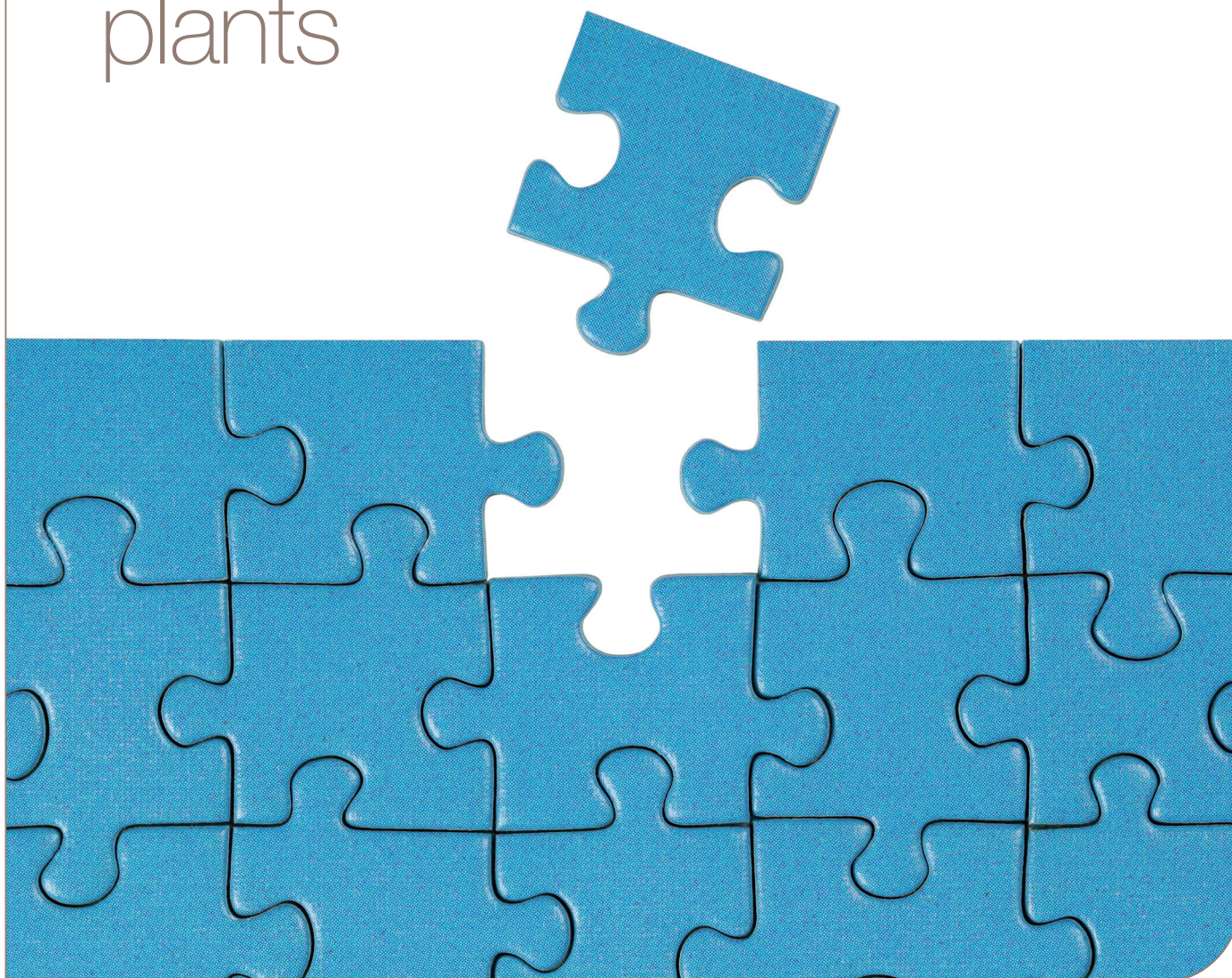
Hexanal in sliced almonds at the end of shelf life



Oxidation of pumpkin seeds under light



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Designing superior phase-change materials from lipids

Michael Floros

Saturated fatty acids and esters are energetic materials which pack together easily. They are frequently used for low-value, bulk applications including biodiesel. Efforts to increase the utility and produce higher-value applications for these types of compounds have inspired our investigation into energy-storage materials. Large-scale energy-storage applications will invariably require significant quantities of material, giving economic advantages to compounds that are inexpensive to produce. This article provides a brief summary of materials derived from saturated lipids and their potential in energy-storage applications.

- Energy-storage techniques are key to increasing both the scope and efficiency of renewable-energy technologies.
- Phase-change materials (PCMs) are effective, low-cost strategies for thermal-energy storage.
- The most commonly used organic PCMs on the market are petrochemical-derived paraffin waxes. Lipid-derived diester PCMs have superior performance to paraffin waxes and represent excellent renewable alternatives.

IMPROVING EFFICIENCIES AND DECREASING WASTED ENERGY

Phase change materials (PCMs) for latent heat-energy storage capture energy in energetic phase transitions. This class of diverse materials is already used in such areas as solar energy, water heating, renewable-energy storage, passive building thermoregulation, and heat recovery. Ideal properties for PCMs are energetic melting and crystallization events (large latent heat) which occur over narrow temperature ranges. In typical applications, energy is transferred to a solid PCM, melting it, and is later recovered in the reverse process, crystallizing the PCM.

Paraffin waxes are the most widely used organic PCMs. They exhibit high latent-heat values (150–200 J/g), minimal reactivity, and are commercially available at low cost with melting points between 20 and 80°C. Paraffin structures generally consist of branched or straight chains of saturated hydrocarbons. Pure straight-chain paraffins display higher latent heats and narrower phase-change profiles than less refined mixtures, but they command significantly higher prices.

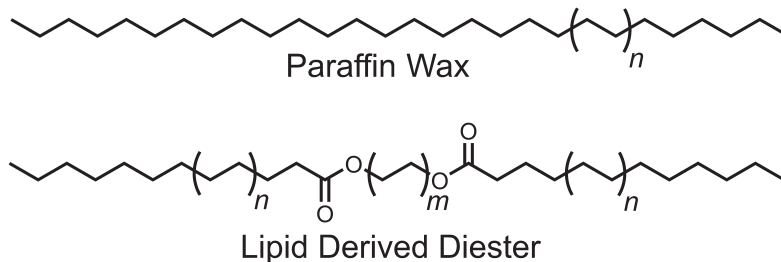


FIG. 1. Generalized structures of paraffin wax- and lipid-derived diester phase-change materials



PREPARATION OF SUPERIOR PHASE CHANGE MATERIALS FROM LIPIDS

Numerous approaches, including investigations into fatty acids and short chain esters, have been used to find renewable substitutes for paraffin PCMs. These investigations resulted in materials which had less-desirable performance characteristics, such as higher vapor pressures, lower latent heats, and reduced temperature ranges. Consequently, they failed to significantly challenge paraffins in the market place.

In an effort to improve the applicability of lipid-derived PCMs, we studied a new approach that involved making higher-molecular-weight derivatives of fatty acids to produce renewable materials with lower vapor pressures, increased melting temperatures, and higher latent heats. Energy-storage approaches must be inexpensive to compete with conventional ones, so complex molecular architectures and

complex syntheses were ruled out. Our approach focused on creating symmetrical saturated diesters from fatty acids and dialcohols (Fig. 1).

Inexpensive saturated stearic (C18), palmitic (C16), myristic (C14), and lauric (C12) fatty acids or fatty acid methyl esters (FAMES) were reacted with dialcohols 2–10 carbon atoms in length in a neat, single-step reaction using small quantities of basic catalyst to produce diesters. Purification of these materials could be accomplished with either vacuum distillation or solvent recrystallization.

Twenty diesters were synthesized to establish the effect of alterations to structure and molecular weight. The melting temperatures of these diesters were between 40 and 77°C (Fig. 2). Increasing the length of the fatty acid from 12 to 18 carbon atoms effectively increased melting points. Latent heats for all of the diesters were between 230 to 260 J/g and significantly higher than paraffin waxes.

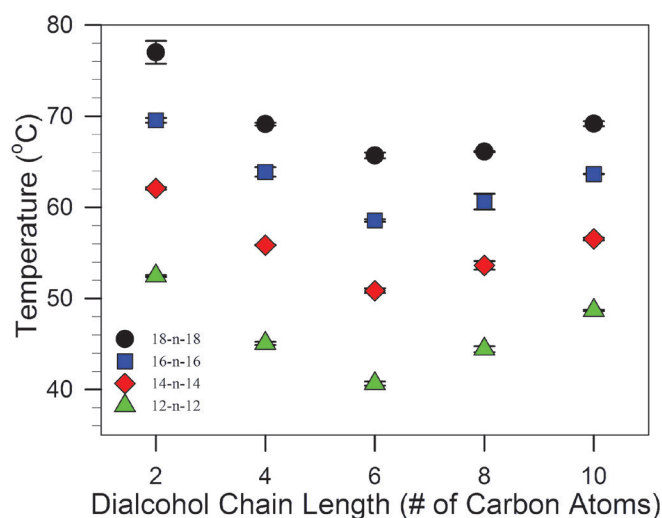
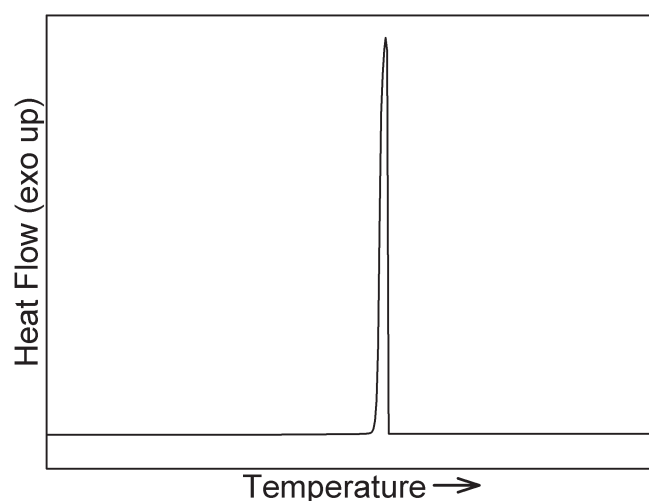


FIG. 2. a. (left) Cooling thermogram of a diester PCM displaying a sharp, highly exothermic crystallization event and minimal sensible heat; b. (right) Diester melting points compared to dialcohol and fatty acid compositions

FOOD AND BEVERAGE APPLICATIONS

While there are numerous potential uses of PCMs, as outlined above, we here demonstrate a simple application using our diesters. The melting points of these diesters are situated in a temperature range associated with hot food and beverage consumption. Frequent coffee consumers are likely familiar with two common issues: 1. Coffee is too hot (above 70°C) to drink immediately after pouring, requiring one to wait for it to cool. 2. Coffee becomes unpleasantly cool (below 50°C) if left too long before consuming.

To address both of these issues, a prototype vacuum-insulated coffee mug was constructed to assess the viability diester PCMs for thermoregulating the temperature of a hot beverage. An optimal amount of diester PCM melting at 63°C (a desirable temperature for hot beverages) was sealed into the wall of a coffee mug with a thin, cylindrical stainless-steel insert. The cup was filled with water preheated to a standard dispensing temperature for coffee (85°C). Continuous temperature readings were taken with the lid on and against a control cup without PCM.

The diester-containing coffee cup cooled the water to 70°C in less than a minute, and the coffee remained above 50°C for 3 hours and 55 minutes. In the control cup, the water took 18 minutes to reach 70°C and remained above 50°C for only 2 hours and 37 minutes. These promising results demonstrate the significant potential of using lipid-derived PCMs made from inexpensive feedstocks for passive thermoregulation of food and beverage temperatures.

PHASE CHANGE MATERIALS AND RENEWABLE ENERGY—AN IDEAL MATCH?

Over the last decade, renewable power from photovoltaic, wind, and solar thermal sources has rapidly increased in mar-

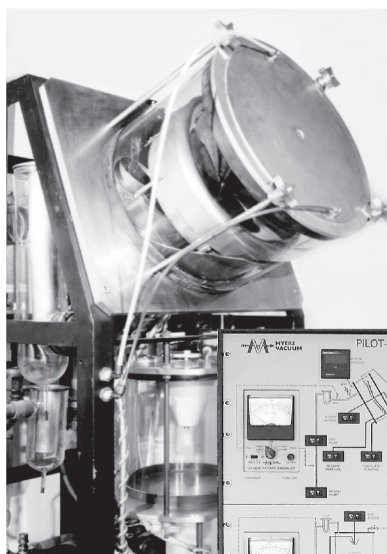
Further reading

- [1] Tessier, M.J., Floros, M.C., Bouzidi, L., and Narine, S.S. (2016) "Exergy analysis of an adiabatic compressed air energy storage system using a cascade of phase change materials." *Energy* 106: 528–534.
- [2] Floros, M.C. and Narine, S.S. (2014) "Saturated linear diesters from stearic acid as renewable- phase change materials." *Materials Letters* 137: 252–255.
- [3] Khudhair, A.M. and Farid, M.M. (2004) "A review on energy conservation in building applications with thermal storage by latent heat using phase change materials." *Energy conversion and management* 45: 263–275.

ket share, growing almost 30% per year. Buoyed by decreasing costs, improving efficiencies, government incentives, and environmentally conscious consumers, the future of renewable energy is bright.

Solar energy is widely used to generate heating for buildings, water, and electricity through direct steam generation. Solar panels and wind turbines have become ubiquitous displays of our transition away from fossil power sources. However, wind and solar energy are intermittent in nature; the sun is not always shining, and the wind is not always blowing. Wind is unpredictable, and solar panels provide peak energy for only a fraction of each day.

For intermittent energy sources to meet a significant percentage of future energy needs, the ability to capture excess energy in times of surplus supply for use during times of high



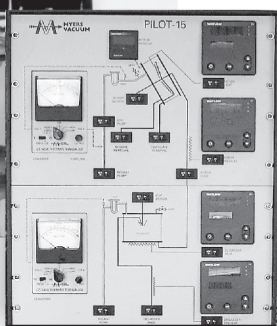
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demand is a necessity. Phase-change materials are under investigation for associated thermal energy storage applications. We are currently investigating an analogous series of diamides based on similar molecular architectures. These diamides have melting temperatures as high as 140°C. With melting temperatures in excess of 100°C, these materials can boil water and generate steam, opening up a whole new set of applications for renewable PCMs.

PCMs can also be used in tandem with other types of energy storage. For example, recovery of waste heat produced during power generation and from other storage techniques with PCMs increases overall energy efficiency. Power storage and generation systems suffer from major reductions in efficiencies due to heat loss. A compressed-air energy-storage system incorporating PCMs for waste heat recovery was predicted to increase the total efficiency by as much as 15% [1]. Further, PCMs can be used to decrease demand for heating and cooling. A significant amount of global energy demand is driven by the need to heat and cool buildings. By incorporating PCMs into building materials like drywall boards, heat during the day can be passively captured and released during the night when temperatures drop.

In conclusion, PCMs derived from saturated feedstocks are highly energetic energy-storage materials. By modifying their structures, a wide range of phase-change temperatures can be met. Our approach uses inexpensive feedstocks typically found in biodiesel to create PCMs that are not only renewable, but also outperform current technologies on the market.

Michael Floros, who earned a Ph.D. in Materials Science in 2015, is a postdoctoral researcher in the Trent Centre for Biomaterials Research at Trent University in Ontario, Canada. His work focuses on lipid-derived materials for energy storage and antimicrobial modifications of biomaterials. He can be reached at mfloros@trentu.ca.



AOCS MEETING WATCH

October 4–7, 2016. World Conference on Fabric and Home Care—Singapore 2016, Shangri-La Hotel, Singapore. <http://singapore.aocs.org>

April 30–May 3, 2017. AOCS Annual Meeting and Industry Showcases, Rosen Shingle Creek, Orlando, Florida, USA. <http://annualmeeting.aocs.org>

September 11–14, 2017. 17th AOCS Latin American Congress and Exhibition on Fats, Oils, and Lipids, Grand Fiesta Americana Coral Beach Hotel, Cancun, Mexico.

For in-depth details on these and other upcoming meetings, visit <http://aocs.org/meetings> or contact the AOCS Meetings Department (email: meetings@aocs.org; phone: +1 217-693-4821; fax: +1 217-693-4865).



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Great science by the Great Salt Lake

Laura Cassiday

- The 2016 AOCs Annual Meeting & Expo, held in Salt Lake City, Utah, USA, May 1–4, offered many interesting and informative oral presentations.
- Those who attended could choose from more than 450 talks given during 69 technical sessions.
- Although complete coverage is not possible, this article summarizes some highlights that capture the breadth and depth of topics.

HARD SURFACE CLEANING

“How a new builder in automatic dishwashing detergent became ready biodegradable in the US: widespread microbial adaptation in the field”

Presented by Jim LePage, AkzoNobel, Chicago, Illinois, USA

Chelators, such as ethylenediaminetetraacetic acid (EDTA), remove the Ca^{2+} “glue” that holds stains together. In 2010, phosphate chelators in autodish detergents were banned in the state of Washington. As a result, AkzoNobel developed the second-generation chelator Dissolvine GLDA as a replacement for EDTA, NTA, and phosphates.

Lab tests showed that GLDA was not readily biodegradable. Factors that influence biodegradation include the presence of specific bacteria and their number, and the chemical structure of the compound. The more exposure to the test chemical in the environment, the larger the population of degrading bacteria will be.

In a collaboration with Procter & Gamble, AkzoNobel scientists did a wastewater treatment simulation test. They found very little degradation of GLDA until several months had passed. The market introduction of GLDA was an unprecedented opportunity to monitor widespread microbial adaptation to a chemical in the field. The researchers collected inoculate from four wastewater treatment plants before and after GLDA introduction. There was negligible degradation of GLDA until 5 months after introduction. At month 7, there was tremendous degradation (Itrich, N. R., <http://doi.org/10.1021/acs.est.5b03649>, 2015).

Prior to market introduction, GLDA failed ready biodegradation tests multiple times. But the lab simulation had shown that it would eventually be degraded, which was confirmed in the field. Thus, this study demonstrated the ability of lab simulation tests to accurately predict widespread microbial adaptation.

“New-to-the-world metathesis-based amide surfactant provides solvent-like function for substantially aqueous cleaners, and a new cleaning mechanism in aqueous formulation with terpenes”

Presented by Ron Masters, Stepan Co., Northfield, Illinois, USA

When vegetable oils are placed in a bioreactor, metathesis (the exchange of double bonds) can occur, resulting in a variety of new molecules, including short-chain monounsaturated fatty esters. Using materials made from this process, Stepan scientists created the new-to-the-world compound *N,N*-dimethyl 9-decenamide (Masters, R. A., *et al.*, *Inform*, 2015).

This compound behaves as a solvent in non-aqueous formulas and as a surfactant in aqueous formulas. Its structure is very hydrophobic, but the compound has enhanced hydrogen-bonding capabilities because of two sets of π electrons. Although *N,N*-dimethyl 9-decenamide has a high critical micelle concentration (CMC), surface tension curves indicate that micelle formation occurs below the solubility limit. The use of more than 0.15% of the compound in a formula may require a co-surfactant.

The apparent micelle radius of *N,N*-dimethyl 9-decenamide is about 7 Å. A small micelle may form because of the compound's short chain and large head group. The small apparent micelle radius might also indicate dimer association rather than true micelle formation. In aqueous solution, the mono-

mer likely adopts a partially looped structure: The π electrons at the end of the carbon chain are about half as electrostatically negative as the oxygen atom of the head group, and thus may be attracted to the electrostatically positive nitrogen of the head group. The rapid wetting of the surfactant in dilute aqueous solution can likely be explained by its partially looped conformation.

A new cleaning mechanism involving synergy between the amide surfactant and terpenes was discovered when cleaning greasy tiles. A product containing 95% water, the new surfactant, and terpenes was formulated. Serendipitously, the researchers discovered that, in addition to removing grease, the new product also cleaned off a permanent marker line on the greasy tiles, producing a “disappearing ink” effect. The ink is a metal charge complex (Co^{2+}) dye that becomes decolorized by the surfactant. The surfactants and terpenes dechelate the dye, causing it to lose intensity.

In bulk solution, the dye and metal center are protected inside a mixed micelle, so the loss of intensity is slow. However, on a surface, the dye and metal center are exposed to surfactant monomers and terpenes from the product, and the loss of intensity is rapid. Possible applications include bloodstain removal, since blood contains the metal complex hemoglobin. The surfactant works better than a commercial peroxide product in removing dried bloodstains from a cotton terry cloth.

Masters performed a live demonstration showing how the cleaning product, made by diluting Stepan's commercial blend with water, is able to disintegrate the color of black permanent marker on several surfaces, including metal, polypropylene, appliance enamel tile, and wood floor tile (Fig. 1). Traditional cleaning by dissolution was demonstrated using red and blue permanent marker stains adjacent to the black marker stains on the same surfaces. When sprayed with the product, the red and blue marker stains dissolved and were cleaned with wiping, but the black marker stains disappeared prior to wiping.



Fig. 1. Twenty seconds after spraying with a hard surface cleaner containing *N,N*-dimethyl 9-decenamide, black marker on a laminate tile is “decolorized” by a new mechanism, whereas red and blue marker are dissolved by traditional cleaning mechanisms (right panel). The left panel shows marker on the same type of laminate tile, 20 seconds after spraying with a commercial multi-purpose cleaner that does not contain *N,N*-dimethyl 9-decenamide. Credit: Ron Masters, Stepan Company

STRUCTURE EFFECTS ON OIL BINDING

“Algal butter, a novel structuring lipid, its similarities and differences in composition, and observed functionality when compared to a conventional shea stearin”

Presented by Alejandro Marangoni, University of Guelph, Ontario, Canada

Compared with cocoa butter, cocoa butter equivalents (CBE) are lower in price, have a better supply, or produce better-quality chocolate than cocoa butter. CBE, which include shea stearin, palm oil midfraction, illipe fat, and kokum fat, are similar in triacylglyceride composition to cocoa butter. When used in a specific ratio to cocoa butter, high-quality chocolate can be produced. In the European Union, CBE can replace cocoa butter at up to 5% of total mass in chocolate.

Solazyme (now TerraVia; South San Francisco, California, USA) has developed algal butters as CBEs that could improve the quality of chocolate. During the chocolate tempering procedure, the crystallization profile of algal butter is similar to that of shea stearin. When algal butter or shea stearin is included in chocolate at 5% or 10%, with 95% or 90% cocoa butter, respectively, the melting properties (solid fat content, SFC) are the same as for 100% cocoa butter. When algal butter or shea stearin is included at 15%, the chocolate shows a slight increase in heat stability compared with 100% cocoa butter.

The researchers examined cocoa butter powder by x-ray diffraction. With 100% cocoa butter, 90% of the crystals were in the 3L form, and 10% were in the 2L form. For cocoa powder containing 100% algal butter, all of the crystals were in the 2L form, similar to shea butter. Mixtures of 5% algal butter/95% cocoa butter and 10% algal butter/90% cocoa butter had mostly 3L and few 2L crystals, like 100% cocoa butter. When algal butter was included at 15%, there was less of the 3L form, and the crystal packing started to change. These properties were the same for algal butter and shea stearin.

MONOUNSATURATED FATS IN THE DIET: BENEFITS AND INGREDIENT SOLUTIONS

“Functionality and stability of monounsaturated vs. polyunsaturated oils in baking, frying, and confectionary”

Presented by Alejandro Marangoni, University of Guelph, Ontario, Canada

Food manufacturers face challenges when replacing saturated fats with unsaturated oils (either monounsaturated or polyunsaturated) in products such as baked goods, processed foods, and fried foods. The two most important challenges involve oxidative stability (particularly during frying, but also important for shelf life) and functionality.

Antioxidants known as tocopherols are often added to polyunsaturated oils to increase stability, but in most cases the tocopherols do not work as well as expected. Generally, the

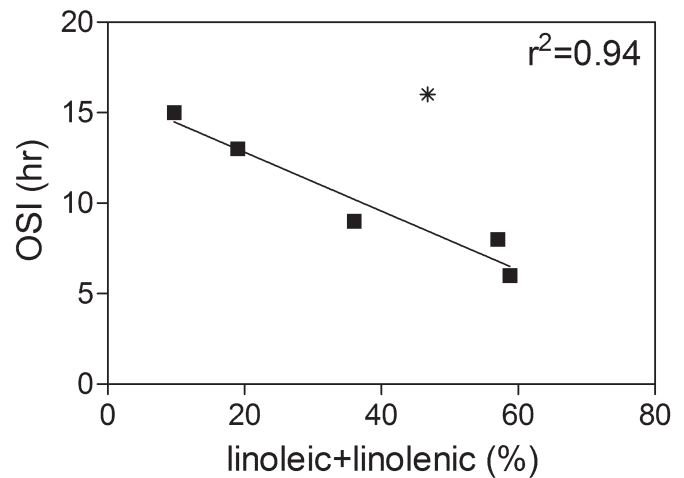


Fig. 2. In general, the oxidative stability index (OSI) of an oil is inversely correlated with the content of polyunsaturated fatty acids (linoleic + linolenic). An exception is pumpkin seed oil (*), which has a high OSI despite having a high linoleic acid content, likely due to the generation of Maillard reaction products during roasting. Credit: Alejandro Marangoni, University of Guelph

oxidative stability of an oil decreases with the content of polyunsaturated fatty acids (e.g., linoleic plus linolenic), regardless of tocopherol content. Interestingly, however, pumpkin seed oil does not follow this trend: Despite having a very high linoleic acid content, pumpkin seed oil has the highest oxidative stability index (OSI) of any oil tested (Fig. 2). This finding could be attributed to the generation of Maillard reaction products, which act as powerful antioxidants, during pumpkin seed roasting.

Vegetable oils do not function as well as fats in baked goods and other processed foods for several reasons. First, fats weaken gluten. Solid fats, oils, and egg yolks coat gluten proteins and prevent them from forming long, strong strands. Fats can also make flour water-resistant. For example, when making tart dough, the first step is to thoroughly work the fat into the flour. Once coated with fat, the flour granules do not absorb as much moisture when wet ingredients such as eggs, cream, or water are added. Therefore, less gluten is formed, and the tart crust stays tender. When using vegetable oils, an ingredient must be added to shorten the gluten, such as an emulsifiable alpha gel.

In addition, the solid particles in fat stabilize air bubbles in foams, a phenomenon known as Pickering stabilization. When using vegetable oils, novel particles (such as, again, alpha gels) must be added to achieve the same functionality. Also, fats provide mechanical strength upon setting, bind oil, and provide a melting sensation in the mouth, all of which must be compensated for with ingredients such as oleogels or hydrocolloids when replacing fats with vegetable oils. Ingredients added to vegetable oils to provide these functions will likely affect the clean label because consumers do not recognize them as natural. However, work is underway to identify more natural ingredients that can fulfill these functions.

BIORENEWABLE POLYMERS

“Moisture-resistant coating for packaging paper from silylated soybean oil”

Presented by Daniel Graiver, Michigan State University, East Lansing, USA

A challenge to developing moisture-resistant packaging paper is that the cellulose in paper is inherently hygroscopic. The moisture absorption depends on factors such as humidity, temperature, and time of contact. Historically, wax was used as a paper coating, but it has been replaced by synthetic polymers. Another alternative, drying oils, produce coatings that are brittle and yellow with age. In addition, a solvent or diluent is required, and they have slow drying rates.

Soy oils are very hydrophobic, but in order to use them as moisture-resistant barriers, they need to be converted from a liquid to a solid form. Chemical modifications to accomplish this include derivitization of the C=C double bond or of ester groups, but traditional modifications are cost-prohibitive.

Silicone paper coatings based on hydrosilylation are well known. Unfortunately, with the exception of chlorosilanes, hydrosilylation is limited to terminal double bonds, and vegetable oils have double bonds in the middle of the chain. The Diers-Alder reaction (-ene reaction) can be used to silylate vegetable oils. There are no byproducts or solvents, and the reaction is a single-step process that uses a free-radical mechanism.

The silylation process can be conducted in a Parr reactor to graft reactive alkoxy silane onto the vegetable oil. The alkoxy silane linkages (Si-O-C) are unstable in the presence of moisture in the air. Thus, hydrolysis to silanols and subsequent condensation lead to a crosslinked network, resulting in moisture-activated curing. The crosslink density of the coating can be adjusted by controlling the composition and the process. The silylation of soybean oil converts a liquid oil into a solid coating, which forms a very hydrophobic surface.

A pilot-scale trial used a conventional gravure roll coating system to coat more than 50,000 square feet of Kraft paper with 5 gallons of the silylated soybean oil in three different trials (4% water, 250 °C). The researchers used scanning electron microscopy (SEM) to examine the coated paper. A thin coating reduced moisture transfer (water vapor transmission rate, WVTR) by about 50%.

The US Department of Defense is interested in this technology because they want to be able to discard biodegradable food wrappers from Navy ships into the ocean. The coated paper is now being tested by the Navy.

ADVANCES IN LIPID OXIDATION AND ANTIOXIDANTS—FUNDAMENTALS AND APPLICATIONS

“Controlling lipid oxidation in oil-in-water emulsions with polyphenol-coated active packaging films”

Presented by Maxine Roman, University of Massachusetts Amherst, USA

Examples of common antioxidants used in foods include ethylenediaminetetraacetic acid (EDTA), butylated hydroxytoluene (BHT), citric acid, and α -tocopherol. EDTA, a metal chelator, is inexpensive and can be used in low amounts that are particularly effective to extend the shelf life of packaged food emulsions. However, many consumers dislike synthetic additives.

As an alternative to antioxidant additives, commercially available active packaging uses oxygen scavengers and ultraviolet (UV) absorbers that are attached to the packaging material or included in sachets within the package. Active packaging enables a “clean” label because it is a food contact material, not a direct additive. Most active packaging has been designed for low-moisture foods, such as meats. To develop a new type of active packaging for emulsions, such as salad dressings, the researchers grafted metal chelators called polyphenols onto packaging material. This packaging is designed to remove prooxidant metals during shipping and storage of packaged food emulsions.

The team drew inspiration from enterobactin, a high-affinity iron chelator from bacteria that contains catechol groups, which bind Fe^{3+} . The researchers used the enzyme laccase to oxidatively polymerize catechol with a related compound, catechin—thereby generating a metal-chelating polyphenol. The team then coated a polypropylene film with the polyphenol. To prevent the polyphenol from migrating out of the packaging material, the researchers added an anchor made of the polysaccharide chitosan.

Next, the researchers screened the polyphenol-coated active packaging film for antioxidant activity by confirming its metal-chelating capacity (40 nmol Fe cm^{-2} at pH 4) and radical-scavenging capacity (up to 52.9 ± 1.8 nmol Trolox eq. cm^{-2}). When the packaging was tested on soybean oil-in-water emulsions, the polyphenol-coated active packaging material could extend the lag time of lipid oxidation by 10 days. However, the material did not perform as well as soluble catechin or EDTA. When the researchers examined lycopene degradation in an oil-in-water emulsion, the polyphenol-coated active packaging material outperformed soluble catechin and EDTA. These findings suggest that polyphenol coatings can be used to prepare antioxidant active packaging materials for preservation of foods.

PLANT LIPID BIOTECHNOLOGY AND GENOMICS

“Sustainable improvement of oil palm through biotechnology”

Presented by G. K. A. Parveez, Malaysian Palm Oil Board

Feeding an estimated 9.1 billion people in 2050 will require a 70% increase in food production. Triple the current oil crop yield will be needed. Oil palm is the most productive oil crop (about 4 tons/ha/year). Although planted on just 5% of the land occupied by oil crops, palm oil contributes 40% of the edible oil.

To improve oil palm yield, classical breeding would take centuries. Conventional breeding has a 10–12-year selection cycle, requires increased land, and is high in cost. Genomics-

guided breeding or epigenetics-guided tissue culture propagation is much faster.

Oil palms are divided into two major species: *Elaeis guineensis*, which mainly originated in equatorial African countries, and *Elaeis oleifera*, from Central and South America. The Malaysian Palm Oil Board has the largest oil palm germplasm in the world. In 40 missions over four decades, researchers have collected 110,000 samples from more than 300 populations of wild palms from 19 countries throughout the world. The oil palm genome has been sequenced. A single representative oil palm from each species was selected for sequencing (Singh, R., *et al.*, <http://doi.org/10.1038/nature12309>, 2013). Super reference genomes were established. Oil palm has 16 chromosomes and contains more than 35,000 genes.

The highest-performing oil palm species, and the one planted commercially, is *E. guineensis*. There are three varieties of modern *E. guineensis*: *dura* (thick-shelled), *pisifera* (shell-less; female-sterile), and *tenera* (thin-shelled; a hybrid between *dura* and *pisifera*). *Tenera* is the variety with the highest yield, producing 36% more oil than the *dura* variety. The *Shell* gene is involved in the production of the palm kernel shell and is responsible for the *tenera* phenotype (Singh, R., *et al.*, <http://doi.org/10.1038/nature12356>, 2013). The SureSawit™ SHELL Kit, based on the *Shell* gene, can differentiate *dura*, *tenera*, and *pisifera* varieties in the field with 100% accuracy. This kit is currently being used to eliminate low-yielding plants of the *dura* and *pisifera* varieties, as early as at the nursery stage.

Within the *tenera* phenotype, the *nigroscens* variety of palm oil fruit is darker in color (dark purple) than the *virescens* variety (green). As the palm fruit ripens, the *nigroscens* turns lighter in color, whereas the *virescens* becomes yellowish. The majority of planted oil palms are *nigroscens*, but it is difficult to differentiate the matured fruit from the *virescens* variety during harvest. The researchers found that five independent mutations in the *VIR* gene, which encodes a transcription factor, account for the *virescens* fruit color (Singh, R., *et al.*, <http://doi.org/10.1038/ncomms5106>, 2014). A commercial kit to dis-

tinguish the *nigroscens* and *virescens* varieties is under development. In addition, the researchers investigated the oil palm mantling phenotype (Fig. 3).

Mantled fruits are produced from palms generated through the tissue culture process, which, in general, increases yield. However, the presence of mantled fruit is undesirable and results in a drastic reduction in yield. Although mantling is a heritable phenotype, it does not result from a change in genome sequence. Therefore, the researchers conducted an epigenome-wide association study, which determined that mantling is caused by a change in DNA methylation at a specific region of the genome (Ong-Abdullah, M., *et al.*, <http://doi.org/10.1038/nature15365>, 2015). A diagnostic kit is being developed to identify and eliminate mantled palms.

BIOFUELS

“Enzymatic biodiesel—single time use of enzyme and one-pot polishing solution”

Presented by A. Rancke-Madsen, Novozymes, Denmark

Using enzymes to produce biodiesel from oils or fats offers feedstock flexibility, lower energy and methanol costs, higher yields and capacity, increased safety, and higher-quality glycerin than the conventional biodiesel production process. Recent improvements have allowed liquid lipases to replace immobilized lipases. Liquid enzymes can handle feedstocks with any content of free fatty acids. In May 2016, Novozymes launched Eversa Transform 2.0, a protein-engineered variant of *Thermomyces lanuginosus* lipase. This liquid lipase has improved thermostability and economy and can process feedstocks with higher melting points, such as animal fats or palm oil.

Novozymes researchers have made improvements to the enzymatic process of biodiesel production. The old process, which required two separation steps, had a 75–82% yield. The



Fig. 3. Cross-section of oil palm fruit, normal (left) and mantled (right). Credit: Dr. Meilina Ong Abdullah, Malaysian Palm Oil Board

DAILY REFERENCE VALUES (DVs) OF VARIOUS NUTRIENTS TO ENCOURAGE AND NUTRIENTS TO LIMIT, FOR ADULTS AND CHILDREN

During the hot topics session on monounsaturated fats in the diet, Fabiola Dionisi, Global Leader for Lipid Research & Development at Nestlé Research Center in Lausanne, Switzerland, explained Nestlé's holistic approach to nutrition in product development. The company uses an evidence-based Nutrient Profiling System (NNPS) to evaluate and (re)formulate foods. The NNPS considers the nutritional impact of specific nutrients to limit and nutrients to encourage, and translates public health recommendations and dietary guidelines into tangible product targets which allow product developers to focus on what matters the most and to deliver nutritious foods. The table represented here includes only a selection of nutrients chosen to match the interest of *Inform* readers. A complete table of the nutrients considered in the nutrient profiling system is available in the open access article by Vlassopoulos, A., *et al.*, "A nutrient profiling system for the (re)formulation of a global food and beverage portfolio," *Eur. J. Nutr.* 1–18, online 2016, <http://link.springer.com/article/10.1007%2Fs00394-016-1161-9>.



TABLE 1. Daily reference values (DVs) of various nutrients to encourage and nutrients to limit, for adults and children

Nutrient	DVs for children aged 4–8 years	DVs for children aged 9–11 years	DVs for adults
Energy	1700 kcal	2000 kcal	2000 kcal
Nutrients to limit			
Total fat	60 g	70 g	70 g
Saturated fat	19 g	20 g	20 g
Trans-fat	<1 % total energy	<1 % total energy	<1 % total energy
Nutrients to encourage			
Vitamin D	5 µg	5 µg	5 µg

new process, which uses the enzyme a single time and requires no enzyme separation step, has a 92–94% yield. The new enzymatic process offers a 10–17% higher primary yield, uses four times less oil volume recycling, and consumes four times less water than the old process.

When used cooking oil was used to make biodiesel in the enzymatic process, free fatty acids (FFAs) were reduced to about 1.5% (bound glycerol less than 0.22%) in 36 hours. "One-pot" caustic washing (with 1.15 equivalents dilute sodium hydroxide) brought the FFAs within biodiesel specifications (approximately 0.1%).

The enzymatic process is robust, allowing almost any feedstock. Novozymes researchers have established guidelines to determine the best pretreatment method. By varying methanol, water, and temperature, polishing can be fine-tuned to enable efficient removal of production residues and solid contaminants. The guidelines also suggest how to use distillation to deal with high levels of diglycerides and metals, such as sulfur.

Economic comparisons were performed for the enzymatic method (using corn oil or acid oil as feedstock) and the chemical method (using soybean oil as feedstock). The cost benefit for the enzymatic process was \$145/ton, mostly due to the ability to use lower-cost feedstock. Another example compared the enzymatic and chemical processes, both using corn oil as feedstock. In this case, the savings for the enzymatic process was \$105/ton, due to reduced use of methanol

and improved yield. In conclusion, the improved pretreatment process and one-pot enzymatic process are superior to the old enzymatic and chemical processes for biodiesel production.

SATIETY AND SENSORY

"Small intestinal sensing of lipid in humans—relationship with appetite and energy intake"

Presented by Christine Feinle-Bisset, University of Adelaide, Australia

Obese individuals have an increased preference for high-fat foods, but high-fat meals are less satiating for them than for lean individuals. The researchers inserted a catheter into the duodenum of human volunteers so that they could infuse nutrients directly into the small intestine. A fat infusion slowed gastric emptying; caused the release of gut hormones CCK, PYY, and GLP-1; and caused a reduction in the "hunger hormone" ghrelin. These events result in the suppression of energy intake.

These effects of fat are dependent on its digestion to free fatty acids. Lipase inhibition with the obesity drug Orlistat suppressed gut effects, resulting in a reduced CCK response, increased pyloric pressure, and increased energy intake. Injecting smaller-sized lipid droplets increased the effects of fat

on the gastrointestinal system and suppressed hunger compared with larger lipid droplets. The effects of fatty acids on gastric emptying were dependent on acyl chain length. Lauric acid (C12) increased pyloric pressure and CCK levels more than capric acid (C10), leading to a greater reduction in energy intake.

Obese people have a reduced small-intestine sensitivity to oleic acid (C18:1; Stewart, J. E., *et al.*, <http://doi.org/10.3945/ajcn.110.007583>, 2011). Some, but not all, studies indicate that obese people also have a reduced oral sensitivity to C18:1 (thus, a higher fat taste threshold), and increased habitual energy and fat intakes.

Volunteers on a 2-week high-fat diet showed increased hunger and decreased pyloric pressure. When volunteers were placed on a 4-day, 70% calorie-restricted diet and then infused with lipids, they showed reduced hunger, energy intake, and pyloric pressure during the infusion (Brennan, I. M., *et al.*, <http://doi.org/10.1038/ijo.2010.153>, 2010). In another study, a 12-week 30% calorie-restricted diet followed by lipid infusion resulted in increased pyloric response (Seimon, R. V., *et al.*, <http://doi.org/10.3945/ajcn.113.067090>, 2014).

The presentations highlighted in this article and other thought-provoking talks at the 2016 AOCs Annual Meeting and Expo sparked interesting and fruitful conversations among meeting attendees. Mark your calendar now for the 2017 AOCs Annual Meeting & Expo, which will take place in Orlando, Florida, USA, April 30–May 3.

Laura Cassiday is an associate editor of *Inform* at AOCs. She can be contacted at laura.cassiday@aocs.org.

MATH MATTERS ON EARTH AND BEYOND

Q: What do Critical Ratios from mass spectrometry of triacylglycerols and the spiral leaf patterns of sunflowers, daisies, cacti, and other plants, as well as orbits of Venus and Earth and also spiral arms of some galaxies have in common?

A: They all have structures that can be described as self-replicating Fibonacci sequences of numbers, in which each subsequent number is the sum of the previous two, and the ratios of these values approximate the Phi Ratio, a.k.a. the Golden Ratio or Golden Mean. During an AM&E technical presentation, “What is a simulacrum and what does it tell you about triacylglycerol structures?,” Craig Byrdwell, a research chemist with the Agricultural Research Service at the United States Department of Agriculture, explained how this mathematical concept can be used to squeeze information out of the abundance ratios generated by Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS). In his second presentation, “What analysis of triacylglycerol structures taught me about space, mass, and the Periodic Table,” Byrdwell went on to describe how APCI-MS of triacylglycerols led to a new understanding of pi and new equations for space, mass and the Periodic Table.

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Highly Detailed Analysis of *cis/trans* FAME Isomers

Using 200 m SP™-2560 and SLB®-IL111 Capillary GC Columns

Over the last half of the previous century, the use of partially hydrogenated vegetable oil (PHVO) replaced the use of animal fats for baking purposes in most western countries. During the process to make PHVO, *cis* fatty acids are converted into *trans* fatty acids, which increases the shelf life of food products. Scientific research over the last decade has shown that the increased intake of *trans* fatty acids coupled with our inability to properly metabolize them can increase the risk of coronary disease. In June 2015, the US FDA mandated that food manufacturers must stop using all artificial *trans* fats (i.e. they can no longer use PHVO) within three years.¹

The qualitative and quantitative testing of *cis/trans* fatty acids is best accomplished using GC after conversion of the fatty acids to fatty acid methyl esters (FAMES). The 200 m SP-2560 and SLB-IL111 are specifically designed and tested for the highly detailed analysis of *cis/trans* FAME isomers. Specifications for both columns are shown in Table 1.

Table 1. Column Specifications

SP™-2560	
USP Code	This column meets USP G5 requirements.
Phase	Non-bonded; poly (biscyanopropyl siloxane)
Temp. Limits	Subambient to 250 °C (isothermal or programmed)
SLB®-IL111	
USP Code	None
Phase	Non-bonded; 1,5-di(2,3-dimethylimidazolium)pentane bis(trifluoromethanesulfonyl)imide
Temp. Limits	50 °C to 270 °C (isothermal or programmed)

C18 FAME Isomer Mix

Some of the most studied fatty acids are the C18 family. A custom mixture was injected in each column, and run conditions were adjusted to maximize resolution. The optimized chromatograms are shown in Figure 1. While neither column can separate all isomers, both provide a high degree of separation of *trans* FAME isomers from *cis* FAME isomers. Of interest is that SLB-IL111 provides resolution of C18:1Δ9c (a *cis* FAME) from all *trans* FAMES. This is significant because C18:1Δ9c often results in a very large peak area while analyzing food extracts. Its entire peak area must be considered as being contributed by a *trans* FAME if there is a co-elution, resulting in *trans* fat values that are biased high.

38-Component FAME Isomer Mix

A custom standard comprised of FAMES ranging from C4 to C24, including key monounsaturated and polyunsaturated fatty acids, was

analyzed on each column under identical conditions. Figure 2 shows the chromatograms obtained from both columns. Of relevance is that SP-2560 provides better resolution of saturated FAME isomers from unsaturated FAME isomers, and that SLB-IL111 provides increased retention of unsaturated FAME isomers.

Rapeseed Oil FAMES with CLA FAME Isomers

A custom mixture containing rapeseed oil FAMES plus four CLA FAME isomers was injected in each column using oven temperature programs which optimized resolution. Rapeseed oil is a simple vegetable oil that contains a series of C14-C24 saturated and unsaturated fatty acids. CLAs are C18:2 fatty acids in which a single carbon-carbon bond separates the two double bonds. The resulting chromatograms are shown in Figure 3. Of note is that the co-elutions on one column are fully resolved on the other, providing complementary data.

Discussion

The SP-2560 / SLB-IL111 pairing allows the most comprehensive fatty acid composition information possible, able to provide accurate results (qualitative and quantitative) for both saturated and *trans* fatty acids. Observations include:

- Analytes elute from SLB-IL111 at a lower oven temperature (Figures 1–3)
- SLB-IL111 provides resolution of C18:1Δ9c from all *trans* FAMES (Figure 1)
- SP-2560 provides better resolution of saturated FAME isomers (Figure 2)
- SLB-IL111 provides increased retention of unsaturated FAME isomers (Figures 2–3)

Ordering Information

Description	Cat. No.
SP-2560, 200 m × 0.25 mm I.D., 0.20 μm	29688-U
SLB-IL111, 200 m × 0.25 mm I.D., 0.20 μm	29689-U

Reference

1. FDA Cuts *Trans* Fat in Processed Foods. <http://www.fda.gov/ForConsumers/ConsumerUpdates/ucm372915.htm> (accessed August 18, 2015)

Related Information

Additional chromatograms, product information, real-time availability, and ordering information is available 24 hours at

sigma-aldrich.com/gc-food

Figure 1. C18:0, C18:1, C18:2, and C18:3 FAME Isomers

column: SP-2560, 200 m × 0.25 mm I.D., 0.20 μm (29688-U)
 column: SLB-IL111, 200 m × 0.25 mm I.D., 0.20 μm (29689-U)
 oven: 175 °C (SP-2560), 150 °C (SLB-IL111)
 inj. temp.: 250 °C
 carrier gas: hydrogen
 detector: FID, 250 °C
 injection: 1.0 μL, 50:1 split
 liner: 4 mm I.D., split type, cup design
 sample: Mix of C18:0, C18:1 (from partially hydrogenated vegetable oil [PHVO]), C18:2, and C18:3 FAME isomers

- | | | |
|---------------|---------------|----------------------|
| 1. C18:0 | 14. C18:1Δ14t | 27. C18:2Δ9t,12t |
| 2. C18:1Δ4t | 15. C18:1Δ6c | 28. C18:2Δ9c,12t |
| 3. C18:1Δ5t | 16. C18:1Δ7c | 29. C18:2Δ9t,12c |
| 4. C18:1Δ6t | 17. C18:1Δ8c | 30. C18:2Δ9c,12c |
| 5. C18:1Δ7t | 18. C18:1Δ15t | 31. C18:3Δ9t,12t,15t |
| 6. C18:1Δ8t | 19. C18:1Δ9c | 32. C18:3Δ9t,12t,15c |
| 7. C18:1Δ4c | 20. C18:1Δ10c | 33. C18:3Δ9t,12c,15t |
| 8. C18:1Δ5c | 21. C18:1Δ11c | 34. C18:3Δ9c,12c,15t |
| 9. C18:1Δ9t | 22. C18:1Δ12c | 35. C18:3Δ9c,12t,15t |
| 10. C18:1Δ10t | 23. C18:1Δ13c | 36. C18:3Δ9c,12t,15c |
| 11. C18:1Δ11t | 24. C18:1Δ16t | 37. C18:3Δ9t,12c,15c |
| 12. C18:1Δ12t | 25. C18:1Δ14c | 38. C18:3Δ9c,12c,15c |
| 13. C18:1Δ13t | 26. C18:1Δ15c | |

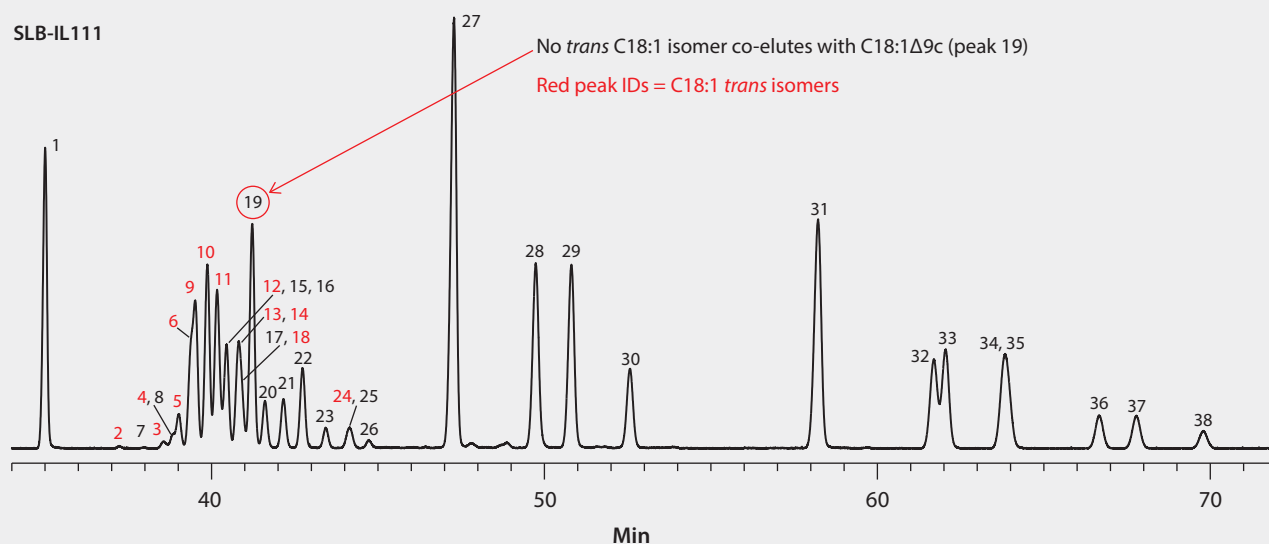
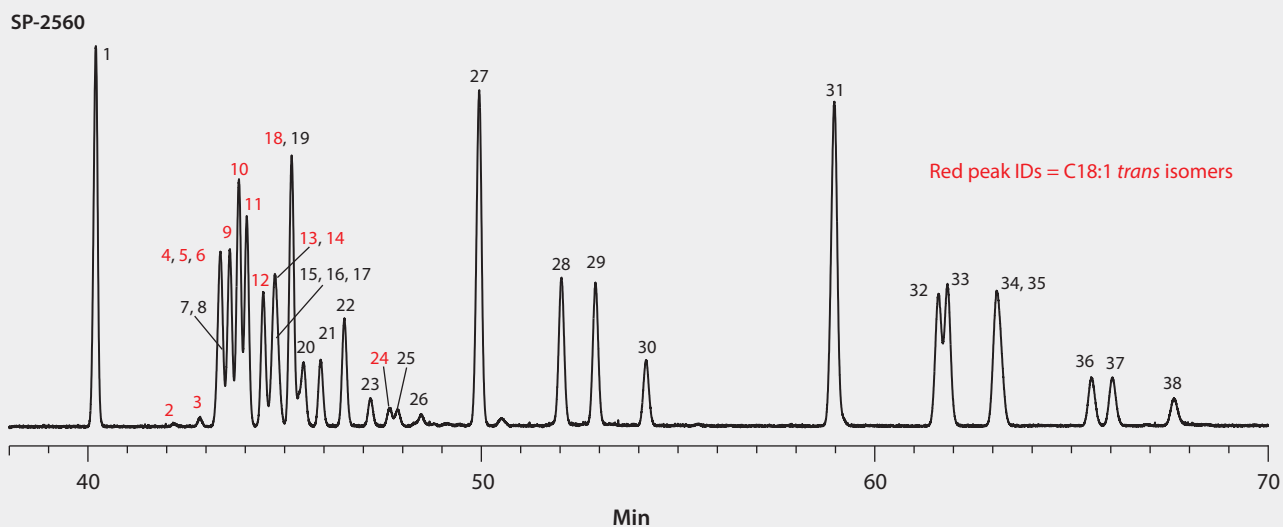


Figure 2. 38-Component FAME Isomers

column: SP-2560, 200 m × 0.25 mm I.D.,
 0.20 μm (29688-U)
 column: SLB-IL111, 200 m × 0.25 mm I.D.,
 0.20 μm (29689-U)
 oven: 100 °C (13 min), 4 °C/min
 to 240 °C (30 min)
 inj. temp.: 250 °C
 detector: FID, 250 °C
 carrier gas: hydrogen, 27 cm/sec
 injection: 1.0 μL, 50:1 split
 liner: 4 mm I.D., split type, cup design
 sample: Supelco 37-Component FAME Mix
 (47885-U) + C22:5n3 FAME

- | | |
|--|---|
| 1. Butyric Acid Methyl Ester (C4:0) | 21. γ-Linolenic Acid Methyl Ester (C18:3n6) |
| 2. Caproic Acid Methyl Ester (C6:0) | 22. α-Linolenic Acid Methyl Ester (C18:3n3) |
| 3. Caprylic Acid Methyl Ester (C8:0) | 23. Arachidic Acid Methyl Ester (C20:0) |
| 4. Capric Acid Methyl Ester (C10:0) | 24. <i>cis</i> -11-Eicosenoic Acid Methyl Ester (C20:1n9) |
| 5. Undecanoic Acid Methyl Ester (C11:0) | 25. <i>cis</i> -11,14-Eicosadienoic Acid Methyl Ester (C20:2) |
| 6. Lauric Acid Methyl Ester (C12:0) | 26. <i>cis</i> -8,11,14-Eicosatrienoic Acid Methyl Ester (C20:3n6) |
| 7. Tridecanoic Acid Methyl Ester (C13:0) | 27. <i>cis</i> -11,14,17-Eicosatrienoic Acid Methyl Ester (C20:3n3) |
| 8. Myristic Acid Methyl Ester (C14:0) | 28. Arachidonic Acid Methyl Ester (C20:4n6) |
| 9. Myristoleic Acid Methyl Ester (C14:1) | 29. <i>cis</i> -5,8,11,14,17-Eicosapentaenoic Acid Methyl Ester (C20:5n3) |
| 10. Pentadecanoic Acid Methyl Ester (C15:0) | 30. Heneicosanoic Acid Methyl Ester (C21:0) |
| 11. <i>cis</i> -10-Pentadecenoic Acid Methyl Ester (C15:1) | 31. Behenic Acid Methyl Ester (C22:0) |
| 12. Palmitic Acid Methyl Ester (C16:0) | 32. Erucic Acid Methyl Ester (C22:1n9) |
| 13. Palmitoleic Acid Methyl Ester (C16:1) | 33. <i>cis</i> -13,16-Docosadienoic Acid Methyl Ester (C22:2) |
| 14. Heptadecanoic Acid Methyl Ester (C17:0) | 34. <i>cis</i> -7,10,13,16,19-Docosapentaenoic Acid Methyl Ester (C22:5n3) |
| 15. <i>cis</i> -10-Heptadecenoic Acid Methyl Ester (C17:1) | 35. <i>cis</i> -4,7,10,13,16,19-Docosahexaenoic Acid Methyl Ester (C22:6n3) |
| 16. Stearic Acid Methyl Ester (C18:0) | 36. Tricosanoic Acid Methyl Ester (C23:0) |
| 17. Oleic Acid Methyl Ester (C18:1n9c) | 37. Lignoceric Acid Methyl Ester (C24:0) |
| 18. Elaidic Acid Methyl Ester (C18:1n9t) | 38. Nervonic Acid Methyl Ester (C24:1n9) |
| 19. Linoleic Acid Methyl Ester (C18:2n6c) | |
| 20. Linolelaidic Acid Methyl Ester (C18:2n6t) | |

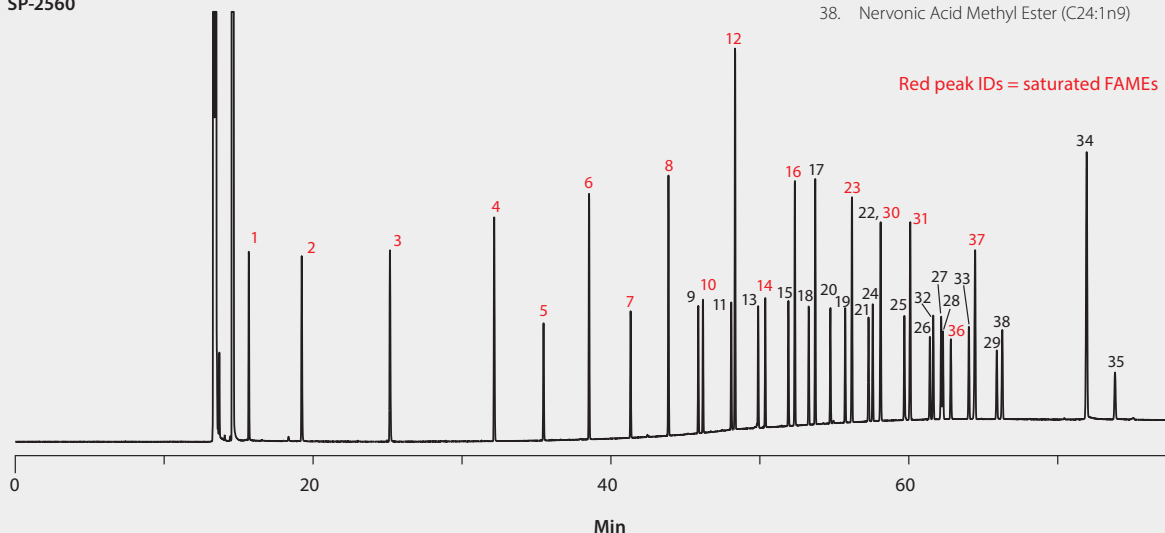
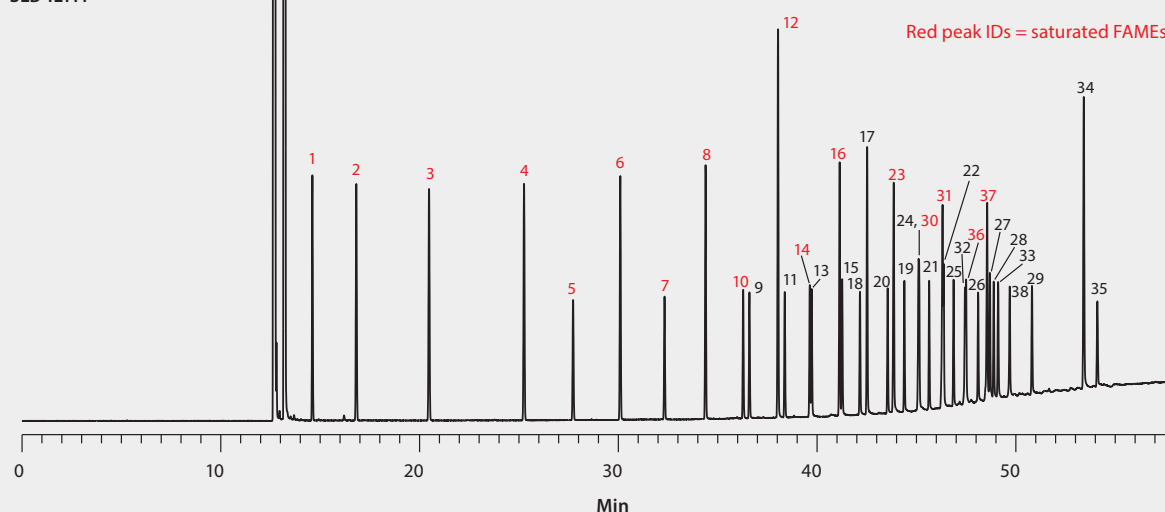
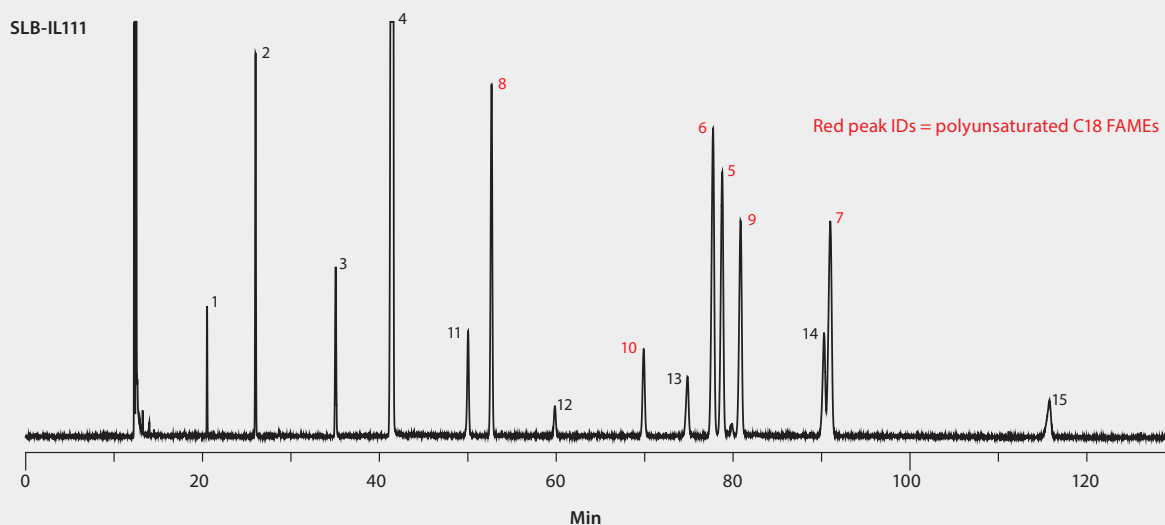
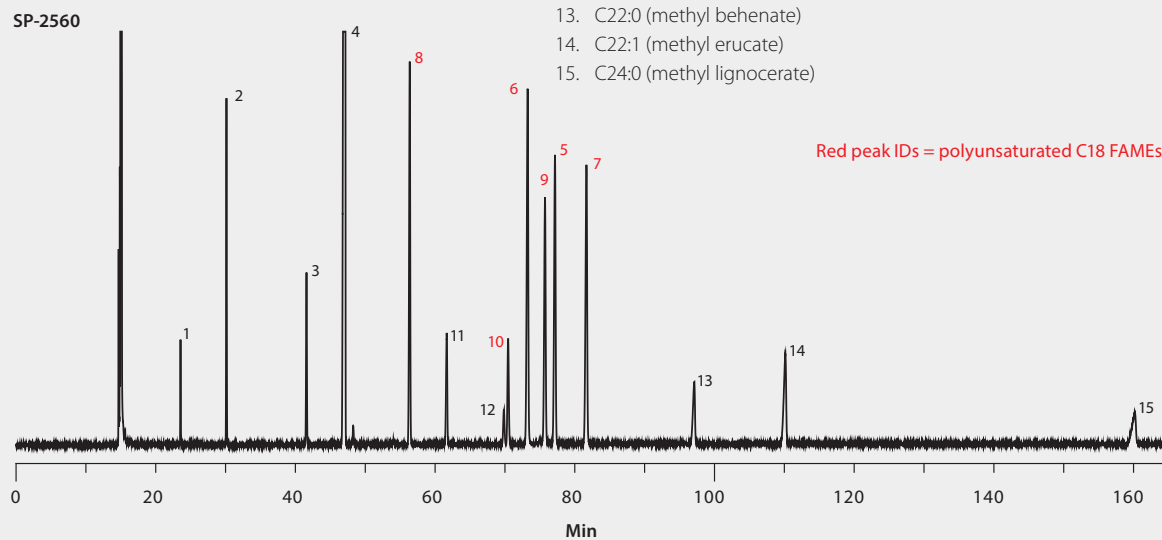
SP-2560

SLB-IL111


Figure 3. Rapeseed Oil FAMES with CLA FAME Isomers

column: SP-2560, 200 m × 0.25 mm I.D., 0.20 μm (29688-U)
 column: SLB-IL111, 200 m × 0.25 mm I.D., 0.20 μm (29689-U)
 oven: 175 °C (SP-2560), 150 °C (SLB-IL111)
 inj. temp.: 250 °C
 carrier gas: hydrogen
 detector: FID, 250 °C
 injection: 1.0 μL, 50:1 split
 liner: 4 mm I.D., split type, cup design
 sample: Mix of rapeseed oil FAME isomers and CLA FAME isomers

1. C14:0 (methyl myristate)
2. C16:0 (methyl palmitate)
3. C18:0 (methyl stearate)
4. C18:1n9c (methyl oleate)
5. C18:2Δ9t,11t (methyl 9-*trans*,11-*trans* octadecadienoate)
6. C18:2Δ9t,11c (methyl 9-*trans*,11-*cis* octadecadienoate)
7. C18:2Δ9c,11c (methyl 9-*cis*,11-*cis* octadecadienoate)
8. C18:2n6c,9c (methyl linoleate)
9. C18:2Δ10c,12t (methyl 10-*cis*,12-*trans* octadecadienoate)
10. C18:3n3c,6c,9c (methyl linolenate)
11. C20:0 (methyl arachidate)
12. C20:1 (methyl eicosenoate)
13. C22:0 (methyl behenate)
14. C22:1 (methyl erucate)
15. C24:0 (methyl lignocerate)



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+1 502-548-7238

James Houghton: Edible Fat
Jack M. Stearns: Edible Fat,
trans Fatty Acid Content

Adams Vegetable Oils, Inc.

Arbuckle, CA 95912 USA
+1 530-668-2072

Abdul Bath: Gas
Chromatography

Admiral Testing Services, Inc.

Luling, LA 70070 USA
+1 985-785-8302

Renato M. Ramos: Oilseed
Meal, Unground Soybean
Meal, Soybean, Soybean Oil,
NIOP Fats and Oils, Aflatoxin
in Corn Meal (test kit)
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North Little Rock, AR 72114
USA
+1 501-771-4255

**Michael White, Brian
Eskridge:** Oilseed Meal,
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Soybean Oil, Aflatoxin
in Cornmeal (test kit),
Phosphorus in Oil

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Celaya GTO 38024 Mexico
+52-01-461-6143504

Fernando Alberto Leon Cruz:
Unground Soybean Meal

Bakels Edible Oils Ltd.

Mount Maunganui 3116
New Zealand
+64 7 9272443

Joy Thompson: Gas
Chromatography

Barrow-Agee Laboratories, Inc.

Memphis, TN 38116 USA
+1 901-332-1590

Joshua Bogan: Oilseed
Meal, Unground Soybean
Meal

Michael Hawkins: Oilseed
Meal, Unground Soybean
Meal, Soybean Oil
www.balabs.com

Barry Callebaut

Pennsauken, NJ 08110 USA
+1 856-486-9978

Joseph Maher: Edible Fat,
Gas Chromatography, trans
Fatty Acid Content,
Solid Fat Content by NMR

BASF A/S

Ballerup 2750 Denmark
+45 29 49 30 50

Maïke Timm Heinrich:
AOCS/GOED Nutraceuical
Oils

Bayer CropScience

Saskatoon, SK S7K 3J9
Canada
+1 306-477-9443

Rudy Fulawka: Gas
Chromatography

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Sanutprakarn 10130
Thailand

+66 2 816 5011
Benjaporn Chatchoochaikul:
Fishmeal
www.betagro.com

Blue Diamond Growers

Sacramento, CA 95811 USA
+1 916-329-3311

Donna Dean-Zavala:
Aflatoxin in Almond

Bunge Oils

Bradley, IL 60915 USA
+1 815-523-8148

Bunge Analytical

Team: Edible Fat, Gas
Chromatography, trans Fatty
Acid Content

California Olive Oil Council (COOC)

Berkeley, CA 94707 USA
+1 888-718-9830

Dean Wilkinson: Olive Oil
Sensory Panel
www.cooc.com

Callaghan Innovation

Lower Hutt 5040 New
Zealand
+64 4 931 3310

Andrew Callaghan: Marine
Oil Fatty Acid Profile
www.callaghaninnovation.govt.nz

Caloy Company LP

Denair, CA 95316 USA
+1 209-874-3381

Nicole Silva: Gas
Chromatography,
Phosphorus in Oil
www.caloyoil.com

Campi Alimentos S.A. de C.V.

Merida, Yucatan 97288
Mexico

+999 40000023

Ana L. Pomar Casares:
Unground Soybean Meal

Canadian Grain Commission

Winnipeg, MB R3C 3G8
Canada

+1 204-983-3354

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Meal, Soybean

Carolina Analytical Services, LLC

Bear Creek, NC 27207 USA
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Stewart:** Oilseed Meal
www.caslabslc.com

Carribex S.A.

Port-Au-Prince Ouest HT
6110 Haiti
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Carl-Henri Cénafils: Palm Oil

Certispec Services, Inc.

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Canada
+1 604-469-9180

Cipriano Cruz: NIOP Fats and
Oils
www.certispec.com

CFIA (Canadian Food Inspection Agency)
Ottawa, ON K1A 0C6 Canada
+1 613-759-1269
Angela Sheridan: Gas Chromatography

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Monopoli, BA 70043 Italy
+39 080 742 777
Georgio Cardone: Olive Oil Part A & B, Olive Oil Sensory Panel

Commodity Inspection Services
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Cumberland Valley Analytical Services
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+1 301-790-1980
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Jeffersonville, IN 47130 USA
+1 812-283-6675
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Darling Analytical Laboratories
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+1 515-289-3718
Shirley Elliott: Tallow and Grease, Gas Chromatography

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River Falls, WI 54022 USA
+1 715-426-0246
Aaron Taylor: Gas Chromatography
Joseph Zalusky: Gas Chromatography
www.eurofinsus.com/biodiagnostics

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+1 504-297-3420
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Keith Persons, Brian Gilchrist: Edible Fat, Tallow and Grease, Cholesterol, AOCS/GOED Nutraceutical Oils, Marine Oil, Marine Oil Fatty Acid Profile, trans Fatty Acid Content, Nutritional Labeling
Anders Thomsen: Edible Fat, Tallow and Grease, Oilseed Meal, Unground Soybean Meal, Soybean, Cholesterol, Fish Meal, AOCS/GOED Nutraceutical Oils, Marine Oil Fatty Acid Profile, Soybean Oil, Aflatoxin in Corn Meal (test kit), Nutritional Labeling

Exact Scientific
Ferndale, WA 98248 USA
+1 360-733-1205
Jamie Barkley: Marine Oil Fatty Acid Profile, Specialty Oils
www.exactscientific.com

Fieldale Farms Corp.
Baldwin, GA 30511 USA
+1 706-778-5100
Janet Smith: Oilseed Meal, Aflatoxin in Corn Meal (test kit)

Fuji Vegetable Oil, Inc.
Savannah, GA 31408 USA
+1 912-433-5331
Gregg Newman: trans Fatty Acid Content, Edible Fat

GC Rieber Oils AS
Kristiansund N 6512 Norway
+47 71683000
Analytical Team: AOCS/GOED Nutraceutical Oils
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San Jose 3657-1000 Costa Rica
+506 2284-1192
Ricardo Arevalo: Gas Chromatography, trans Fatty Acid Content, Trace Metals in Oil, Solid Fat Content by NMR
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In Con Processing
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+1 630-761-1180
Christopher Stefan: DDGS from Cornmeal

Indelab SDN BHD
Port Klang, Selangor 42000 Malaysia
+60 3-3167 6929
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Lidieth Solera Carranza: Edible Fat, Unground Soybean Meal, Soybean
Josue Nunez Moya: Unground Soybean Meal, Soybean, Soybean Oil, trans Fatty Acid Content
Jesus Gomez Salgado: Edible Fat, Unground Soybean Meal, trans Fatty Acid Content, Soybean

Inspectorate America
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+1 713-451-2121
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Sandra Holloway: Aflatoxin in Cornmeal (test kit)
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Tuyen Mai: Oilseed Meal, Soybean, Gas Chromatography, NIOP Fats and Oils, DDGS from Cornmeal, Aflatoxin in Cornmeal (test kit)

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Odessa 65003 Ukraine
+38 0487202475
Irina Kushnir: Palm Oil
www.intertek.com

Intertek Testing Services
Saskatoon, SK S7N 3R2
Canada

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Tetiana Tseona: Oilseed Meal

Isotek, LLC

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USA

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+1 901-525-0519

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Unground Soybean Meal

Land O'Lakes

Arden Hills, MN 55112 USA

+1 651-375-1586

Julie Honsa: Edible Fat, Gas
Chromatography, trans Fatty
Acid Content

Lysi hf

Reykjavik 101 Iceland

+354 525-8100

Arnar Halldorsson: AOCS/
GOED Nutraceutical Oils,
Marine Oil, Marine Oil Fatty
Acid Profile
www.lysi.com

**Malaysian Palm Oil Board,
AOTD**

Selangor 43000 Malaysia

+603-8769-4288

Ms. Hajar Musa: Palm Oil,
Gas Chromatography, trans
Fatty Acid Content

Merieux Nutrisciences

Markham, ON L3R 5V5

Canada

+1 905-305-2218

Jocelyn Alfieri: Cholesterol,
Gas Chromatography,
Marine Oil FAP, Specialty
Oils, trans Fatty Acid
Content, Aflatoxin in Peanut
Paste (test kit), Nutritional
Labeling

**Modern Olives Laboratory
Services**

Lara, VIC 3212 Australia

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Claudia Guillaume: Olive
Oil (Parts A, B), Olive Oil
Sensory Analysis

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Services**

Woodland, CA 95776 USA

+1 530-669-6921

Natalie Ruiz: Olive Oil Part A

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Oil Sensory Panel
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National Beef

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Mike Clayton: Tallow and
Grease

**National Beef Packing
Company**

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+1 620-626-0646

Sherry Robertson: Tallow
and Grease
www.nationalbeef.com

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+1 609-882-6800

Pete Cartwright: Oilseed
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**NSW Department of
Primary Industries**

Wagga Wagga, NSW 2650

Australia

+61 02-69381-818

Jamie Ayton: Gas
Chromatography, Olive Oil
(Part A, B), trans Fatty Acid
Content

NSF INASSA S.A.C

Lima 32 Peru

+51-1-616-5200

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Altona North VIC 3025

Australia

Nathaniel Irving: Marine Oil
Fatty Acid Profile

Nutegrity-Omega Protein

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USA

+1 630-220-1119

Rita Kazmi: Marine Oil

**Olam Food Ingredients
UK, LTD**

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Kingdom

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Ingredients: Gas

Chromatography

Olvea Fish Oils

Saint Leonard 76400 France

+33 1 35 29 28 54

Melanie Delvaux: Marine
Oil Fatty Acid Profile

Omega Protein, Inc.

Houston, TX 77040 USA

+1 713-574-7190

Holly Edwards: Marine Oil
Fatty Acid Profile

Juan Li: Marine Oil

http://omegaprotein.com

**Omega Protein, Inc.—
Health and Science Center**

Reedville, VA 22539 USA

+1 804-453-3830

Otelia Robertson: Marine
Oil, Marine Oil Fatty Acid
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Nancy Roman: Marine Oil

Melissa V. Thrift: Marine Oil

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+1 270-686-6628

OGEO Lab: Soybean Oil,
trans Fatty Acid Content

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Baltimore, MD 21224 USA

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Parts (A, B), Olive Oil
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www.pompeian.com

POS Bio Sciences

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+1 306-978-2866

Angie Johnson: Oilseed
Meal, Cholesterol, Marine
Oil Fatty Acid Profile,
trans Fatty Acid Content,
Phosphorus in Oil

PT Musim Mas

North Sumatra 20371

Indonesia

+62 61 6871123

Goh Tiam Huat: Gas
Chromatography, Trace
Metals in Oil, Palm Oil,
Solid Fat Content by NMR,
trans Fatty Acid Content,
Phosphorus in Oil

PT Sukses

BVersana Surveyor

Indonesia

Medan, Sumatera Utera

20119 Indonesia

+62 61 8881 3225

Martua Saragih: Palm Oil

Richardson Oilseed

Lethbridge AB T1H 6P5
Canada
+1 403-329-5537

Adel Ghabour: Edible Fat,
Gas Chromatography, Trace
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for Color Only, Phosphorus
in Oil

Richardson Oilseed

Yorkton, SK S3N 2X3 Canada
+1 306-828-2255

Eoin Moloney: Edible
Fat, Trace Metals in Oil,
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www.richardson.ca

Russell Marine Group—PNW, LLC

Portland, OR 97210 USA
+1 503-224-9325

Robert Carr: Oilseed Meal,
Soybean

Sanimax-ACI, Inc.

Levis, QC G6X 2L9 Canada
+1 418-832-4645

Jean-Francois Harvey:
Tallow and Grease

Sanimax San

Montreal, QC H4C 2P4
Canada
+1 514-648-6001

Montreal Analytical Team:
Tallow and Grease
www.sanimax.com

SDK Laboratories

Hutchinson, KS 67502 USA
+1 620-665-5661

Dennis Hogan: Tallow
and Grease, Aflatoxin in
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from Cornmeal
www.sdklabs.com

Select Supplements, Inc.

Carlsbad, CA 92008 USA
+1 760-431-7509

**Kristin Dershem, Irene
Nguyen:** Marine Oil Fatty
Acid Profile

Ser-Agro S.A.

Chinandega Nicaragua
+505 2340-3493

Norma Hernandez: Peanut,
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Setton Pistacho of Terra Bella

Terra Bella, CA 93270 USA
+1 559-535-6050

Wendy Keith: Aflatoxin in
Pistachio and Almond
www.settonfarms.com

SGS Canada

Burnaby, BC V5A 4W4
Canada
+1 604-638-2349

Cathy Sun: Oilseed Meal,
Soybean Oil

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+1 281-478-8181

Aaron K. Jusko: Oilseed
Meal, NIOP Fats and Oils

SGS North America

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William Spence: Oilseed
Meal, Olive Oil (Part A),
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Adam Powell: Aflatoxin in
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Eddie L. Baldwin, Helen

Cianciolo, Derek Gumm:
Gas Chromatography, trans
Fatty Acid Content, Solid Fat
Content by NMR, Edible Fat
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Kong Khim Chong: Palm Oil

Texas A&M Agrilife Research

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Anne Muiruri: Aflatoxin in
Cornmeal (test kit)
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The FDA's new guidance for voluntary sodium reduction: worthwhile, or taken with a grain of salt?

Olio is an Inform column that highlights research, issues, trends, and technologies of interest to the oils and fats community.

Laura Cassiday

On June 1, 2016, the US Food and Drug Administration (FDA) issued a draft guidance for voluntary sodium reduction (<http://tinyurl.com/FDA-salt-guidance>). The document calls on food manufacturers and restaurants to help reduce Americans' average daily sodium intake 11.8% over 2 years, and an additional 23.3% in 10 years, by formulating lower-salt versions of 150 processed and prepared foods. The guidelines, although voluntary at this time, present additional challenges to formulators, many of whom are already striving to reduce fat and sugar in their products. Like fat, salt has long been vilified as a key contributor to cardiovascular disease. However, some studies have questioned whether population-wide salt reduction strategies will actually impact the incidence of cardiovascular disease.

Salt, or sodium chloride, consists of 40% sodium and 60% chloride by weight. On average, Americans consume 3,400 mg of sodium per day—almost 50% more than the 2,300 mg recommended by the US Dietary Guidelines. However, sodium intake by Americans is not particularly high compared with other regions of the world, notably Eastern Europe (4,180 mg/day) and Central Asia (5,510 mg/day) (Powles, J., *et al.*, <http://dx.doi.org/10.1136/bmjopen-2013-003733>, 2015). Worldwide, the average estimated sodium intake in 2010 was 3,950 mg/day. In the US and Europe, most sodium comes from processed and prepared foods, whereas in many Asian countries, soy sauce and salt added during cooking are the primary sources.

Sodium plays important roles in the human body, such as maintaining cell membrane potential, blood volume, and blood pressure. However, too much sodium in the diet has been linked with elevated blood pressure, which is a major risk

factor for cardiovascular disease. As early as 1960, researchers observed an apparently linear relationship between daily salt intake and the prevalence of hypertension (Elliott, P., and Brown, I., <http://tinyurl.com/WHO-salt>, 2007). Populations that consume very little salt, such as Alaskan Eskimos, had essentially no high blood pressure, whereas those that consumed high levels of salt, such as Northern Japan (up to 10,600 mg/day sodium) had a high prevalence of hypertension (up to 40% of the population). Indeed, in patients with existing hypertension, reducing dietary sodium typically lowers blood pressure.

The link between sodium and cardiovascular disease is less clear. Some studies have found that sodium intake correlates with cardiovascular disease risk, whereas others have not. A 2013 report commissioned by the US Centers for Disease Control and Prevention found insufficient scientific rationale for reducing sodium levels below 2,300 mg/day



(Strom, B. L., *et al.*, <http://tinyurl.com/salt-CDC>). Some studies have even found evidence of harm for reduced sodium intake. For example, a 2016 *Lancet* study that examined health records of more than 130,000 subjects with both normal and high blood pressure in 49 countries concluded that the prevalence of heart disease, stroke, and death were higher among those on a low-salt diet (less than 3,000 mg/day) than a moderate-salt diet (4,000–5,000 mg/day) (Mente, A., *et al.*, [http://dx.doi.org/10.1016/S0140-6736\(16\)30467-6](http://dx.doi.org/10.1016/S0140-6736(16)30467-6)). Reducing sodium can boost triglyceride levels, insulin resistance, and the activity of the sympathetic nervous system, all of which can increase cardiovascular disease risk. However, critics claim that studies finding adverse effects of low-sodium diets suffer from methodological errors (Cogswell, M. E., *et al.*, <http://dx.doi.org/10.1056/NEJMs1607161>, 2016).

In some respects, the salt story parallels that of saturated fat. Saturated fat has long been maligned for raising total cholesterol levels, although many studies have failed to find an association between saturated fat intake and cardiovascular disease (likely due to its propensity to raise “good” cholesterol, or HDL). Likewise, sodium appears to increase blood pressure, a risk factor for cardiovascular disease, but perhaps does not promote cardiovascular disease itself.

A 2011 article in *Scientific American*, entitled “It’s time to end the war on salt,” is reminiscent of similar stories on saturated fat: Early animal and epidemiological studies implicated salt in cardiovascular disease, but recent studies have failed to uphold, or have even overturned, the link (Wenner Moyer, M., <http://tinyurl.com/SciAm-salt>). The author of this article points to research showing that low-salt diets, compared with normal-salt diets, would have the effect of lowering blood pressure in healthy people only very slightly—like going from 120/80 to 119/79. Only a small percentage of the population that is hypersensitive to salt may realize greater benefits. Despite the tenuous link between sodium intake and cardiovascular disease, the FDA conjectures in its draft guidance that “lowering US sodium intake by about 40 percent [to below

Information

Cogswell, M. E., *et al.* (2016) “Dietary sodium and cardiovascular disease risk—measurement matters.” *N. Engl. J. Med.*, e-published ahead of print. <http://dx.doi.org/10.1056/NEJMs1607161>

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Strom, B. L., *et al.* (2013) “Sodium intake in populations: assessment of evidence.” The National Academies Press. <http://tinyurl.com/salt-CDC>

Wenner Moyer, M. (2011) “It time to end the war on salt.” *Scientific American*, July 8, 2011. <http://tinyurl.com/SciAm-salt>

2,300 mg] over the next decade could save 500,000 lives and nearly \$100 billion in healthcare costs.”

The FDA’s new guidance will challenge formulators to reduce salt in processed foods without increasing fat and sugar to improve consumer acceptance. The document states that, in addition to monitoring the prevalence of sodium in the food supply, “to avoid the potential for unintended consequences, we plan to monitor the levels of other nutrients (e.g., added sugars and saturated fat); such monitoring will be done by, for example, consulting product nutrition information and ingredient lists to ensure that no broad trends emerge that negatively affect the nutritional quality of the foods.” Instead of drastic sodium reductions, the FDA recommends small reductions in a variety of foods, with the net result of lowering sodium in the US population’s diet. Over time, as consumers’ taste buds adjust to lower-sodium products, further reductions can be made. The guidance includes both a short-term (2-year) sodium target of 3,000 mg/person/day, and a long-term (10-year) target of 2,300 mg/person/day.

Salt serves multiple purposes in food, including taste, texture, stability, and preservation. Some options for replacing salt include savory herbs and spices, salt blends, or other flavorings or aroma compounds. Also, changing the structure of a food or of the salt crystals may allow quicker sodium release from a food and increased salt perception (Kloss, L., *et al.*, <http://dx.doi.org/10.1016/j.nfs.2015.03.001>, 2015). To maintain shelf life, substantial sodium reductions may require the addition of other antimicrobial agents, such as organic acids or potassium chloride.

Many food companies have already invested in sodium-reduction initiatives. Between 2007 and 2012, Mars reduced sodium in its products by 25%, and has pledged to cut an additional 20% by 2021. With the help of the Nestlé Nutritional Profiling System (NNPS), a product reformulation tool, Nestlé has reduced sodium by an average of 10% in 250 products,

without increasing sugar or fat. “When reducing salt content in our products that do not yet meet [our] criteria, we typically start with a gradual reduction,” says Kirsteen Rodger, R&D External Senior Communication Specialist at Nestlé. “A second approach we apply systematically is the culinary reformulation of our products. Here, our chefs use their expertise to compensate for reduced salt content by selecting and optimizing the best ingredients to rebalance the taste profile, for example, with the addition of spices.” Rodger says that Nestlé welcomes the FDA’s voluntary sodium reduction guidelines, which “can create a meaningful reduction in population sodium intake over time and help consumer taste preferences adjust.”

Olio is produced by Inform’s associate editor, Laura Cassiday. She can be contacted at laura.cassiday@aocs.org.



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Walmart releases high-priority chemical list

Regulatory Review is a regular column featuring updates on regulatory matters concerning oils- and fats-related industries.

Kelly Franklin

In July, US giant retailer Walmart revealed a list of eight “high priority chemicals (HPCs)” that it has been targeting to phase out from products on its shelves.

The announcement came three months after Walmart reported that it had achieved a 95% by weight reduction of these HPCs from certain products sold in US locations.

The HPCs were selected from Walmart’s broader list of priority chemicals, and were identified by such criteria as listing status on authoritative hazard lists, high volume of use and exposure, and consideration of emerging regulations and stakeholder concern.

The HPCs, identified for suppliers to phase out, are:

- toluene;
- dibutyl phthalate (DBP);
- diethyl phthalate (DEP);
- nonylphenol ethoxylates (NPEs, encompassing nine individual Cas numbers);
- formaldehyde;
- butylparaben;
- propylparaben; and
- triclosan (except when present as an active ingredient providing therapeutic benefit, and approved by the FDA New Drug Application process).

In addition to revealing the eight chemicals, Walmart disclosed chemical volume reduction figures and details around ingredient transparency efforts.

Walmart launched its policy on sustainable chemistry in consumables in 2013. It seeks to reduce or eliminate the use of chemicals of concern from personal care, paper, cleaning, and pet and baby products it sells, covering approximately 90,000 individual products from 700 suppliers.

Zach Freeze, Walmart director of sustainability, told *Chemical Watch* that the company initially elected to withhold the identity of the HPCs to give suppliers time to reformulate products. But he said that with suppliers having made “such significant progress,” the company decided to increase transparency to recognize those efforts.

The company is “very proud” of the progress its suppliers and products have made, he added.

Environmental Defense Fund’s (EDF) Michelle Mauthe Harvey said: “Walmart is the one company in the world that could drive over 11,500 tons—23m pounds—of chemicals out of so much product in less than 24 months.”

The NGO has worked closely with the company to develop and implement its chemicals management plan.

WORK REMAINS

The company’s recently released data showed that 15% of products covered by its program still contain HPCs, and 39% of suppliers are still using substances from the list.

Additionally, more than two thirds of covered products contain priority chemicals, and some 80% of suppliers covered by the policy still use listed chemicals.

Harvey acknowledged that more work remains to be done, but that Walmart deserves credit for its accomplishments.

“The business case can be thin to none,” said Harvey. “When you talk about chemicals, people’s eyes glaze over—or they panic. Few-to-no marketing wins exist here.”

She told *Chemical Watch* that to maintain its momentum, Walmart should “keep up the pressure to meet its current commitments, expand into more product categories, and take this effort global.” The NGO also hopes that the company will:

- meet its commitments to expand products certified under Safer Choice;
- offer “more meaningful” ingredient disclosure;
- fully eliminate HPCs, through sharing supplier success stories and working across the supply chain to identify issues hindering their widespread elimination; and
- strengthen monitoring to ensure hazardous ingredients are not replaced with “regrettable substitutions.”

“Publicizing the journey is also important,” added Harvey. “We need Walmart’s leadership on chemicals to continue to resonate with the public and provide an incentive for other retailers to follow Walmart’s lead.”

The company announced that it will continue to encourage and work with suppliers to disclose ingredients in all the markets, where they operate—beyond just the United States—“as we believe everyone should have access to information about their products.”

Kelly Franklin is editor, North America, for Chemical Watch.

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Can doughnuts survive PHO replacement?

The results of a deep-frying study conducted by Qualisoy in collaboration with Stratas Foods LLC demonstrated that they will.

Reproducing the characteristically delicious color, texture, mouthfeel, and shelf-life of doughnuts fried in partially hydrogenated oils (PHO) is not easy. In 2013, doughnuts topped *Time* magazine's list of "The 7 foods that won't be the same if trans fats are banned." (<http://healthland.time.com/2013/11/07/7-foods-that-wont-be-the-same-if-trans-fats-are-banned/>). Why?

Partial hydrogenation makes vegetable oil more stable during frying and storage, which extends both its frying and shelf life. PHO is also semi-solid at room temperature, so the oil is less likely to leach out, or "weep" at room temperature, as happens when doughnuts are fried in oils that are liquid at room temperature. Weeping produces doughnuts with an oily, soggy taste and mouthfeel. It can lead to inconsistent covering of sugar coatings and glazes (or runny frosting), and excessive weeping can result in greasy and stained packaging.

Oil Weeping Averages

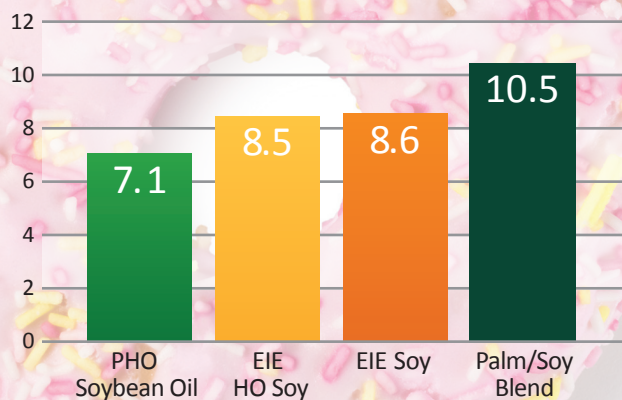


FIG. 1. Oil weeping is when oil leaches out of the doughnut, producing an oily taste and mouthfeel.

Total Polar Materials (%TPM)

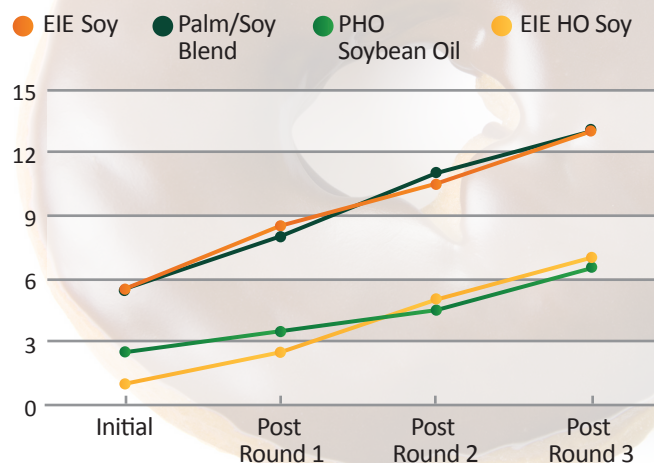


FIG. 2. Total Polar Materials (TPM) measures oil fry life. The TPM percentage rises as the oil is used. Consequently, oils with a lower TPM rise and overall content have a longer fry life.

A cake doughnut deep-frying study performed earlier this year by Qualisoy in collaboration with Stratas Foods LLC compared the performance of a typical PHO soybean doughnut shortening with a palm/soy blend, enzymatically interesterified (EIE) conventional soybean oil, and EIE high-oleic soybean oil. Because the fatty acid profile of EIE high oleic soybean oil is close to that of traditional PHO doughnut shortenings, the belief was that doughnuts fried in the interesterified high-oleic soybean oil would very closely resemble those fried in PHO (since interesterified oils are semi-solid at room temperature), and that its high content of oleic acid would give it stability similar to PHO during frying.

Sure enough, in Total Polar Materials (TPM) testing, the stability of EIE high-oleic soybean oil during frying was similar to PHO and significantly outperformed the other oils (Fig. 1).

EIE high oleic soybean oil was also second only to PHO soybean oil when it came to weeping (Fig. 2), and doughnuts fried in EIE-high oleic soybean oil were closest to those fried in the PHO soybean oil in terms of color, mouthfeel, texture, structure, and uniformity (<http://tinyurl.com/hn7awes>).

According to Frank Flider, an edible oils consultant for Qualisoy, the PHO soybean oil slightly outperformed the others with respect to all measures, but "the small gap between EIE high oleic soybean oil and PHO soybean oil can be closed even further by optimizing the fatty acid profiles prior to interesterification." Ergo, Homer Simpson can continue to say, "Mmmmm...doughnuts."



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Uruguayan Cheeses Rich in Conjugated Linoleic Acid (CLA)

Leslie Kleiner

Conjugated linoleic acid (CLA) is of current interest due to its associated health benefits. Consequently, milk from pasture-fed cattle (cow, sheep, and goats)—which is naturally rich in CLA—is also of interest. To learn more about CLA-rich cheese from Uruguayan pasture-fed cattle, I interviewed Professor Ignacio Vieitez from the Laboratorio de Grasas y Aceites, Facultad de Química, Universidad de la República, Uruguay.


Q: What are conjugated linoleic acid (CLA) and trans-vaccenic acid (TVA), and how are they produced in nature?

It is well-established that some trans fatty acids are generated from dietary lipids by partial biohydrogenation under “natural” conditions in the rumen. This process is responsible for the occurrence of up to 18 isomers of conjugated linoleic acids (CLA). CLA comprise a family of positional and geometric isomers, all conjugated dienes of linoleic acid (18:2 *cis*-9, *cis*-12). The *cis*-9, *trans*-11 isomer is the most abundant in dairy products (90% of total). CLAs are thus formed as a result of incomplete rumen biohydrogenation, and can therefore be considered natural constituents of milk products and fat from ruminants. Biohydrogenation of unsaturated acids by rumen bacteria first results in the isomerization of *cis*-12 linoleic acid to form the *cis*-9, *trans*-11 isomers (to form 9/11CLA). The second reaction is reduction of the *cis*-9 CLA double bond, and the fatty acid becomes mono-unsaturated with 18 carbons. The structure formed with a single unsaturation, *trans*-11, is vaccenic acid, also termed *trans*-vaccenic acid (TVA).

There is another pathway for formation of 9/11CLA. This reaction takes place in the liver and mammary gland of ruminants. TVA produced in the rumen can be desaturated at carbon 9 by the enzyme $\Delta 9$ -desaturase (forming 9/11CLA). Activity is also found in intestinal, hepatic, and mammary glands, and can convert TVA to CLA. Accordingly, the total content of 9/11CLA in ruminant milk is due to the sum of these two metabolic pathways.

Q: What are the nutritional and health advantages of CLA- and TVA-rich dairy products?

Recently published papers underscore the importance of CLA and link its consumption to anticarcinogenic, antioxidant, and hypocholesterolemic effects, as well as improvement of



Latin America Update is a regular Inform column that features information about fats, oils, and related materials in that region.

the immune system. Therefore, they are different from the trans fatty acids generated industrially via the process of partial hydrogenation of oils, which the US Food and Drug Administration (FDA) removed from the Generally Regarded as Safe (GRAS) status and initiated a phase out period until June 2018. For this reason it is important to differentiate CLA and TVA ("natural" trans fatty acids) from trans fats derived from the process of partial hydrogenation. CLA and TVA do not fall under FDA's prohibition.

Q: Uruguay and Argentina are known for pasture-fed cattle. How does a pasture-based diet influence CLA content in cow's milk?

Some factors that influence CLA content in cow's milk are: diet (e.g., the type of pasture and quantity consumed, dietary restrictions, and oil supplements), the environmental condition of the animals (e.g., free in fields, restricted to pens, and so on), breed, and age.

A number of studies have indicated that depending on fat supplementation rations and the availability of pastures (which vary with the seasons), the 9/11CLA content in milk can be significantly increased (e.g., 50% increase). Consequently, we could expect significant variation in the 9/11CLA content in milk from cows arising from different countries.

Q: How do Uruguayan cheeses derived from cow, goat, and sheep's milk compare in terms of CLA and TVA to those produced in other countries?

An emerging perspective from studies performed at the Laboratory of Fats and Oils (Laboratorio de Grasas y Aceites, Facultad de Química, Universidad de la República), is that, in general, the content of TVA and CLA in the milk fat from Uruguayan cow, sheep, and goat is relatively higher than that found in milk studied from other countries of origin.

Despite seasonal variations, analyzed cheeses derived from Uruguayan cow's milk had consistently higher levels of both CLA and TVA than those found in the cheeses from other origins. Uruguayan cheeses derived from goat and sheep's milk, respectively, are also richer in "good" trans fatty acids (TVA + CLA).


Q: Would other dairy products also contain high levels of CLA and TVA?

Higher levels of TVA + CLA could be found in a variety of dairy products from Uruguay and Argentina; an additional example is that of butter made from cow's milk fat.


By extension, the higher levels of these potentially beneficial trans fatty acids in a variety of dairy products from Uruguay and Argentina may be associated with health or nutritional added value for these products.

Latin America Update is produced by Leslie Kleiner, R&D Project Coordinator in Confectionery Applications at Roquette America, Geneva, Illinois, USA, and a contributing editor of *Inform*. She can be reached at LESLIE.KLEINER@roquette.com.








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PATENTS

Human sebum mimetics derived from botanical sources and methods for making the same

Brown, J.S., *et al.*, International Flora Technologies Ltd., US9289373, March 22, 2016

Human sebum mimetics and methods for producing human sebum mimetics are provided. In one exemplary embodiment, a human sebum mimetic comprises a wax ester derived from interesterification of refined botanical oil comprising palmitoleic acid and refined jojoba oil, a phytosterol, and phytosqualene. A method for producing a human sebum mimetic comprises mixing refined macadamia oil and refined jojoba oil, interesterifying the refined macadamia oil and the refined jojoba oil, adding a phytosterol after the interesterifying, and adding phytosqualene after the interesterifying.

Curable and cured compositions

Campbell, C.J., *et al.*, 3M Innovative Properties Co., US9290683, March 22

Curable compositions, cured compositions, and articles that include the cured compositions are described. The curable composition contains a) an epoxy resin, b) a curing agent, c) a reactive liquid modifier, and d) a toughening agent. The reactive liquid modifier is an acetoacetate ester of a polyol that is a vegetable oil, that is prepared from a vegetable oil, or that is a mixture thereof. The cured compositions can be used as adhesives such as structural adhesives or as polymeric coatings.

Reducing astringency in compositions containing phenolic compounds

Bortlik, K. *et al.*, Nestec S.A., US9265276, February 23, 2016

The present invention in general relates to the field of taste. In particular it relates to the reduction of astringency. One embodiment of the present invention relates to the use of at least one phospholipid for the preparation of a phenol containing composition to reduce the astringency of the composition.

Epoxy acid thermoset resins and composites that can be hot-fashioned and recycled

Ludwik, L., *et al.*, Arkema France, Centre Nat. Rech. Scient., US9266292, February 23, 2016

Resins and thermoset composites comprising them, these materials being able to be hot-fashioned. These compositions resulting from placing at least one thermosetting resin precursor,

this thermosetting resin precursor comprising hydroxyl functions and/or epoxy groups, and optionally ester functions, in contact with at least one hardener chosen from carboxylic acids, in the presence of at least one transesterification catalyst whose total molar amount is between 5% and 25% of the total molar amount of hydroxyl and epoxy contained in the thermosetting resin precursor. Process for manufacturing these materials, process for transforming, and process for recycling these materials. New solid forms of resins and of thermoset composites that may be used in the implementation of these processes.

Coating composition and method for the protection of complex metal structures and components used in submerged environments

Fink, T. G. and E. Hall, Oxifree Holdings Corp., US9267040, February 23, 2016

A coating composition for application to a subsea component or structure has cellulose acetate an amount of approximately 47% by weight of the total composition, diisooctyl phthalate in an amount of approximately 17% by weight of the total composition, a fatty acid ester in an amount of approximately 23% by weight of the total composition, a vegetable oil in an amount of approximately 8% by weight of the total composition, a stabilizer and a silica amorphous in which the stabilizer and the silica amorphous are in amount of approximately 5% by weight of the total composition. The stabilizer can be either titanium dioxide or aluminum dioxide. The vegetable oil is canola oil.

Crystal growth inhibitor for fats and oils

Hiroyuki, K., *et al.*, Taiyo Kagaku K.K., US9271512, March 1, 2016

An inhibitor for crystal growth of fats and oils, containing a polyglycerol fatty acid ester, which is an esterified product formed between a polyglycerol and a fatty acid, the polyglycerol having a hydroxyl value of 850 mg KOH/g or less and a ratio of primary hydroxyl groups to all the hydroxyl groups of the polyglycerol of 50% or more, wherein the polyglycerol fatty acid ester has a hydroxyl value of 100 mg KOH/g or less. Since the inhibitor for crystal growth of fats and oils of the present invention can inhibit crystal growth of fats and oils by adding the inhibitor to fats and oils, storage property of the fats and oils in a refrigerator, cold climates, or the like, so that the inhibitor can be suitably used in liquid fats and oils such as salad oil for which transparency is important.

Composition comprising a sucrose ester and a polyglycerol ester

Poletti Mickael, L'Oreal, US9272165, March 1, 2016

Composition containing an aqueous phase, a lipophilic compound and an emulsifying system containing a fatty acid ester of sucrose and a fatty acid ester of polyglycerol, and to its use in the cosmetics field, in particular for cleansing and/or for removing makeup from keratin materials.

Solvent-based coating compositions

Li, C., *et al.*, Akzo Nobel Coatings Int. B.V., US9273226, March 1, 2016

Coating compositions are disclosed. In some embodiments, the coating compositions are used to coat substrates such as packaging materials and the like for the storage of food and beverages. The coating compositions can be prepared by reacting an epoxidized vegetable oil and a hydroxyl functional material in the presence of an acid catalyst to form a hydroxyl functional oil polyol, mixing the hydroxyl functional oil polyol (with or without epoxidized polybutadiene) with a functional polyolefin copolymer to form a mixture, reacting the mixture with an ethylenically unsaturated monomer component in the presence of an initiator to form a graft copolymer, and crosslinking the graft copolymer with a crosslinker to form the coating composition.

Human breast milk lipid mimetic as dietary supplement

Meiri Bendek, I., *et al.*, Enzymotec Ltd., US9282748, March 15, 2016

Disclosed is an enzymatically prepared fat base composition comprising a mixture of vegetable-derived triglycerides, characterized in that it has a total palmitic acid residues content of at most 38% of the total fatty acid residues, and in that at least 60%, preferably 62% of the fatty acid moieties at the sn-2 position of the glycerol backbone are palmitic acid residues, at least 70% of the fatty acid moieties at the sn-1 and sn-3 positions of the glycerol backbone are unsaturated, at least 40%, preferably 40–60%, of the unsaturated fatty acid moieties at the sn-1 and sn-3 positions are oleic acid moieties and at least 6%, preferably 6–17 percent, of the unsaturated fatty acid moieties at the sn-1 and sn-3 positions are linoleic acid moieties, its preparation and its various uses in the field of infant formulas.

Use of a fatty acid composition comprising at least one of EPA and DHA or any combinations thereof

Bryhn, M. and J. Kopecky, Pronova Biocare A. S.; Pronova BioPharma Norge A.S., US9282760, March 15, 2016

A method is disclosed for treatment and prevention of obesity, an overweight condition or for controlling body weight reduction, wherein an effective amount of a fatty acid composition comprising at least one of (all-Z omega-3)-5,8,11,14,17-eicosapentaenoic acid (EPA) and (all-Z omega-3)-4,7,10,13,16,19-docosahexaenoic acid (DHA) or any combinations thereof, is administered to a human or an animal. Additionally, a dietary product is disclosed, containing a fatty acid composition comprising at least one of EPA and DHA or any combinations thereof, for non-medical treatment of obesity, an overweight condition and/or for supporting and controlling body weight reduction. Finally, a method is disclosed for supplementing a dietary product with a fatty acid composition mentioned above.

Conveyor-based frying apparatus and methods of use

Hockett, W.T., *et al.*, ConAgra Foods Lamb Weston Inc., US9282852, March 15, 2016

A fryer can include a base having a reservoir for receiving oil for frying a food product and a hood coupled to the base. The fryer can have an inlet at an upstream section and an outlet at a downstream section. At least one conveyor can move food product from the inlet to the outlet. A first baffle member and second baffle member can be positioned over the conveyor to define a frying chamber there between. The first and second baffle members can restrict air from flowing into the frying chamber from outside of the frying chamber.

Pharmaceutical compositions for local administration

Panzner, S., *et al.*, Marina Biotech Inc., US9283186, March 15, 2016

A pharmaceutical composition for local application is disclosed, said composition comprising a nucleic acid as a therapeutic agent, an excipient and a pharmaceutically acceptable vehicle therefore, said excipient comprising a liposome. The excipient comprises an amphoteric liposome having an isoelectric point between 4 and 7.4 and said composition is formulated to have a pH in the range 3 to 5. The composition may administered in the form of a colloidal suspension and may be buffered to the lower pH at the time of use by the addition of a suitable acidifying means to a substantially neutral suspension of the nucleic acid and excipient that may be more suitable for long-term storage of the composition. Alternatively, the composition may be lyophilised at the lower pH for subsequent reconstitution just prior to use with a suitable aqueous medium, such for example as substantially unbuffered water or saline.

Methods and compositions for improving cognitive function

French, S., *et al.*, Mars Inc., US283203, March 15, 2016

This invention relates to compositions, and methods of use thereof, for (i) enhancing executive cognitive function(s) (for example, decision making, planning, working memory, multitasking, judgment, numerical problem-solving, reading comprehension), and/or (ii) increasing blood flow in brain vasculature, comprising administering to a subject in need thereof, certain polyphenols such as flavanols, procyanidins, or pharmaceutically acceptable salts or derivatives thereof.

Patent information is compiled by Scott Bloomer, a registered US patent agent with Archer Daniels Midland Co., Decatur, Illinois, USA. Contact him at scott.bloomer@adm.com.



10 most-cited 2015 AOCS journal articles

In case you missed them, here are the 10 articles from each of our AOCS journals that received the most citations in 2015. We congratulate the authors and give the editorial team a big round of applause.



Journal of the American Oil Chemists' Society

1. Doan, C.D., D. Van de Walle, K. Dewettinck, and A.R. Patel, Evaluating the oil-gelling properties of natural waxes in rice bran oil: rheological, thermal, and microstructural study
2. Li, Y., D. Wang, and X.S. Sun, Oxirane cleavage kinetics of epoxidized soybean oil by water and UV-polymerized resin adhesion properties
3. Tokay, F. and S. Bagdat, Determination of iron and copper in edible oils by flame atomic absorption spectrometry after liquid-liquid extraction
4. Siyanbola, T.O., *et al.*, Development of functional polyurethane-ZnO hybrid nanocomposite coatings from thevetia peruviana seed oil
5. Wu, Y., A. Li, and K. Li, Pressure-sensitive adhesives based on oleic acid
6. Al-Rimawi, F., Development and validation of a simple reversed-phase HPLC-UV method for determination of malondialdehyde in olive oil
7. Balvardi, M., K. Rezaei, J.A. Mendiola, and E. Ibanez, Optimization of the aqueous enzymatic extraction of oil from iranian wild almond
8. Zhao, X., *et al.*, XRD, SEM, and XPS analysis of soybean protein powders obtained through extraction involving reverse micelles
9. Mozzon, M., D. Pacetti, N.G. Frega, and P. Lucci, Crude palm oil from interspecific hybrid *Elaeis oleifera* x *E. guineensis*: alcoholic constituents of unsaponifiable matter
10. Behr, A. and S. Toepell, Comparison of reactivity in the cross metathesis of allyl acetate-derivatives with oleochemical compounds

Lipids

Lipids

1. Okla, M., J-H. Ha, R.E. Temel, and S. Chung, BMP7 drives human adipogenic stem cells into metabolically active beige adipocytes
2. Seet, E.L., *et al.*, Maternal high-fat-diet programs rat offspring liver fatty acid metabolism
3. Honda, K.L., S. Lamon-Fava, N.R. Matthan, D. Wu, and A.H. Lichtenstein, EPA and DHA exposure alters the inflammatory response but not the surface expression of toll-like receptor 4 in macrophages
4. Hammann, Simon, C. Wendlinger, and W. Vetter, Analysis of intact cholesteryl esters of furan fatty acids in cod liver
5. Li, G., *et al.*, Oxidized low-density lipoprotein inhibits THP-1-derived macrophage autophagy via TET2 down-regulation
6. MacPherson, R.E K., *et al.*, A maternal high-fat diet has long-lasting effects on skeletal muscle lipid and plin protein content in rat offspring at young adulthood
7. Vahmani, P., *et al.*, Individual *trans* 18:1 isomers are metabolised differently and have distinct effects on lipogenesis in 3T3-L1 adipocytes
8. Takahashi, H., *et al.*, 13-Oxo-9(Z),11(E),15(Z)-octadecatrienoic acid activates peroxisome proliferator-activated receptor gamma in adipocytes
9. Hancock, S.E., M.G. Friedrich, T.W. Mitchell, R.J.W. Truscott, and P.L. Else, Decreases in phospholipids containing adrenic and arachidonic acids occur in the human hippocampus over the adult lifespan
10. Rao, L.N., *et al.*, Hypercholesterolemia-induced immune response and inflammation on progression of atherosclerosis in Apob (tm2Sgy) Ldlr (tm1Her)/J mice

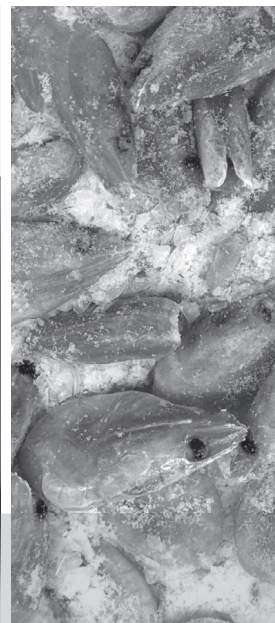
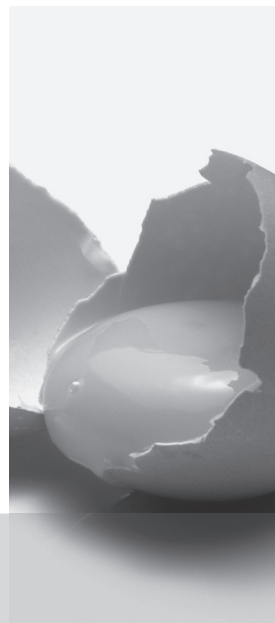


JOURNAL OF SURFACTANTS AND DETERGENTS

Journal of Surfactants and Detergents

1. Negm, N.A., S.M. Tawfik, E.A. Badr, M.I. Abdou, and F.M. Ghuiba, Evaluation of some nonionic surfactants derived from vanillin as corrosion inhibitors for carbon steel during drilling processes
2. Mondal, S., S. Das, and S. Ghosh, Interaction of myoglobin with cationic gemini surfactants in phosphate buffer at pH 7.4
3. Negm, N.A., S.M. Tawfik, M.I. Abdou, E.A. Badr, and F.M. Ghuiba, Evaluation of some nonionic surfactants derived from tannic acid as additives for water-based mud
4. Tawfik, S.M. and M.F. Zaky, Synthesis, structure characterization and biological activity of Co (II), Cu (II), and Zn (II) complexes with (Z)-3-((3-hydroxybenzylidene) amino)pyridin-1-ium 4-(dodecan-4-yl)benzenesulfonate surfactant
5. Vecino, X.; G. Bustos, R. Devesa-Rey, J. Manuel Cruz, and A. Belen Moldes, Salt-free aqueous extraction of a cell-bound biosurfactant: a kinetic study
6. Fan, Ye, Y. Fang, L. Ma, and H. Jiang, Investigation of micellization and vesiculation of conjugated linoleic acid by means of self-assembling and self-crosslinking
7. Tang, Y., R. Wang, and Y. Wang, Constructing gemini-like surfactants with single-chain surfactant and dicarboxylic acid sodium salts
8. Kawase, T., M. Kagawa-Ohara, T. Aisaka, and T. Oida, Synthesis of succinic gemini surfactants and the effect of stereochemistry on their monolayer behaviors
9. Deyab, M.A.M., Corrosion inhibition and adsorption behavior of sodium lauryl ether sulfate on L80 carbon steel in acetic acid solution and its synergism with ethanol
10. Chauhan, S., R. Singh, K. Sharma, and K. Kumar, Interaction study of anionic surfactant with aqueous non-ionic polymers from conductivity, density and speed of sound measurements

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Phase behavior of binary blends of four different waxes

Martini, S. and S. Jana, *J. Am. Oil Chem. Soc.* 93: 543–554, April 2016, <http://dx.doi.org/10.1007/s11746-016-2789-6>.

The objective of this study was to investigate the phase behavior of binary blends of four waxes—beeswax (BW), paraffin wax (PW), sunflower wax (SFW), and rice bran wax (RBW)—using differential scanning calorimetry (DSC) and polarized light microscopy (PLM). Blends of BW/PW, RBW/PW, SFW/PW, SFW/RBW, SFW/BW, and RBW/BW were crystallized in a DSC, and their melting behavior was used to build binary phase diagrams. The microstructure of the crystalline networks formed in these blends was analyzed using PLM. BW/PW, SFW/PW, SFW/BW, and RBW/BW blends showed eutectic phase behavior, while RBW/SFW showed continuous solid solution and the RBW/PW blend showed monotectic behavior. Results from the box-counting fractal dimension (D_b) measurement of crystal morphology showed higher D_b values for the 20 and 80% wax blends, irrespective of crystallization temperature or wax type. D_b values of single waxes decrease as temperature increases.

A conjugated fatty acid present at high levels in bitter melon seed favorably affects lipid metabolism in hepatocytes by increasing NAD⁺/NADH ratio and activating PPAR α , AMPK, and SIRT1 signaling pathway

Chen, G.-C., et al., *J. Nutr. Biochem.* 33: 28–35, 2016, <http://dx.doi.org/10.1016/j.jnutbio.2016.03.009>.

α -Eleostearic acid (α -ESA), or the *cis*-9, *trans*-11, *trans*-13 isomer of conjugated linolenic acid, is a special fatty acid present at high levels in bitter melon seed oil. The aim of this study was to examine the effect of α -ESA on hepatic lipid metabolism. Using H4IIEC3 hepatoma cell line, we showed that α -ESA significantly lowered intracellular triglyceride accumulation compared to α -linolenic acid (LN), used as a fatty acid control, in a dose- and time-dependent manner. The effects of α -ESA on enzyme activities and mRNA profiles in H4IIEC3 cells suggested that enhanced fatty acid oxidation and lowered lipogenesis were involved in α -ESA-mediated triglyceride lowering effects. In addition, α -ESA triggered AMP-activated protein kinase (AMPK) activation without altering sirtuin 1 (SIRT1) protein levels. When cells were treated with vehi-

cle control (VC), LN alone (LN; 100 μ mol/L), or in combination with α -ESA (LN+ α -ESA; 75+25 μ mol/L) for 24 h, acetylation of forkhead box protein O1 was decreased, while the NAD⁺/NADH ratio, mRNA levels of *NAMPT* and *PTGR1* and enzyme activity of nicotinamide phosphoribosyltransferase were increased by LN+ α -ESA treatment compared to treatment with LN alone, suggesting that α -ESA activates SIRT1 by increasing NAD⁺ synthesis and NAD(P)H consumption. The antisteatosis effect of α -ESA was confirmed in mice treated with a high-sucrose diet supplemented with 1% α -ESA for 5 weeks. We conclude that α -ESA favorably affects hepatic lipid metabolism by increasing cellular NAD⁺/NADH ratio and activating PPAR α , AMPK and SIRT1 signaling pathways.

Effect of dietary docosahexaenoic acid (DHA) in phospholipids or triglycerides on brain DHA uptake and accretion

Kitson, A.P., et al., *J. Nutr. Biochem.* 33: 91–102, 2016, <http://dx.doi.org/10.1016/j.jnutbio.2016.02.009>.

Tracer studies suggest that phospholipid DHA (PL-DHA) more effectively targets the brain than triglyceride DHA (TAG-DHA), although the mechanism and whether this translates into higher brain DHA concentrations are not clear. Rats were gavaged with [3 H]PL-DHA and [3 H]TAG-DHA and blood sampled over 6 h prior to collection of brain regions and other tissues. In another experiment, rats were supplemented for 4 weeks with TAG-DHA (fish oil), PL-DHA (roe PL) or a mixture of both for comparison to a low-omega-3 diet. Brain regions and other tissues were collected, and blood was sampled weekly. DHA accretion rates were estimated using the balance method. [3 H]PL-DHA rats had higher radioactivity in cerebellum, hippocampus, and remainder of brain, with no differences in other tissues despite higher serum lipid radioactivity in [3 H]TAG-DHA rats. TAG-DHA, PL-DHA or a mixture were equally effective at increasing brain DHA. There were no differences between DHA-supplemented groups in brain region, whole-body, or tissue DHA accretion rates except heart and serum TAG where the PL-DHA/TAG-DHA blend was higher than TAG-DHA. Apparent DHA β -oxidation was not different between DHA-supplemented groups. This indicates that more labeled DHA enters the brain when consumed as PL; however, this may not translate into higher brain DHA concentrations.

Short- and medium-chain fatty acids in energy metabolism: the cellular perspective

Schönfeld, P. and L. Wojtczak, *J. Lipid Res.* 57: 943–954, 2016, <http://dx.doi.org/10.1194/jlr.R067629>.

Short- and medium-chain fatty acids (SCFAs and MCFAs), independently of their cellular signaling functions, are important substrates of the energy metabolism and anabolic processes in mammals. SCFAs are mostly generated by colonic bacteria and are predominantly metabolized by enterocytes and liver, whereas MCFAs arise mostly from dietary triglycerides, among them milk and dairy products. A common feature of SCFAs and MCFAs is

their carnitine-independent uptake and intramitochondrial activation to acyl-CoA thioesters. Contrary to long-chain fatty acids, the cellular metabolism of SCFAs and MCFAs depends to a lesser extent on fatty acid-binding proteins. SCFAs and MCFAs modulate tissue metabolism of carbohydrates and lipids, as manifested by a mostly inhibitory effect on glycolysis and stimulation of lipogenesis or gluconeogenesis. SCFAs and MCFAs exert no or only weak protonophoric and lytic activities in mitochondria and do not significantly impair the electron transport in the respiratory chain. SCFAs and MCFAs modulate mitochondrial energy production by two mechanisms: they provide reducing equivalents to the respiratory chain and partly decrease efficacy of oxidative ATP synthesis.

Bioavailability of lutein in corn distillers dried grains with solubles relative to lutein in corn gluten meal based on lutein retention in egg yolk

Shin, H.S. *et al.*, *J. Sci. Food Agric.* 96: 3401–3406, 2016, <http://dx.doi.org/10.1002/jsfa.7520>.

Dietary lutein and its food sources have gained great attention due to its health-promoting effects on humans, especially for certain eye diseases. However, relative bioavailability (RBV) of lutein among lutein-rich feed ingredients that lead to lutein-enriched egg production has not been determined. Thus, the RBV of lutein in corn distillers dried grains with solubles (DDGS) as compared to lutein in corn gluten meal (CGM) was evaluated based on lutein retention in egg yolk. Increasing inclusion levels of DDGS or CGM in diets increased (linear, $P < 0.01$) Roche colour score and lutein concentrations of egg yolk without affecting laying performance. Multiple regression analysis revealed that the bioavailability of lutein in DDGS was less ($P < 0.05$) than that of lutein in CGM, with the RBV of lutein in DDGS being 61.6% when the bioavailability of lutein in CGM was assumed to be 100% for lutein retention in egg yolk. The results of the present experiment indicate that the DDGS can be a potential ingredient for laying hens to improve egg yolk colour and lutein concentrations of egg yolk although lutein in DDGS is less bioavailable than lutein in CGM.

Improvement of β -carotene bioaccessibility from dietary supplements using excipient nanoemulsions

Salvia-Trujillo, L. and D.J. McClements, *J. Agric. Food Chem.* 64: 4639–4647, 2016, <http://dx.doi.org/10.1021/acs.jafc.6b00804>.

The influence of excipient nanoemulsions on β -carotene bioaccessibility from commercial dietary supplements (tablets or soft gels) was studied employing an in vitro gastrointestinal tract (GIT) model. Excipient nanoemulsions were formulated from long or medium chain triglycerides (LCT or MCT) to determine the impact of lipid type on carotenoid bioaccessibility. Dietary supplements were tested using the GIT model in the absence or presence of excipient nanoemulsions. β -carotene bioaccessibility from tablets (0.3%) or soft gels (2.4%) was low when tested in isolation. LCT nanoemulsions greatly improved β -carotene bioaccessibility from tablets (20%) and slightly improved it from soft gels (5%), whereas MCT nanoemulsions only slightly improved bioaccessibility. These results were attributed to the ability of large carotenoid molecules to be incorporated into large mixed micelles formed by LCT digestion but not by small ones formed by MCT digestion. Our results indicate that excipient nanoemulsions have considerable potential for improving nutraceutical bioavailability from dietary supplements.

Inhibition of fat accumulation by hesperidin in *Caenorhabditis elegans*

Peng, H., *et al*, *J. Agric. Food Chem.* 64: 5207–5214, 2016, <http://dx.doi.org/10.1021/acs.jafc.6b02183>.

Hesperidin, abundant in citrus fruits, has a wide range of pharmacological effects, including anticarcinogenic, anti-inflammatory, antioxidative, radioprotective, and antiviral activities. However, relatively few studies on the effects of hesperidin on lipid metabolism have been reported. Here, using *Caenorhabditis elegans* as a model animal, we found that 100 μ M hesperidin significantly decreased fat accumulation in both



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high-fat worms cultured in nematode growth medium containing 10 mM glucose ($83.5 \pm 1.2\%$ versus control by Sudan Black B staining and $87.6 \pm 2.0\%$ versus control by Oil Red O staining; $p < 0.001$) and *daf-2* mutant worms ($87.8 \pm 1.4\%$ versus control by Oil Red O staining; $p < 0.001$). Furthermore, 50 μ M hesperidin decreased the ratio of oleic acid/stearic acid (C18:1 Δ 9/C18:0) ($p < 0.05$), and supplementation of oleic acid could restore the inhibitory effect of hesperidin on fat accumulation. Hesperidin significantly downregulated the expression of stearoyl-CoA desaturase, *fat-6*, and *fat-7* ($p < 0.05$), and mutation of *fat-6* and *fat-7* reversed fat accumulation inhibited by hesperidin. In addition, hesperidin decreased the expression of other genes involved in lipid metabolism, including *pod-2*, *mdt-15*, *acs-2*, and *kat-1* ($p < 0.05$). These results suggested that hesperidin reduced fat accumulation by affecting several lipid metabolism pathways, such as *fat-6* and *fat-7*. This study provided new insights into elucidating the mechanism underlying the regulation of lipid metabolism by hesperidin.

Lipids and cardiovascular/metabolic health effects of dietary saturated and n-6 polyunsaturated fatty acids on the incorporation of long-chain n-3 polyunsaturated fatty acids into blood lipids

Dias, C.B., *et al.*, *Eur. J. Clin. Nutr.* 70: 812–818, 2016, <http://dx.doi.org/10.1038/ejcn.2015.213>.

Omega-3 polyunsaturated fatty acids (n-3PUFA) are better absorbed when they are combined with high-fat meals. However, the role of different dietary fats in modulating the incorporation of n-3PUFA in blood lipids in humans has not been previously explored. Omega-6 polyunsaturated fatty acids (n-6PUFA) are known to compete with n-3PUFA in the metabolic pathways and for the incorporation into phospholipids, whereas saturated fats (SFA) may enhance n-3PUFA incorporation into tissues. In a randomized parallel-design trial, we aimed to investigate the long-term effects of n-3PUFA supplementation in subjects consuming a diet enriched with either SFA or n-6PUFA on fatty acid incorporation into plasma and erythrocytes and on blood lipid profiles (total cholesterol, low-density lipoprotein cholesterol (LDL-C), high-density lipoprotein cholesterol (HDL-C) and triglycerides). Dietary supplementation with n-3PUFA co-administered with SFA for 6 weeks resulted in a significant rise in total cholesterol (0.46 ± 0.60 mmol/L; $P=0.020$) and LDL-C (0.48 ± 0.48 mmol/L; $P=0.011$) in comparison with combination with n-6PUFA. The diet enriched with SFA also induced a greater increase in eicosapentaenoic acid (2.07 ± 0.79 vs 1.15 ± 0.53 ; $P=0.004$), a smaller decrease in docosapentaenoic acid (-0.12 ± 0.23 vs -0.30 ± 0.20 ; $P=0.034$) and a similar increase in docosahexaenoic acid (3.85 ± 1.14 vs 3.10 ± 1.07 ; $P=0.128$) percentage in plasma compared with the diet enriched with n-6PUFA. A similar effect was seen in erythrocytes. n-3PUFA supplementation resulted in similar changes in HDL-C and triglyceride levels. The results suggest that dietary substitution of SFA with n-6PUFA, despite maintaining low levels of circulating cholesterol, hinders n-3PUFA incorporation into plasma and tissue lipids.

Molecular species composition of plant cardiolipin determined by liquid chromatography mass spectrometry

Zhou, Y., *et al.*, *J. Lipid Res.* 57: 1308–1321, 2016, <http://dx.doi.org/10.1194/jlr.D068429>.

Cardiolipin (CL), an anionic phospholipid of the inner mitochondrial membrane, provides essential functions for stabilizing respiratory complexes and is involved in mitochondrial morphogenesis and programmed cell death in animals. The role of CL and its metabolism in plants are less well understood. The measurement of CL in plants, including its molecular species composition, is hampered by the fact that CL is of extremely low abundance, and that plants contain large amounts of interfering compounds including galactolipids, neutral lipids, and pigments. We used solid phase extraction by anion exchange chromatography to purify CL from crude plant lipid extracts. LC/MS was used to determine the content and molecular species composition of CL. Thus, up to 23 different molecular species of CL were detected in different plant species, including *Arabidopsis*, mung bean, spinach, barley, and tobacco. Similar to animals, plant CL is dominated by highly unsaturated species, mostly containing linoleic and linolenic acid. During phosphate deprivation or exposure to an extended dark period, the amount of CL decreased in *Arabidopsis*, accompanied with an increased degree of unsaturation. The mechanism of CL remodeling during stress, and the function of highly unsaturated CL molecular species, remains to be defined.

α -Tocopherol attenuates the triglyceride- and cholesterol-lowering effects of rice bran tocotrienol in rats fed a Western diet

Shibata, A., *et al.*, *J. Agric. Food Chem.* 64: 5361–5366, 2016, <http://dx.doi.org/10.1021/acs.jafc.6b02228>.

Previous studies demonstrated the ability of tocotrienol (T3) to lower levels of lipids, including cholesterol (Cho) and triglycerides (TG). Although α -tocopherol (α -Toc) reportedly inhibits the hypocholesterolemic effect of T3, there is no information about whether α -Toc influences the TG-lowering effect of T3 in vivo. In this study, we investigated the influence of α -Toc on the antihyperlipidemic effects (Cho- and TG-lowering) of rice bran tocotrienols (RBT3) in F344 rats fed a western diet. α -Toc attenuated both the Cho- and TG-lowering effects of RBT3 *in vivo*, whereas α -Toc alone exhibited no hypolipidemic effects. RBT3-induced *Cpt-1a* and *Cyp7a1* gene expression was reduced by α -Toc. Furthermore, coadministration of α -Toc decreased liver and adipose tissue concentrations of tocotrienols in F344 rats. These results indicate that α -Toc has almost no antihyperlipidemic effect in vivo, but abrogates the antihyperlipidemic effect of RBT3 by reducing tissue concentrations of tocotrienols and regulating expression of genes involved in lipid metabolism. Understanding the underlying mechanism of the beneficial effects of T3 on lipid metabolism and the interaction with α -Toc will be important for developing T3-based therapeutics.

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Chemical characteristics of cold-pressed blackberry, black raspberry, and blueberry seed oils and the role of the minor components in their oxidative stability

Li, Q., *et al.*, *J. Agric. Food Chem.* 64: 5410–5416, 2016, <http://dx.doi.org/10.1021/acs.jafc.6b01821>.

The chemical characteristics of cold-pressed blackberry, black raspberry, and blueberry seed oils were evaluated for their fatty acid composition, positional distribution of fatty acids, triacylglycerol (TAG) profile, and minor component profile. The role of minor components, including tocopherols and pigments, on the oxidative stability was also investigated using high-temperature- and fluorescent-lighting-induced oxidation before and after tested berry seed oils were stripped of their minor components. The results indicated that all tested berry seed oils contained significant levels of palmitic (C16:0), stearic (C18:0), oleic (18:1), linoleic (C18:2 ω -6), and α -linolenic (C18:3 ω -3) acids, along with a favorable ratio of ω -6/ ω -3 fatty acids (1.49–3.86); palmitic, stearic, oleic, and α -linolenic acids were predominantly distributed on the terminal positions. Six TAGs, namely, L_nL_nL_n, L_nLL_n, LLL_n, LLL, OLL, and OLL_n, were the major species detected in the tested berry seed oils. Total tocopherol contents were 286.3–1302.9 mg/kg, which include α -, γ -, and δ -tocopherols as well as δ -tocotrienol. Oxidative stability of the three berry seed oils was compromised after the removal of tocopherols under high-temperature-induced oxidation, while the loss of pigments (chlorophylls) led to weak oxidative stability when exposed to fluorescent lights.

Changes in the fatty acid profile and phospholipid molecular species composition of human erythrocyte membranes after hybrid palm and extra virgin olive oil supplementation

D. Pacetti, D., *et al.*, *J. Agric. Food Chem.* 64: 5499–5507, 2016, <http://dx.doi.org/10.1021/acs.jafc.6b01903>.

This work aims to evaluate and compare, for the first time, the effects of extra virgin olive oil (EVOO) and hybrid palm oil (HPO) supplementation on the fatty acid profile and phospholipid (PL) molecular species composition of human erythrocyte membranes. Results supported the effectiveness of both HPO and EVOO supplementation (3 months, 25 mL/day) in decreasing the lipophilic index of erythrocytes with no significant differences between HPO and EVOO groups at month 3. On the other hand, the novel and rapid ultraperformance liquid chromatography–tandem mass spectrometry method used for PL analysis reveals an increase in the levels of phosphatidylcholine and phosphatidylethanolamine species esterified with polyunsaturated fatty acids. This work demonstrates the ability of both EVOO and HPO to increase the degree of unsaturation of erythrocyte membrane lipids with an improvement in membrane fluidity that could be associated with a lower risk of developing cardiovascular diseases.

The increasing use of interesterified lipids in the food supply and their effects on health parameters

Mensink, R.P., *et al.*, *Adv. Nutr.* 7: 719–729, 2016, <http://doi.org/10.3945/an.115.009662>.

A variety of modified fats that provide different functionalities are used in processed foods to optimize product characteristics and nutrient composition. Partial hydrogenation results in the formation of trans FAs (TFAs) and was one of the most widely used modification processes of fats and oils. However, the negative effects of commercially produced TFAs on serum lipoproteins and risk for cardiovascular disease resulted in the Institute of Medicine and the 2010 US Dietary Guidelines for Americans both recommending that TFA intake be as low as possible. After its tentative 2013 determination that use of partially hydrogenated oils is not generally regarded as safe, the FDA released its final determination of the same in 2015. Many food technologists have turned to interesterified fat as a replacement. Interesterification rearranges FAs within and between a triglyceride molecule by use of either a chemical catalyst or an enzyme. Although there is clear utility of interesterified fats for retaining functional properties of food, the nutrition and health implications of long-term interesterified fat consumption are less well understood. The Technical Committee on Dietary Lipids of the North American Branch of the International Life Sciences Institute sponsored a workshop to discuss the health effects of interesterified fats, identify research needs, and outline considerations for the design of future studies. The consensus was that although interesterified fat production is a feasible and economically viable solution for replacing dietary TFAs, outstanding questions must be answered regarding the effects of interesterification on modifying certain aspects of lipid and glucose metabolism, inflammatory responses, hemostatic parameters, and satiety.

Lipid Oxidation

Mitochondrial DNA fragmentation to monitor safety and quality in roasted peanuts

Caldwell, J.M., *et al.*, *Peanut Science*, online first 2016, <http://doi.org/10.3146/PS15-9.1>.

Abstract Mitochondrial DNA (mtDNA) fragmentation has been proposed as a time-temperature integrator (TTI) for high-moisture thermal processes using low-acid, high-temperature and high-acid, low-temperature protocols. In this study, dry roasted peanuts were assayed using the same novel molecular TTI. *Enterococcus faecium* was evaluated as a *Salmonella* surrogate for process validation and compared to fragmentation of intrinsic peanut mtDNA and Hunter L color, a quality indicator, for dry roasting. Reduction curve data for *E. faecium* were highly repeatable as similar kinetics were observed when compared to another study which used a commercial, contract laboratory to validate this same surrogate for use with dry roasted peanuts processes (4-log reduction after 10 min at 167°C). Mitochondrial DNA fragmentation was not linear

compared to time at a given temperature, but exhibited a long lag time. D and z-values were calculated using *E. faecium*, threshold cycle (Ct) and Hunter L color values. D values for *E. faecium*.

Primary and secondary antioxidants to prevent oil degradation during repeated frying of french fries and chicken nuggets

Rocha-González, D.G., *et al.*, In 2016 ASABE Annual International Meeting (p. 1), American Society of Agricultural and Biological Engineers, <http://tinyurl.com/z2ssyu8>.

Fried foods are highly appreciated and marketed in the world. Due to they absorb the oil in which they are cooked, the quality of frying oil is very important. Antioxidants are employed to maintain good quality during oil storage, and also, to avoid degradation during repeated frying. In this work, the performance during repeated frying of oil free of antioxidants or added with a blend of primary and secondary antioxidants was analyzed. The frying oil was a blend of hydrogenated canola oil with high-oleic sunflower oil. The antioxidants were added at concentration of 200 ppm (TBHQ as a primary antioxidant with 20% of citric acid as a secondary antioxidant). The performance was evaluated for two fried foods separately: french fries or chicken nuggets. A batch (80 g of frozen food) was fried for 3 min at 180°C; 50 batches were fried daily during 4 days. At the beginning of every day, the used oil was filtered and the fryer was refilled with fresh oil. These conditions are similar to those practiced in restaurants and fast food establishments. According to the parameters of free fatty acids, peroxides, p-anisidin, total polar compounds, color and viscosity, no effects of the antioxidants were observed in the oil when employed for repeated frying of french fries ($p > 0.05$). However, oil with antioxidants had higher performance than oil without antioxidants when it was employed for repeated frying of chicken nuggets ($p > 0.05$). Thus, the type of food affected the oil performance. The oil was resistant by itself for repeated frying when employed for repeated frying of french fries, and the blend of antioxidants was not able to prevent the oil oxidation when used for repeated frying of chicken nuggets.

Effect of sodium ascorbate and sodium nitrite on protein and lipid oxidation in dry fermented sausages

Berardo, A., *et al.*, *Meat Sci.* 121: 359–364, 2016, <http://doi.org/10.1016/j.meatsci.2016.07.003>.

The effects of sodium nitrite and ascorbate on lipid and protein oxidation were studied during the ripening process of dry fermented sausages. Samples were taken at day 0, 2, 8, 14, 21 and 28 of ripening to assess lipid (malondialdehyde) and protein (carbonyls and sulfhydryl groups) oxidation. Sodium ascorbate and nitrite were separately able to reduce the formation of malondialdehyde. Their combined addition resulted in higher amounts of carbonyl compounds compared to their separate addition or the treatment without any of both compounds. Moreover, sodium nitrite limited the formation of γ -glutamic semialdehyde whereas sodium ascorbate showed a pro-oxidant effect. A loss of thiol groups was observed during ripening, which was not affected by the use of

sodium ascorbate nor sodium nitrite. In conclusion, sodium nitrite and ascorbate affected protein and lipid oxidation in different manners. The possible pro-oxidant effect of their combined addition on carbonyl formation might influence the technological and sensory properties of these products.

Removal of rancid-acid odor of expeller-pressed virgin coconut oil by gamma irradiation: evaluation by sensory and electronic nose technology

Ghosh, P. K., *et al.*, *Food Bioprocess Tech.*, 1–11, online first 2016, <http://doi.org/10.1007/s11947-016-1752-8>.

Expeller-pressed virgin coconut oil, known to have disagreeable rancid-acid odor due to the presence of octanoic acid, was subjected to gamma (γ) irradiation for removal of the same. Sensory evaluation in tandem with electronic nose (Heracles and ENOVISION) analyses established that the oil irradiated at 4.2 kGy had no rancid-acid odor (absence of octanoic acid) at the end of 28 days of storage at $23 \pm 2^\circ\text{C}$. Therefore, 4.2 kGy was established as the “appropriate irradiation dose” for removal of rancid-acid odor of virgin coconut oil. A “deodorization index” with respect to rancid-acid odor was also developed using electronic nose for confirmation of this “appropriate dose” and thereby provided possible means of preventing detrimental effects of high dose of γ -irradiation in oils. GC–MS analysis of hydrocarbons extracted from oil irradiated at 4.2 kGy by supercritical carbon dioxide extraction revealed radiolysis of octanoic acid resulting in elimination of rancid-acid odor. Further, γ -irradiation at 4.2 kGy did not affect the antioxidant potency of coconut oil rendering it a safe and healthy alternative to conventional deodorization techniques for oils. Development of methodology for assessment of rancid-acid odor of coconut oil using electronic nose has been reported for the first time in this work.

Peach skin powder inhibits oxidation in cooked turkey meat

Y. Zhang, *et al.*, *Poultry Sci.* 00:1–6, 2016, <http://dx.doi.org/10.3382/ps/pew139>.

The objective of this study was to measure the antioxidant activity of peach skin and test the antioxidant effect of peach skin powder on cooked ground turkey meat during 12 d of refrigerated storage. Antioxidant activity of 3 cultivars of peaches grown in South Carolina was first evaluated by three antioxidant assays. The peach variety O’Henry showed the greatest antioxidant effect and therefore was used for further study. Two levels of peach skin powder (0.5%, 1%) and 0.01% butylated hydroxyanisole (BHA) were applied to ground turkey meat. Oxidation of cooked turkey meat was measured by detection of hexanal using gas chromatography-mass spectrometry. Results indicated that all levels of peach skin powder used in this study had an antioxidant effect on ground turkey with a greater effect at the higher concentration. O’Henry peach skin powder was as effective as BHA in preventing oxidation at the levels tested.

Development and validation of a novel microwave-assisted extraction method for fish lipids

Costa, D. dos S. V., and N. Bragagnolo, *Eur. J. Lipid Sci. Technol.*, online first 2016, <http://doi.org/10.1002/ejlt.201600108>.

A novel microwave-assisted extraction (MAE) method for fish lipids was optimized by means of a central composite design and validated using a fish tissue standard reference material (SRM, 1946, NIST). Scanning electron microscopy showed that MAE caused total disruption of the fish tissue, thus lipid migration to the extraction solvent was more efficient and faster in comparison to the Folch method. The lipid content of the SRM obtained by MAE (10.1 ± 0.2 g/100 g) was similar to that declared on the certificate (10.2 ± 0.5 g/100 g). The use of microwave energy did not alter the fatty acid composition of the fish nor formed lipid oxidation derived compounds at higher levels than in the Folch method. The MAE method was applied to fishes with different lipid contents, tilapia, pacu, and hake. MAE is a fast and robust technique with low solvent consumption when compared to the Folch method. MAE presented the following advantages over the Folch method: the lipids can be extracted from up to 12 samples simultaneously, it reduces the extraction time by up to 90%, produces less residues, reduces solvent consumption proportionally to the mass used by up to 25%, and contributes to a reduction in toxicity in the environment by substituting chloroform with ethyl acetate.

Industrial Applications

Technoeconomic analysis of small-scale, farmer-owned camelina oil extraction as feedstock for biodiesel production: a case study in the Canadian prairies

Mupondwa, E., *et al.*, *Ind. Crops Prod.* 90: 76–86, 2016, <http://doi.org/10.1016/j.indcrop.2016.05.042>.

This study evaluated costs and profitability associated with small-scale camelina oil extraction plant in the Canadian prairies for the purpose of selling camelina oil for further biodiesel production. In this case, *Camelina sativa* is targeted for production on underutilized summer fallow land to avoid displacement of crop lands. Saskatchewan soil zone 7A has the capacity to provide camelina for oil extraction based on small scale capacities of 30,000–120,000 t annum⁻¹ and capital investment of \$10–24 million. Oil production price is reduced with increased camelina oil content, field yield, plant scale, and camelina meal price. Oil production costs range from \$0.39 to \$1.88 L⁻¹ when camelina meal has a market value of \$0.30 kg⁻¹. These results provide an informative basis for investment decisions by farmers and investors vis-à-vis the advancement of farm adoption of camelina as a dedicated industrial crop, as well as the development of an integrated camelina-to-processing oilseed value-chain.

Synthetic Biology

Metabolic engineering of cyanobacteria and microalgae for enhanced production of biofuels and high-value products

Gomaa, M. A., *et al.*, *J. Appl. Microbiol.*, online first July, 2016, <http://doi.org/10.1111/jam.13232>.

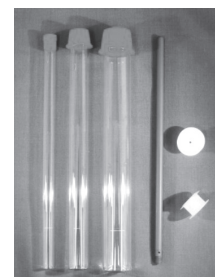
A lot of research has been performed on cyanobacteria and microalgae with the aim to produce numerous biotechnological products. However, native strains have a few shortcomings, like limitations in cultivation, harvesting and product extraction, which prevents reaching optimal production value at lowest costs. Such limitations require the intervention of genetic engineering to produce strains with superior properties. Promising advancements in the cultivation of cyanobacteria and microalgae have been achieved by improving photosynthetic efficiency through increasing RuBisCO activity and truncation of light-harvesting antennae. Genetic engineering has also contributed to final product extraction by inducing autolysis and product secretory systems, to enable direct product recovery without going through costly extraction steps. In this review, we summarize the different enzymes and pathways that have been targeted thus far for improving cultivation aspects, harvesting and product extraction in cyanobacteria and microalgae. With synthetic biology advancements, genetically engineered strains can be generated to resolve demanding process issues and achieve economic practicality. This comprehensive overview of gene modifications will be useful to researchers in the field to employ on their strains to increase their yields and improve the economic feasibility of the production process.

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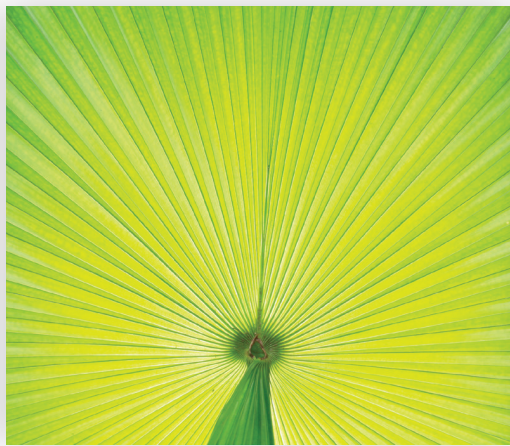
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