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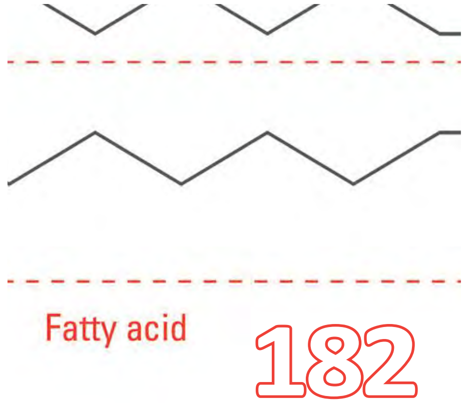

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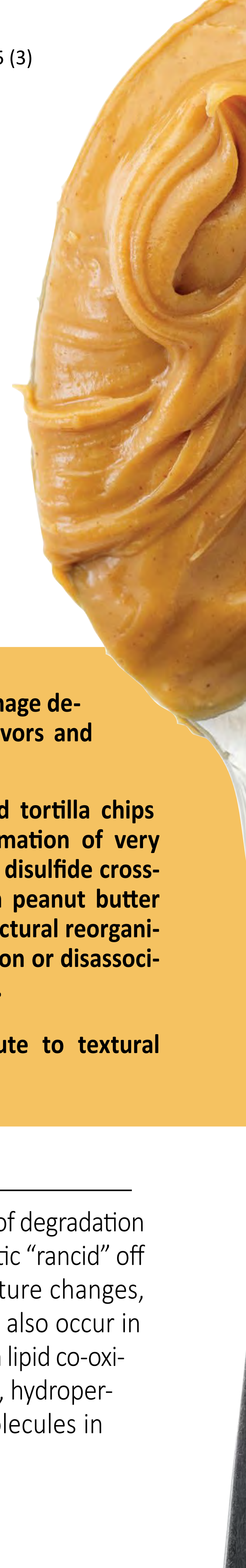
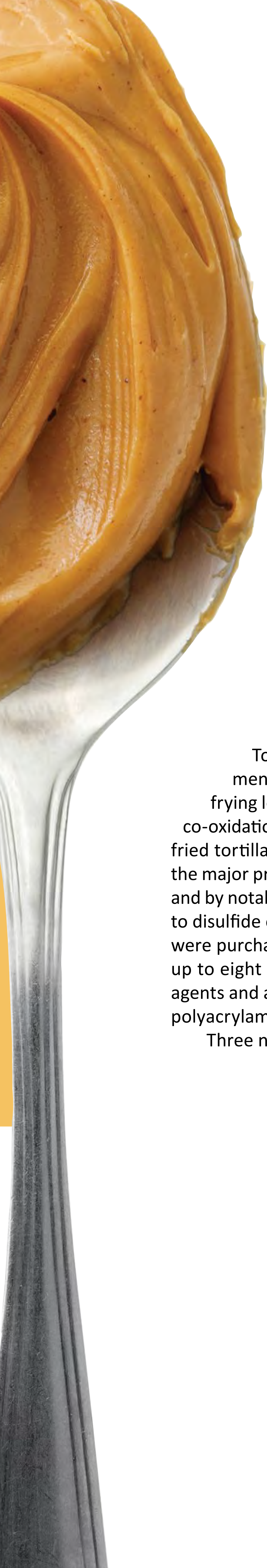


LIPID CO-OXIDATION OF PROTEINS: ONE SIZE DOES NOT FIT ALL

- **Oxidizing lipids transfer damage to proteins. Such damage degrades food quality beyond production of rancid flavors and odors.**
- **Lipid co-oxidation of maize proteins in fried tortilla chips causes protein surface modifications and formation of very large protein aggregates with free radical and disulfide crosslinks, while lipid co-oxidation of proteins in peanut butter leads to extensive surface modification, structural reorganization of arachins, and notable fragmentation or disassociation of arachin and conarachin complexes.**
- **Both types of modifications contribute to textural hardening in these foods.**

K.M. Schaich

Lipid oxidation is the major chemical cause of degradation in foods during storage, and the characteristic "rancid" off odors and flavors are well recognized. Texture changes, browning and color fading, and vitamin loss also occur in conjunction with lipid oxidation, resulting from lipid co-oxidations—interactions of lipid oxidation radicals, hydroperoxides, aldehydes, and epoxides with other molecules in foods and biological tissues.



These co-oxidations paradoxically make analyzed lipid oxidation appear to be less than it actually is by removing lipid oxidation products from the reaction stream, when, in fact, oxidation has been broadcast past lipids to affect the entire system. Co-oxidations provide footprints of lipid oxidation that must be measured along with lipid oxidation products to accurately determine the full extent of oxidation (Schaich, 2008).

In foods, proteins are key targets of lipid co-oxidation. Studies in model systems have documented that all stages of lipid oxidation—radicals, hydroperoxides, epoxides, and carbonyl products—damage proteins extensively. Results are formation of protein radicals that lead to oxidation of amino acid side chains, lipid adducts, scissions, aggregation and crosslinking, loss of solubility, denaturation and changes in conformation, modification of surface residues that increase surface hydrophobicity and alter protein functionality, and loss of nutritional value.

Theoretically, one size does not fit all in protein co-oxidations, that is, the exact pattern of damage should vary with protein conformation and amino acid content, with lipid/protein ratios, and with reaction environment. However, there is relatively little validation of this expectation since protein co-oxidation is rarely tracked in intact materials. The importance of co-oxidation is rarely recognized, it is difficult to separate damage induced by processing (e,g., hear and shear), and the analytical challenges of determining detailed protein changes and the lipid oxidation products responsible are significant. To begin building a database of protein co-oxidation, we have investigated protein modifications in a number of different foods. Results in two systems—baked vs. fried tortilla chips, and peanut butter—demonstrate clearly that protein co-oxidation varies with the protein, system composition, and system environment.

CO-OXIDATION OF PROTEINS IN TORTILLA CHIPS

Tortilla chips were selected as a test system because the composition and treatment of the corn base are the same, including the heating temperature, except frying leads to adsorption of significant amounts of oil that oxidizes and mediates co-oxidations. Thus, baked tortilla chips provide a control of processing effects while fried tortilla chips reflect added changes from oxidizing lipids. Zeins and glutelins, the major proteins in the corn base, are characterized by very high hydrophobicity and by notable sulfur amino acid content that makes them particularly susceptible to disulfide crosslinking. Commercial tortilla chips from the same manufacturer were purchased from a local grocery store and incubated at 40°C and 60°C for up to eight weeks. Proteins were then extracted with and without reducing agents and analyzed for change by chemical analyses, antibody reactions, and polyacrylamide gel electrophoresis (PAGE).

Three notable changes occurred in the maize proteins:

i. Crosslinking of zeins and glutelins. Crosslinking was predominantly disulfide in baked chips, but both disulfide (reducible) and free radical (nonreducible) in fried chips. Crosslinking was obvious even in fresh products, and the changes became more extensive with incubation time and temperature, particularly after frying (Fig. 1, page 136). Crosslinking began almost immediately in the fried chips; and by six weeks at 40°C and two weeks at 60°C, most of the peptide bands were no longer detectable in the gel. Only very low levels of fluorescent products were detectable so Schiff base adducts or Michael additions were not likely sources of crosslinking. Hardening of texture accompanied protein crosslinking in the fried chips.
ii. Modification of surface residues. Proteins from fried (but not baked) tortilla chips lost the ability to bind Coomassie blue dye in PAGE

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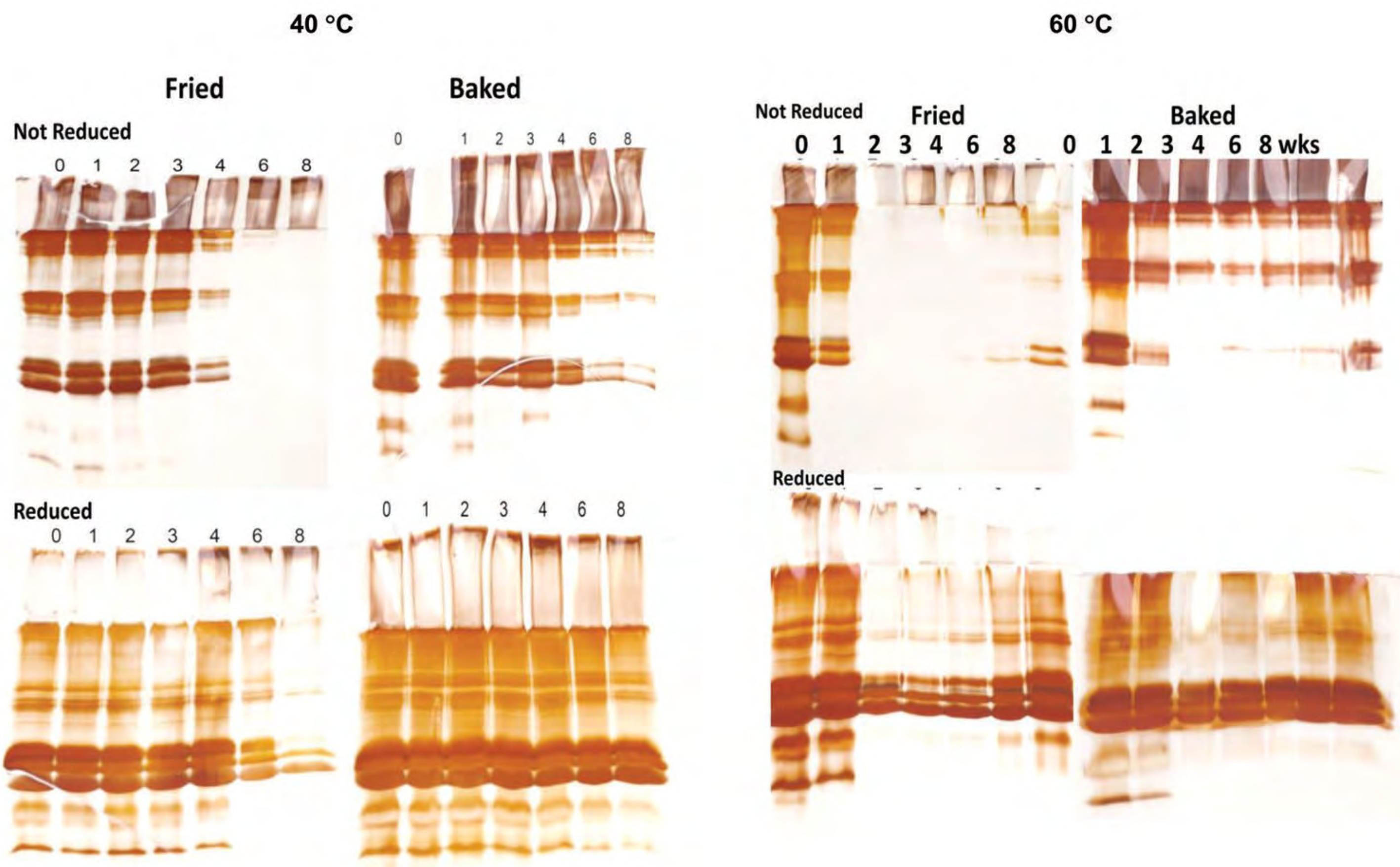

FIG. 1. SDS-PAGE [sodium dodecyl sulfate-polyacrylamide electrophoresis] gels showing modifications of proteins in baked and fried tortilla chips during incubation at 40°C and 60°C. Silver staining, reduction with 2-mercaptoethanol. Source: Dong, 2011.

gels. At the same time, reaction with Coomassie blue in solution was retained.

iii. Formation of protein carbonyls (oxidation products detected by antibody reactions) in every protein fraction. Surprisingly, the oxidation base was established during processing, most extensively in proteins from baked chips, and oxidation levels were relatively constant during incubation.

The details of chemical changes in maize proteins are still under investigation, but current data suggest that in fried tortilla chips oxidizing lipids crosslink zeins and glutelins by reversible S–S bonds and permanent radical links to form loosely associated masses too large to enter the PAGE stacking gel but open enough for accessibility to dyes in solution. These polymeric masses are likely responsible for the observed texture hardening. Lipid radicals and/or hydroperoxides appear to be the most active inducers of crosslinking; other oxidation products may be involved in modification of amino acid side chains (Fig. 2).

Tortilla chips have a dry, porous protein matrix with relatively low lipid concentrations. Peanut butter, in contrast, is high fat (45–50%) and has a protein matrix dispersed in a definite lipid phase. Thus, the contacts between lipid and protein in peanut butter are very different from in tortilla chips. In addition, the lipid oxidation products available for co-oxidation are likely to differ from those formed on the surface of tortilla chips, so the same damage patterns should not be expected. Most importantly, peanut proteins are unique structurally in having non-homogeneous distribution of acidic and basic amino acid residues among peptide fractions.

CO-OXIDATION OF PROTEINS IN PEANUT BUTTER

Peanut butter in military MRE (meals ready to eat) laminate packages stored at 25°, 40°, and 60°C was monitored for lipid oxidation and associated changes in protein and physical properties for up to 12 weeks. Hardness of the peanut butter increased significantly ($p < 0.05$) with incu-

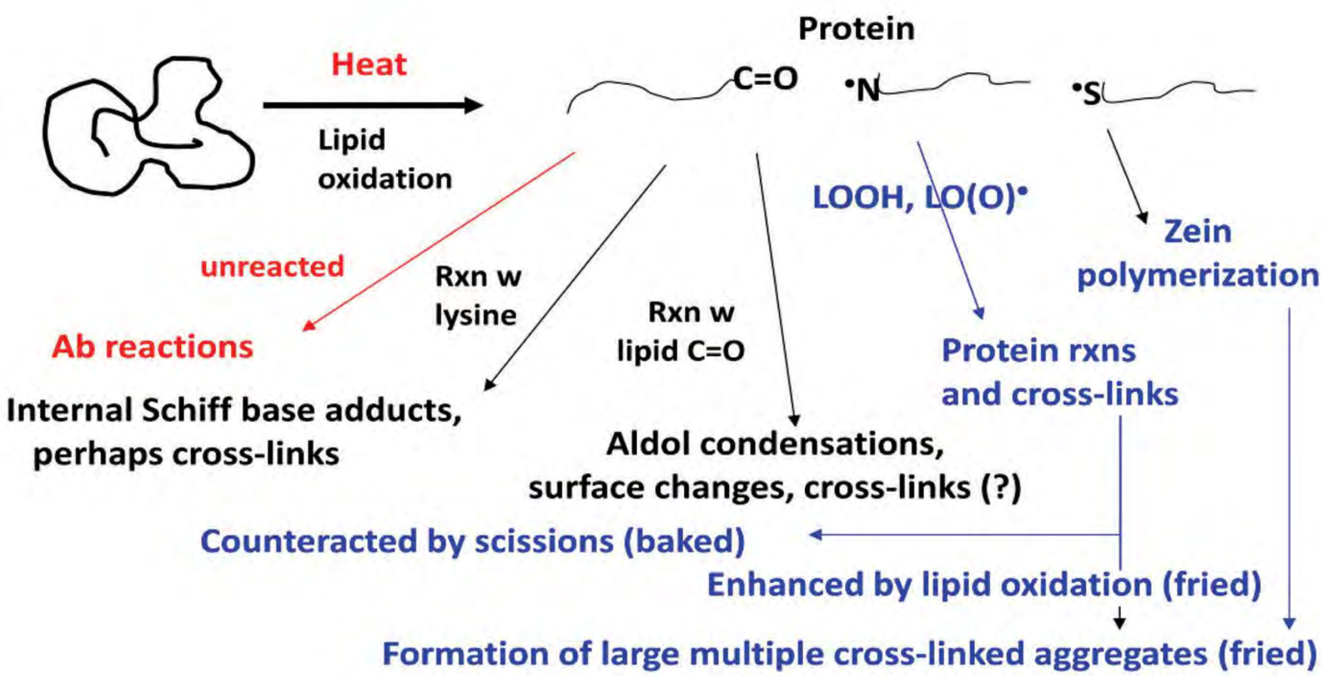

FIG. 2. Proposed lipid-protein co-oxidation reactions occurring in tortilla chip proteins. Abbreviations: rxn, reaction; L, lipid. Source: Dong, 2011.

bation time and temperature. At the same time, the peanut butter lost its cohesiveness (did not hold together well) but became increasingly sticky, rubbery, and chewy. Moisture content did not change, so this texture deterioration most likely resulted from oxidation of lipids and proteins. The peanut butter also darkened significantly over time, particularly at 60°C.

Lipid oxidation products (conjugated dienes, hydroperoxides, carbonyls) remained low throughout the incubation and tended to decrease rather than increase over time, even while peanut butter quality was obviously deteriorating. Parallel to this, protein solubility progressively decreased and protein modification increased, providing a cogent example of how co-oxidation moves system oxidation away from lipids to other molecules.

Unexpectedly, Coomassie blue and silver staining revealed very different peptide patterns in peanut proteins, whereas they usually detect proteins identically. Since silver binds to acidic amino acids and Coomassie blue binds to basic amino acids, this differential staining indicates that binding amino acids in peanut proteins are selectively concentrated in specific peptides, rather than being generally distributed as in most proteins. This difference turns out to be important in directing co-oxidation modifications.

CONTINUED ON NEXT PAGE

INFORMATION

- Dong, Y., Protein modifications in baked versus fried tortilla chips, M.S. Thesis, Department of Food Science, Rutgers University, New Brunswick, New Jersey, USA, 2013.
- Schaich, K.M., Co-oxidations of oxidizing lipids: Reactions with proteins, in Lipid Oxidation Pathways, Vol. 2, edited by A. Kamal-Eldin and D. Min, AOCS Press, Urbana, Illinois, USA, 2008, pp. 183–274.
- Wanibadullah, W., Lipid-protein interactions in peanut butter, Ph.D. dissertation, Department of Food Science, Rutgers University, New Brunswick, New Jersey, USA, 2013.

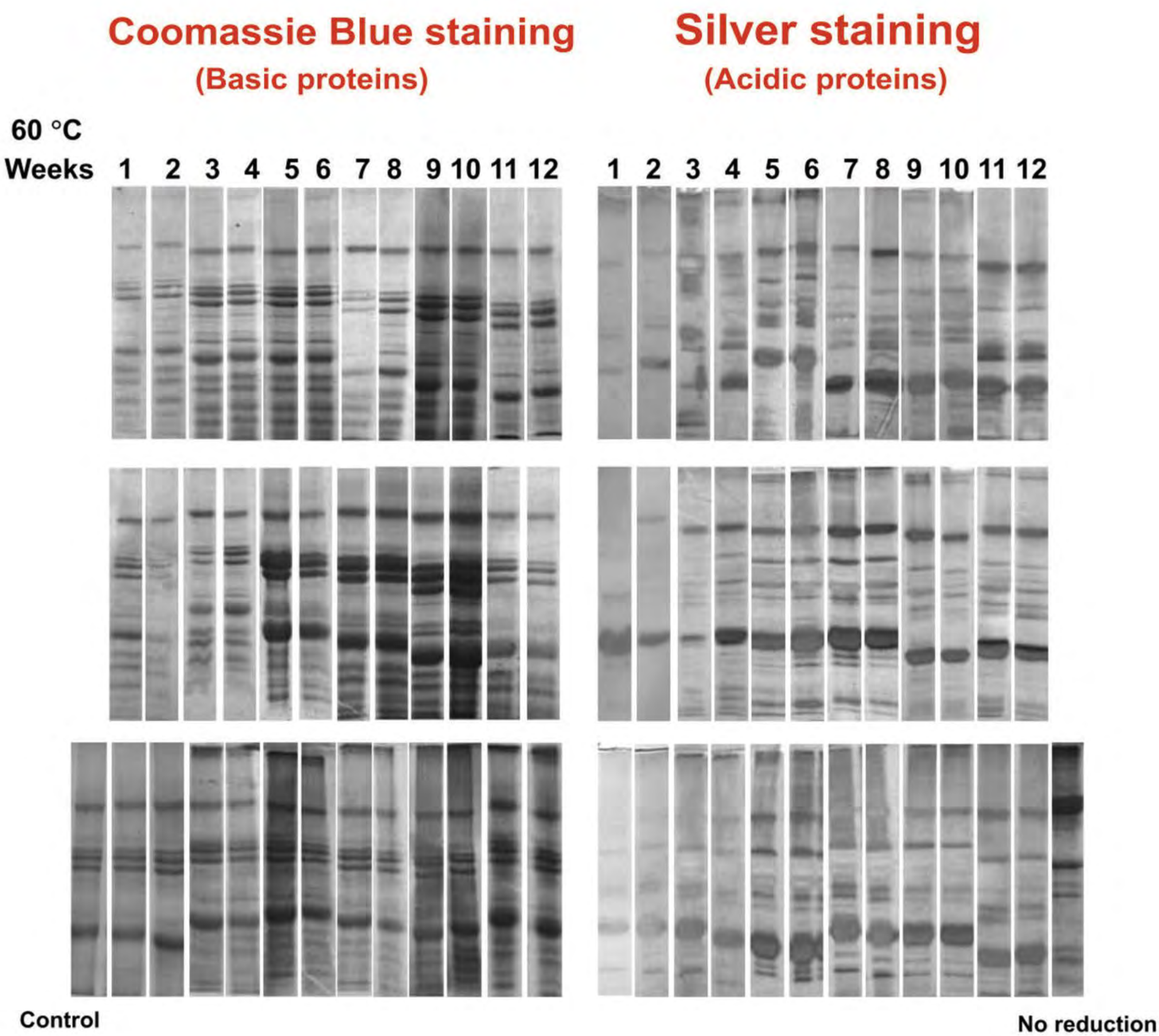

FIG. 3. SDS-PAGE gels showing differential changes in basic and acidic proteins during storage of peanut butter at 60°C. For abbreviations see Figure 1. Source: Wanibadullah, 2013.

WANT MORE ON THIS TOPIC?

Author Karen Schaich also contributed two chapters in the AOCS Press title, *Lipid Oxidation: Challenges in Food Systems*. Learn more about this title by reading the book review by Laurence Eyres, a consultant with Food Inc. in Aukland, New Zealand, available via this issue's supplement (digital and mobile editions only).

In marked contrast to changes in maize proteins in tortillas, peanut proteins showed little crosslinking, but there was notable fragmentation or dissociation of arachins. Rather, the dominant changes were surface modifications and reorganization of arachin and conarachin sub-units (Fig. 3). Coomassie blue dye binding decreased in all fractions. Basic protein fractions (mostly albumins) showed a progressive decrease in molecular weight, while acidic globulins rearranged, fragmented, and aggregated.

Peptides from both albumins and globulins became more hydrophobic due to surface or configuration changes, decarboxylation, deamination, some aldehyde reactions, and moved to the SDS (sodium dodecyl sulfate)-soluble fraction. In fresh peanut butter, the SDS-soluble fraction had little material, but by the end of incubation, this was the dominant fraction containing a large proportion of the modified peptides (Fig. 3). Surface modifications resulted primarily from extensive protein oxidation, especially in the SDS-soluble fraction, along with low levels of carbonyl–amine reactions (Schiff base or Michael addition) and some decarboxylation of acidic residues. Protein modifications followed the same cycling pattern as lipid oxidation, suggesting that lipid oxidation products did not accumulate because lipid radicals, hydroperoxides, and to a lesser extent aldehydes reacted preferentially with proteins, broadcasting oxidation to these non-lipid molecules. Hardening of the peanut butter appears to be directly related to surface modifications and structural reorganization of the proteins mediated by oxidized lipids.

Both of these studies established a direct correlation between lipid oxidation and protein degradation and demonstrated quite clearly how measuring only lipid oxidation can grossly underestimate oxidation in complex systems. Evidence suggests that lipid free radicals and hydroperoxides are the most active species damaging proteins during the first few months of shelf life in foods, but the results in the tortilla chips and peanut butter are quite different—peptide crosslinking leading to very large molecular complexes of maize proteins in dry fried tortilla chips vs. marked surface modifications, structural reorganization and disassociation of protein subunits, and protein fragmentation in the emulsions of peanut butter. In both cases, a major consequence of protein co-oxidation was deterioration of food textures, though certainly not by the same mechanisms. Results demonstrate clearly that "one size does not fit all" in protein co-oxidations and that measuring protein changes along with lipid oxidation is critical for accurately assessing the extent of oxidative deterioration in foods.

K.M. Schaich is an associate professor in the Department of Food Science at Rutgers University in New Jersey, USA. She can be contacted at schaich@AESOP.Rutgers.edu.

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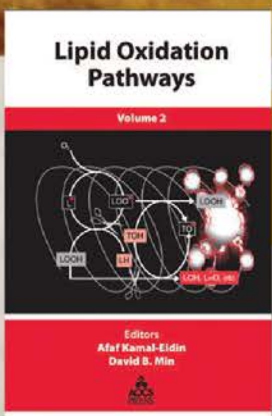

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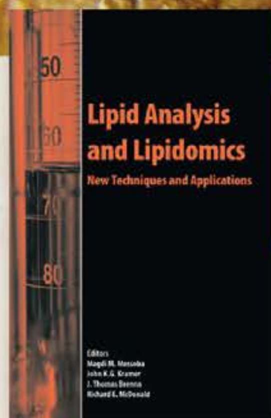

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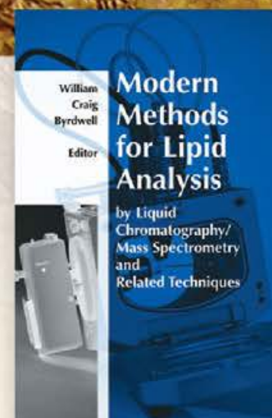

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List: ~~$223~~ $123 • Member: ~~$165~~ $65

Edited by Afaf Kamal-Eldin and David B. Min. ISBN 978-1-893997-56-1. 324 pages. Hardback. 2008.

This book complements *Lipid Oxidation Pathways*, Volume 1, by focusing on the oxidation kinetics and mechanisms governing the behavior of different molecular species involved in lipid oxidation reactions. It provides a detailed review of the reactions of lipid molecules other than conventional polyunsaturated fatty acids.

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Edited by Magdi M. Mossoba, John K.G. Kramer, J. Thomas Brenna, and Richard E. McDonald. ISBN 978-1-893997-85-1. 458 pages. Softbound. 2006.

New applications and methods for the analysis of edible oils, fats, and cellular lipids are always in development. These methods apply to biological and food matrices, edible oils and fats, as well as cellular fats of pathogenic bacteria and spores, and will cover many research applications in lipidomics, food analysis, food safety, food security, and counter-terrorism. *Lipid Analysis* offers the lipid analyst an array of essential analytical tools in the fields of chromatography, mass spectrometry, spectroscopy, magnetic resonance, and chemometrics. This book also serves as a reference for recent developments, and reviews the rapidly evolving field of lipid methodologies.

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List: ~~$234~~ $134 • Member: ~~$175~~ $75

Edited by William Craig Byrdwell. ISBN 978-1-893997-75-2. 588 pages. Hardback. 2005.

As the number of commercially available instruments with atmospheric pressure ionization (API) interfaces has increased, interest in liquid chromatography/mass spectrometry (LC/MS) for lipid analysis has blossomed. Research into novel techniques for LC/MS is a lively source of journal article material, most notably regarding electrospray ionization and atmospheric pressure chemical ionization for analysis of lipids. The summary of LC/MS in this book serves as a valuable reference and resource for those interested in moving into the field of lipid analysis using modern instrumentation. *Modern Methods* describes previous work that helped establish the foundation of the field, while also demonstrating new data that are quickly defining a new level of "state-of-the-art." Described herein are the methods that will be applied to lipids into the next decade and hopefully beyond.

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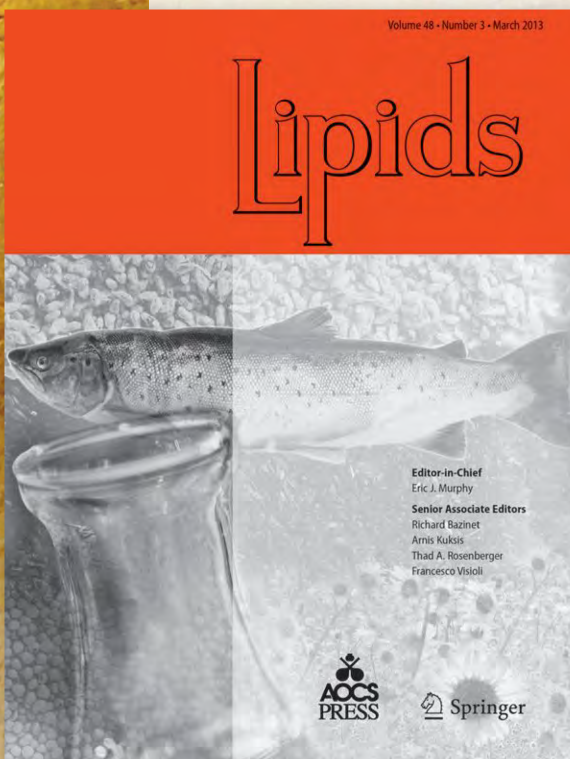

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Eric J. Murphy is a tenured associate professor in the Department of Pharmacology, Physiology, and Therapeutics at the University of North Dakota, Grand Forks, USA. He has served as editor-in-chief of *Lipids* since 2006 and as an associate editor with the *Journal of Neurochemistry* since 2004.

Be sure to read the feature article "Lipidomics Comes of Age" in last month's issue of *Inform*.

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Rebecca Hobden

Viesel Fuel, in collaboration with Novozymes and Tactical Fabrication, has developed and implemented a biodiesel production process using enzymes to produce at a rate of 5 million gallons (19 million liters) annually. The company says its process can be easily scaled to larger capacities. Recovery and reuse of the enzymes to catalyze several batches makes the enzymes economically feasible, and simple resin-based technology is used to bring the crude biodiesel into ASTM specifications. Additionally, this process requires a lower capital investment, works at a production cost per gallon that is comparable to that of traditional biodiesel, and most importantly, allows the use of less expensive, more varied feedstocks with free fatty acid content as high as 100%.

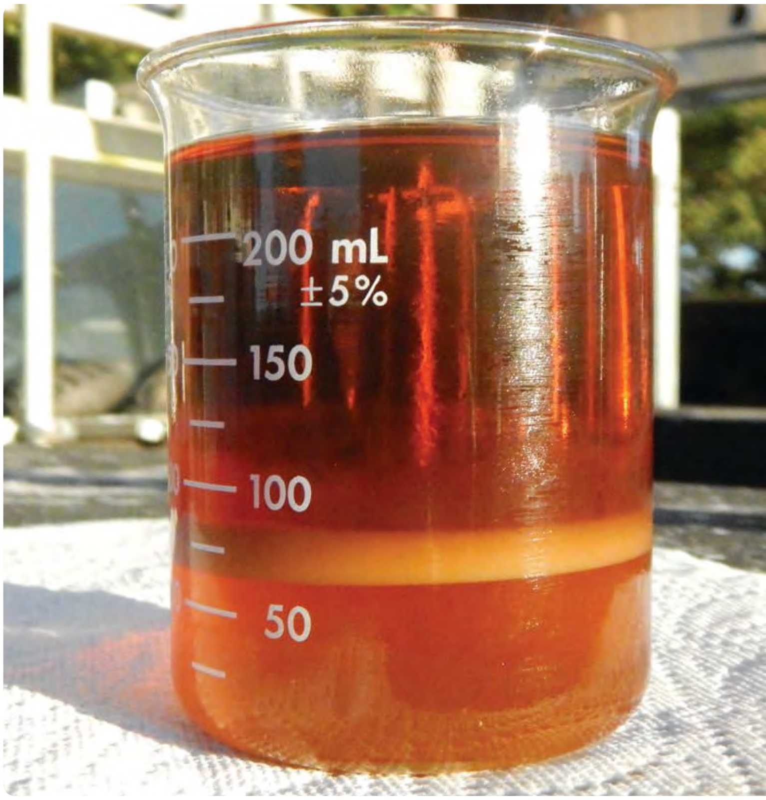

FIG. 1. Clear separation: a sample of enzyme-catalyzed product is shown with the glycerin phase on the bottom, the enzyme phase in the middle, and the biodiesel phase on top.

FEEDSTOCKS IN THE MARKET

Demand for biodiesel in recent years has greatly increased due to consumer acceptance as well as incentives and mandates, such as the renewable fuel standard (RFS), which are in place through state and federal governments. Consequently, the economic viability of many biodiesel facilities relies heavily on the ever-changing policies related to biodiesel. Because the cost of feedstock is the largest single expenditure in the production of biodiesel, the flexibility enzymes allow to use any feedstock that may appear in the marketplace, from brown grease to virgin oil, is economically advantageous and offers a reprieve for biodiesel

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- **Enzyme-catalyzed biodiesel production has long been on the cusp of revolutionizing the way biodiesel is produced.**
- **Historically, the high cost of enzymes has outweighed any benefits they might offer, such as (i) their ability to convert low-quality, high free fatty acid (FFA) feedstocks, (ii) savings on energy consumption, and (iii) coproduction of technical-grade glycerin.**
- **Recently, the hurdle of making the process economically viable on a commercial scale has been overcome.**

producers whose sustainability shifts and destabilizes with the changing value of tax credits and RIN [renewable identification number] prices.

Pretreatment of feedstock is required to remove impurities that may be harmful to the reaction kinetics (in this case the enzymes) and/or prohibit compliance with ASTM D6751 standards. The use of low-quality feedstocks has been problematic for traditional processes and catalysts, even after all other impurities have been neutralized, due to their high FFA content. A major advantage of enzymes is their ability to easily convert FFA to fatty acid methyl esters (FAME) at temperatures around 95°Fahrenheit (35°C), and with less methanol. The appropriate pretreatment method depends on the feedstock and might include water washes and settling, neutralization of pH, or filtration. Sulfur is one of the more troublesome contaminants in low-quality feedstocks, but research and development of technologies including filtration and resins for sulfur reduction to 15 ppm in either feedstock or crude biodiesel assists in making inexpensive, high-FFA feedstock a viable option.

ENZYMATIC REACTION

The enzymes are able to convert high-FFA feedstock because the reaction chemistry occurs in two steps: The glycerides are first hydrolyzed to FFA, and then the FFA and methanol are esterified to produce FAME. When using high-FFA feedstock, the hydrolysis step has already occurred and the main job of the enzyme becomes the conversion of FFA to FAME. In the esterification step, water is produced and absorbed into the heavy phase, which also consists of glycerol, excess methanol, and enzymes. Conveniently, water is a necessary component to activate the enzymes and does not lead to soapy contaminants, as it does in many traditional processes.

Careful monitoring during the reaction of methanol, water, and enzymes in the heavy phase; temperature; and rate of conversion is critical to ensure high-quality finished biodiesel and optimum number of enzyme reuses. The "happier" the enzymes are, the longer they will remain active, and the more economical they become.

ENZYME RECOVERY AND REUSE

So that the manufacturer can recover the enzymes, the reaction mixture must go through two different stages of settling. Initial settling results in a heavy phase that includes glycerol, methanol, water, and enzymes as well as a light phase of crude biodiesel. At this point, the crude biodiesel can be withdrawn from the reactor and refined, while the heavy phase requires further separation. The second stage of settling results in a transparent glycerin phase, which falls to the bottom of the reaction vessel, and the enzymes, which migrate to the interface between crude biodiesel and glycerin. This second separation can be expedited by the use of flocculants or by mechanical separation with membranes. A portion of the glycerin phase is withdrawn and refined, while the remaining glycerin and the layer of active enzymes are retained in the reactor and reused to catalyze the next reaction (Fig. 1, page 143).

Combining proper feedstock pretreatment and optimized reaction conditions allows Viesel to run a series with a minimum of eight to 10 enzyme reuses, with a 10% addition of fresh enzymes to each batch.

The glycerin can be cleaned easily to 80% purity with simple vacuum distillation to remove methanol and water. If a processor chooses to add additional processing, such as resins, filtration, or active carbon, this glycerin could be purified to greater than 97%. In either event, the glycerin can be sold into value-added applications not normally available for crude glycerin.

BIODIESEL REFINING

The use of enzymes results in a crude biodiesel with 1.5–2.0% unreacted FFA. Viesel Fuel initially used a caustic wash to turn this FFA to soap, followed by washes and centrifugation to remove the soap and water. The recovered soap was acidulated back to FFA, for reuse as a blend component in the feedstock.

Viesel Fuel has most recently adopted the use of resin technologies, both as a catalyst to convert FFA to FAME and in an ion exchange capacity to adsorb any remaining FFA. The optimization of resins makes the refining process simpler, reduces yield loss, and has allowed Viesel Fuel to transition to a continuous flow process for the biodiesel refining section of the plant. Viesel Fuel will further develop the capability to convert the current batch enzymatic reaction process into a continuous process throughout 2014.

CONCLUSION

The benefits of enzyme catalysts in the production of biodiesel have long been apparent, but until now their adoption on a commercial scale has not been economically feasible. With production approaching 150 batches in six months, Viesel Fuel's process has demonstrated that the enzymes require less energy and fewer chemicals. When coupled with resin technologies for refining to ASTM specifications, the process becomes cost comparable to traditional catalysts. But the true economic benefit of enzymes comes in their ability to handle a variety of inexpensive feedstocks, making enzymes a financially prudent route for biodiesel producers, allowing them to thrive despite low RIN prices and the disappearance of tax incentives.

Rebecca Hobden is a chemical engineer with Viesel Fuel LLC, headquartered in Florida (USA). She can be reached at rhobden@vieselfuel.com.

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BRIEFS

New research shows that a cocoa butter equivalent (CBE) made from mango seed fat and palm stearin could help manufacturers produce chocolate that can withstand high temperatures. This could be a boon to companies looking to boost their presence in developing countries with warm climates such as Brazil and India. The study was led by M.H.A. Jahurul of the Universiti Sains Malaysia and found that the mango/palm CBE maintained fat structure at 37.5°C. This compares favorably with the average melting temperature of cocoa butter, which is around 34°C. The work appeared in *Food Chemistry* (http://dx.doi.org/10.1016/j.foodchem.2013.11.098, 2013).

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Cargill Cocoa & Chocolate broke ground in December 2013 on a $48 million project to double the capacity of its chocolate production facility in Mouscron, Belgium. The additional capacity will meet growing demand for chocolate in confectionary, bakery, dairy, and artisanal applications from European customers, Cargill said. The new facility is expected to be operational in the second quarter of 2014.

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Archers Daniels Midland Co. (ADM; Decatur, Illinois, USA) announced in January 2014 that it is building a $6.5 million refining plant within the ADM processing complex in Decatur. The new facility, scheduled for completion in the second half of 2014, will be used to refine crude vegetable oil into an acidulated form that improves the nutritional value of animal feeds and can allow livestock feeders to use less grain in their animals' rations. The plant will have a production capacity of 800,000 pounds (about 400 metric tons) per day, according to ADM. ■

NEWS & NOTEWORTHY

FSMA marches on

The tangled web of interrelated proposed regulations and comment period deadlines mandated by the US Food Safety Modernization Act (FSMA) of 2010 continued to move toward final implementation at the close of 2013 as the US Food and Drug Administration (FDA) made several important announcements. Implementation is complicated by the fact that a federal court has ordered that all FSMA rules be made final by June 30, 2015, despite FDA's assertion that it needs more time to adequately review and write final regulations. (See *Inform* 25:16–19, 2014.)

The agency's troubles creating and implementing the massive overhaul of the US food safety system are encapsulated in an FDA announcement made on December 19, 2013. In a blog post (see http://tinyurl.com/FDA-FSMA-2), FDA's Michael Taylor, deputy commissioner for foods and veterinary medicine, began by writing: "You spoke. We heard you." Input from farmers, Taylor said, led to an FDA decision to revise two of the proposed rules affecting farmers under the Food Safety Modernization Act (FSMA). Revised rules for the proposed regulations—originally released in January 2013—on produce safety and preventive controls for human food will be released early in the second quarter of 2014, he said.

Next, on December 24, 2013, the agency released its proposed rule on food defense. (See http://tinyurl.com/FSMA-adulteration.) That left only one remaining regulation to be released—a proposed rule on the sanitary transport of food and feed—which was presented on January 31, 2014 just as this issue of *Inform* was going to press. More information on it will appear in the April issue.

FSMA RULE ON ADULTERATION

"Under the proposed rule on Focused Mitigation Strategies to Protect Food against Intentional Adulteration, a food facility would be required to have a written food defense plan that addresses significant vulnerabilities in its food production process," explains William Kanitz, president of Scoring System, Inc. in Venice, Florida, USA. Scoring System is the developer of ScoringAg, an online food safety record-keeping system.

CONTINUED ON NEXT PAGE

"Facilities then would have to identify and implement strategies to address these vulnerabilities," noted Kanitz.

The aim of the proposed rule is to protect food from intentional adulteration when the intent is to cause large-scale public harm. FDA has identified four key activities within the food production system that are most vulnerable to such forms of adulteration. They are:

- Bulk liquid receiving and loading;
- Liquid storage and handling;
- Secondary ingredient handling (the step where ingredients other than the primary ingredient of the food are handled before being combined with the primary ingredient); and
- Mixing and similar activities.

Under the proposed rule, facilities would be required to review their production systems to determine if they engage in any of these activities or else complete their own vulnerability assessments. Once that is completed, they would need to identify actionable process steps, "which are points, steps, or procedures in a food process that will require focused mitigation strategies to reduce the risk of intentional adulteration," FDA said.

The cost of the proposed rule to both domestic and foreign firms, according to the agency, annualized over 10 years at a 7% discount rate, is between $260 million and $470 million. The first-year cost is between $520 million and $860 million. The average annualized cost per firm is about $37,000, with initial costs of $70,000. (This is an average per-firm cost, and firms may have more than one facility. The annualized cost for a one-facility firm with 100 employees is about $13,000.) "The expected benefit of preventing a catastrophic terrorist attack on the US food supply is about $130 billion, which means that the benefits of this rule outweigh the costs to Americans if the rule has a 1 in 730 or better annual chance of preventing such an attack," FDA said in the proposed rule.

COMMENT PERIODS EXTENDED

The comment period for the proposed rule on adulteration closes on March 31, 2014. Meanwhile, FDA extended the comment periods for two previously released FSMA proposed regulations. Comments on the proposed rule on food for animals and the draft risk assessment for animal feed operations co-located on a farm are now due on March 31 instead of February 26.

ADM to create global headquarters in Chicago

Archer Daniels Midland Co. (ADM; Decatur, Illinois, USA) announced in mid-December 2013 that it has selected Chicago as the location for its global headquarters and customer center.

"While we considered other global hubs, Chicago emerged as the best location to provide efficient access to global markets while maintaining our close connections with US farmers, customers, and operations," said ADM Chairman and CEO Patricia Woertz.

"In keeping with our intention to establish our global center in a cost-effective manner, we expect to locate a small corporate team of about 50 to 75 employees in the new center," Woertz commented. In addition, she noted that the company will now evaluate alternative sites for its new Information Technology (IT) and support center, where it expects to locate about 100 new IT jobs. The company said it will continue to consider potential locations for the IT center in several states and expects to make a decision by mid-year 2014.

Woertz said that ADM will continue to have a significant presence in Decatur, which will be designated the company's North American headquarters, and that the company does not plan any layoffs in connection with the move to a new global center.

Trade implications of the Panama Canal expansion

The Panama Canal is in the midst of its largest expansion in nearly a century. The $5.25 billion project, expected to be complete in 2015, centers on the construction of a new set of locks to allow for the passage of wider, longer, and more heavily loaded ships. (For more, see www.pancanal.com/eng/expansion.)

Upon completion of the expansion project, the cost to transport grain from the US Corn and Soybean Belt to Asia will drop by an estimated 12%, thus enhancing the cost competitiveness of the United States as a grain exporter to Asia, Rabobank forecasts.

In a new report, "Panama Canal: Expanding the Gateway for US Grain to the East," Rabobank says the expansion of the Canal will accommodate grain-laden ships with 25% more capacity than before, resulting in a shift in US grain-shipping routes.

Rabobank predicts the decline in shipping cost, coupled with the increased capacity, will help ports along the US Gulf of Mexico to regain export volume lost to ports in the Pacific Northwest over the last decade and also benefit large grain traders and exporters with operations in the US Gulf region. Ocean freight accounts for 60% of total shipping cost, so increased shipping capacity has a material effect on cost savings.

The Panama Canal is the main artery for US grain exports, with the US Gulf currently accounting for about two-thirds of volume. For decades, the shipping route from the central US corn and soybean belt down the Mississippi River to the Gulf and through the Panama Canal has been the dominant avenue for US grain exports. However, with the rising importance of Southeast Asia in the global grain trade over the past decade, the US Pacific Northwest has taken more than 10% market share from US Gulf ports over the past decade.

Rabobank also found that:

- *More than $225 million in US transportation costs will be saved.* The expansion of the canal will push down the cost of shipping a bushel of corn or soybeans from the United States to Asia from approximately $2/bushel to $1.75/bushel. With an estimated 900 million bushels (between 23 and 25 million metric tons) of grain shipped each year, the actual cost savings to US grain traders and exporters will be $225 million annually, a significant benefit to companies in the sector.
- *The "draw area" in Minnesota, Iowa, and Missouri will be doubled.* The Canal expansion is expected to approximately double the overall draw area in these three grain-producing states to 50% of all corn acres (up from 26% currently) and 48% of all soybean acres (up from 28%

SUSTAINABILITY WATCH

Two of the five Presidential Green Chemistry Challenge Awards presented in December 2013 recognized innovations involving vegetable oils (and chicken feathers, as it turns out). The awards, given annually for the past 18 years, are administered by the US Environmental Protection Agency's Green Chemistry Program.

"It's hard not to be in awe of these accomplishments," chemistry professor Bruce H. Lipshutz of the University of California, Santa Barbara, told *Chemical & Engineering News* magazine. "But the world has a long way to go. Research and development in this direction, whether in industry or academia, must be desperately expanded."

The winner of the individual award is Richard P. Wool of the University of Delaware (Newark, USA), who has created several high-performance materials using biobased feedstocks, including vegetable oils, chicken feathers, and flax to produce a range of products such as adhesives, composites, foams, a leather substitute, and even computer circuit boards.

The other vegetable oil-related award was given to Cargill, Inc.'s unit in Brookfield, Wisconsin, for developing a soybean oil-based dielectric fluid for use in high-voltage electric transformers. (See http://tinyurl.com/transformer-fluid for *Inform*'s 2008 look at the development of several different vegetable oil-based dielectric fluids.)

For more information on the awards, see http://tinyurl.com/EPA-Green-2013.

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AkzoNobel has joined the Together for Sustainability (TfS) initiative (see http://tinyurl.com/Akzo-TsF and www.tfs-initiative.com/). TfS, which was founded in 2011 and is based in Germany, aims to develop and implement a global supplier engagement program that assesses and improves sustainability sourcing practices, including ecological and social aspects. "Technically, suppliers now only have to complete one form instead of multiple questionnaires [for all the companies involved in TfS]," the TfS website notes. "Additionally, buyers can access the information through a shared platform." The other members of the initiative are BASF, Bayer, Evonik Industries, Henkel, LANXESS, and Solvay.

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Sustainable palm oil remains in the news as pressure on the industry continues to come from environmental groups, investors, and large buyers. In December 2013, Wilmar International, the Singapore-based palm oil and food ingredients company, made a commitment to supplying sustainable palm oil. Toward that end, Wilmar and global consumer products manufacturer Unilever signed a Memorandum of Understanding (MoU) that "aims to accelerate sustainable market transformation for palm oil," Wilmar said in a news release. "In parallel, and [as a] key part of the MoU, Wilmar launched a new 'No Deforestation, No Peat, No Exploitation' policy that aims to advance an environmentally and socially responsible palm oil industry." See http://tinyurl.com/Wilmar-MoU for more information. ■

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currently). The doubled draw area will comprise 15% of total corn and soybean acres in the United States, up from 8% currently.

- *Whereas US Gulf ports will see growth, the Pacific Northwest ports will remain static.* Over the next decade, the estimated share of US grain exports from the Gulf region is expected to rise to 72% of the total. This increase will come mainly from a rise in US grain exports overall, rather than from cannibalization.
- *The impact on overall exports is uncertain.* The effect of the Canal expansion on overall US export volume is harder to quantify, with weather volatility, export growth in Brazil and Eastern Europe, and concerns over US yield potential clouding the US export picture. The demand side is equally murky owing to changes in the US ethanol mandate and China's grain stocks. Rabobank views US Department of Agriculture baseline projections of less than 1% growth in soybean exports and 5% growth in corn exports over the next decade as best-case scenarios.

The Rabobank Group (www.rabobank.com) is a global financial services cooperative providing wholesale and retail banking, asset management, leasing, real estate services, and renewable energy project financing to agribusiness. ■

At the 7th International Algae Conference held in Hamburg, Germany, in December, Dutch company Evodos won the Algae Innovation Award for 2013 for producing the best innovation in the algae industry. The company's harvesting technique, a dynamic settler with spiral plate technology, outperforms traditional separation/harvesting equipment. Separation efficiency exceeds 95%, and the dry weight of the resultant algae paste is 1.5–2 times better compared with traditional centrifuges. Furthermore, even the smallest and most fragile cells remain intact and undamaged during the process. For further information see www.evodos.eu.

■■■

A number of drivers of diesel cars in eastern England and Scotland began experiencing breakdowns in November and December 2013. Blockage of the fuel filters by the formation of a gel-like substance in the diesel fuel was identified as the cause. The initial culprit was suspected to be the increase in biofuel content—up to 7% added to all road diesel—required by European Union law. Experience in years past with filter-clogging during colder months was alleviated with fuel additives. In the current situation, as the weather warms, the gel does not dissolve back into the fuel, meaning a new filter must be installed.

■■■

In a report entitled "Global Algae Biofuel Technologies Market 2014–2018," MarketResearchReports.Biz predicts a compound annual growth rate for algal fuel of 43.4% for 2013–2018. See http://tinyurl.com/algae-biotech-fuel for further information.

■■■

In December 2013 BiofuelsDigest.com released a compilation of biofuels mandates and targets around the world (http://tinyurl.com/biofuels-mandates-targets). Sixty-two countries were identified as having mandates: 13 in the Americas (including individual standards for the Canadian provinces), 12 in Asia-Pacific, 10 in Africa, and the remaining 27 in the European Union. The article presents details on both biodiesel and ethanol mandates. ■

BIOFUELS+

Algae feedstock. Image courtesy of the US Department of Energy's Pacific Northwest National Laboratory.

Algae to oil in minutes

Engineers at the US Department of Energy's Pacific Northwest National Laboratory (PNNL; Richland, Washington) have created a continuous chemical process that produces useful crude oil from algae in minutes. Their starting material is an aqueous slurry of algae having dry solids concentrations of up to 35 wt%.

PNNL scientists and engineers simplified the production of crude oil from algae by combining several chemical steps into one continuous process that incorporates a number of methods, thus reducing the cost of producing algal fuel. The most important cost-saving step is that the process works with wet algae. Many current processes require the algae be dried first, which is energy intensive.

"Not having to dry the algae is a big win in this process," according to Douglass Elliott, leader of the PNNL research team. "Then there are bonuses, like being able to extract usable gas from the water and then recycle the remaining water and nutrients to help grow more algae, which further reduces costs."

The PNNL system runs continuously, processing about 1.5 liters of algal slurry per hour in the reactor. Instead of using hexane to extract the oil, the whole algal biomass is subject to an aqueous extraction at high temperature (~350°C) and high pressure (~3,000 psi, or 20 MPa). Both hydrothermal liquefaction and catalytic hydrothermal gasification take place.

Products of the process include:

- Crude oil, which can be converted to aviation fuel, gasoline, or diesel fuel. In the PNNL experiments 50–70% of the algal carbon is converted to energy in crude oil
- Clean water, which can be re-used to grow more algae
- Fuel gas, which can be burned to make electricity or cleaned to make natural gas
- Nutrients such as nitrogen, phosphorus, and potassium, which can be recycled to help grow more algae.

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A biofuels company, Utah-based Genifuel Corp., has licensed the technology and is working with an industrial partner to build a pilot plant using the technology.

The research was reported in a paper by D.C. Elliott, T.R. Hart, A.J. Schmidt, G.G. Neuenschwater, L.J. Rotness, *et al.*, Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor, *Algal Research* 2:445–454 (2013). Also see http://tinyurl.com/algae-processing.

"Not having to dry the algae is a big win in this process."

Jatropha beginning to pick up?

Although the shrub *Jatropha curcas* has been promoted as a source of non-edible vegetable oil for use in making biodiesel, success in commercializing this tropical plant has been quite uneven. One of the initial attractions of the plant as a biodiesel feedstock had been the possibility that the plant could be grown on unused land (e.g., in hedgerows) without additional inputs. However, researchers have found that without additional water and fertilizer, oil production is not always sufficient to generate a profit.

Researchers in both the United States and India are finding ways to increase oil production in the plant. SGB, Inc., located in San Diego, California, USA, has been using molecular genetics and DNA sequencing technology to develop hybrid strains of jatropha that, it says, produce oil in quantities to make it competitive with petroleum priced at $99 a barrel. (The US Energy Information Administration has projected that Brent crude oil will average $105/barrel in 2014 and $102/barrel in 2015. For further information see www.eia.gov/forecasts/steo.) The challenge will to achieve high yields out in the field, as opposed to in a greenhouse.

SGB has contracts to plant 250,000 acres (100,000 hectares) of jatropha in Brazil, India, and other countries. From these, the company projects production of about 70 million gallons (260 million liters) of fuel a year (http://tinyurl.com/jatropha-USA-SGB). At these levels, jatropha oil could act as a hedge against spikes in petroleum prices—and as a way to meet government mandates to use biobased fuels.

In a December 2013 interview with *The New York Times*, Jim Rekoske, vice president for renewable energy and chemicals for Honeywell International, Inc., said that jatropha "is one of the few biofuels that I think has the potential to supply a large fraction of the aviation fuel currently used today."

One key to the success SGB has had in developing new hybrid strains of jatropha has been the discovery of just how genetically diverse jatropha plants can be. Costs of mapping a plant's genetics are falling rapidly, reportedly $150,000 per plant in 2008, and about $50 per plant in 2014 (http://tinyurl.com/jatropha-USA-SGB).

JOil (S) Pte. Ltd., headquartered in Singapore and India, has also been working to develop high-yielding jatropha. Using two open-pollinated JOil-developed jatropha varieties, the company reports it has achieved an average seed yield of 3.53 metric tons per hectare (MT/ha) in the third year of its large-scale Indian field trials. It anticipates yields of 4.5 MT/ha in year 4 (http://tinyurl.com/JOil-jatropha-yield).

In a December 2013 company statement, JOil's Chief Technology Officer Srinivasan Ramachandran said, "The results of the India field trials take jatropha closer to commercial viability, which we believe is within two years from now, once a yield of 5 MT/ha is achieved."

JOil is also working with genetically modified seedlings in its efforts to reach commercial cultivation.

REG to acquire Syntroleum

On December 17, 2013, Renewable Energy Group (REG; Ames, Iowa, USA) announced it would acquire the assets of Syntroleum Corporation (Tulsa, Oklahoma, USA) and assume substantially all of the material liabilities of Syntroleum. The cost was 3.8 million shares of REG common stock, valued at $40.08 million on December 17. Preliminary estimates were that Syntroleum stockholders would receive 0.3809 shares of REG common stock for each outstanding share of Syntroleum common stock. The asset sale was expected to close in the first quarter of 2014.

Syntroleum pioneered Fischer-Tropsch gas-to-liquids and renewable diesel fuel technologies. As of December it had 101 patents issued or pending. Syntroleum also owned a 50% interest in Dynamic Fuels, a joint venture with Tyson Foods, Inc., located in Geismar, Louisiana, USA. That facility has the capacity to process waste animal fat or other low-margin greases into75 million gallons (284 million liters) annually of renewable fuel for use in planes or trucking fleets.

According to REG President and Chief Executive Officer Daniel J. Oh, "This will help us grow our advanced biofuel business, enhance our intellectual property portfolio, expand our geographic footprint, and launch REG into new customer segments."

Furthermore, Oh said, "Syntroleum and its 50%-owned subsidiary Dynamic Fuels represent an attractive entry path for REG into renewable diesel. They have invested substantial resources in their Bio-Synfining technology, which enables the economical conversion of lipid-based biomass into diesel and jet fuel. Their technology and products complement our core biodiesel business."

As of December 2013 REG had a combined nameplate production capacity of 257 million gallons of biodiesel per year at its eight active biodiesel refineries in four states and was distributing biodiesel through a national network of distribution terminals.

Post-completion of the sale, Syntroleum will represent about 10% of REG shares, and REG's capacity will increase 15%

(~37.5 million gallons annually). Furthermore, the increase in gallons will have a higher margin that what REG currently produces. Thus, at least one analyst predicts the Syntroleum purchase should boost REG's earnings per share (http://tinyurl.com/REG-SYNM-EPS).

The Syntroleum plant has not operated since October 2012, when it shut down for a turnaround. It had been scheduled to reopen in July 2013, but doing so would have cost Syntroleum $10 million, to which the cash-strapped company was reluctant to commit. Syntroleum's President and CEO Gary Roth said the deal was the best way forward for the company (http://tinyurl.com/BatonRouge-Syntroleum).

At least one stock analyst questioned the wisdom of REG's purchase, saying that 2014 will be a difficult year for biodiesel producers because of the expiration of the Blenders Tax Credit on December 31, 2013, an oversupply of biodiesel, and proposed reductions in federal mandates for incorporation of biofuels into the nation's energy supply (http://tinyurl.com/REG-Syntroleum-critique), However, the consensus seems to be favorable.

Biodiesel in the Philippines

The *Manila Standard Today* newspaper reported on January 2, 2014, that biodiesel producers in the Philippines have increased their annual capacity by 70.3 million liters in advance of implementation of a higher biodiesel blend in petroleum products. Nine accredited coco-methyl ester production plants accounted for the additional capacity, including five that expanded their facilities. These five, taken together, now can produce 345.3 million liters annually.

Coco-methyl ester producers as well as the Philippine Coconut Authority have been pushing for an increase by 2015 from the current 2% blend of coco-methyl esters into diesel to 5%, as a means to accelerate development of the coconut industry. Before this can happen, though, the Energy Department's Renewable Energy Management Bureau is waiting for a price and supply impact study from the National Economic and Development Authority.

Three conditions must be met before an increase to 5%: adequate supplies of copra, coconut oil, and coco-methyl ester.

In these discussions, the question of the destruction wreaked in November 2013 by Typhoon Haiyan, known as Typhoon Yolanda in the Philippines, comes up. The *Wall Street Journal* newspaper reported that Haiyan destroyed as many as 15 million coconut trees on 42,000 hectares for a loss of $38 million, but that 300 million trees remain (http://tinyurl.com/coconuts-diesel-Philippines). According to Ben Evardone, congressman from the province of Eastern Samar, where most of the island's coconut plantations suffered heavy losses, it would take 7–10 years for traditional coconut varieties to produce after replanting, but some of the new varieties would bear fruits in 3–5 years.

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Neste using only certified palm oil

Neste Oil, headquartered in Porvoo, Finland, has achieved its long-term target of using only certified palm oil as an input for its renewable diesel production process. The original target, set in 2009, was that 100% of the raw palm oil used would be certified by the end of 2015, but Neste achieved this goal in 2013. All the renewable inputs used by Neste Oil have been traced back to the plantations and production sites from which they come. Certification verifies that the sustainability criteria set for biofuels are met throughout the supply chain.

US Secretaries push for biofuels

US Secretary of Defense Chuck Hagel, Secretary of Agriculture Thomas Vilsack, and Secretary of Energy Ernest Moniz joined on January 2, 2104, to support the Defense Production Act biofuels effort, calling it an important element of a comprehensive US government investment in national energy security. Their joint letter of support was sent to Harry Reid, Senate Majority Leader; John Boehner, Speaker of the House of Representatives; Dianne Feinstein, chair of the Senate subcommittee on energy and water development; and Mike Simpson, chair of the House of Representatives subcommittee on energy and water development. The secretaries urged support of the US Navy's efforts to procure drop-in, cost-competitive advanced biofuels and to supply funding for this effort.

These letters followed the December 13, 2013, unveiling of the Farm to Fleet Program of the US Department of Agriculture and the US Navy. Through this program the Navy will begin to add biofuels into its regular domestic purchases of approximately 77 million gallons (290 million liters) of jet fuel (JP-5) and marine diesel (F-76) each year. Requests for proposals will go out in the second quarter of 2014, initial fuel contracts will be issued in 2015, and first deliveries are to be scheduled for mid-2015. The fuels will be blends of 10–50% biofuel, with the rest being conventional petroleum-based fuels.

The December announcement marked the first time alternative fuels such as advanced drop-in biofuels would be available for purchase through regular procurement practices. It lowered barriers for alternative domestic fuel suppliers to do business with Department of Defense. Preliminary indications from the Defense Production Act Title III Advanced Drop-in Biofuels Production Project are that drop-in biofuels will be available for less than \$4 per gallon (~\$1 per liter) by 2016, making them competitive with traditional sources of fuel.

The USDA and Navy also sponsored an Industry Day in Washington, DC, on January 30, 2014, to provide more information for stakeholders in the Farm to Fleet Program.

Further information is available at http://tinyurl.com/Dec-FarmtoFleet, http://tinyurl.com/biofuels-USSecretaries, and http://tinyurl.com/biofuel-defense. ■

A study in *Food Research International* (http://dx.doi.org/10.1016/j.foodres.2013.10.044, 2014) attempts to establish the secret to producing the perfect chip (French fry). In work led by John S. Lioumbas of Greece's Aristotle University of Thessaloniki, researchers explored the effect of gravitational force on the deep-fat frying of potato chips. Researchers fried chips at varying gravity levels (1.8-, 3.0-, 6.0-, and 9.0*G* and found that this affected the crust thickness of the chips. "Temperature recordings and crust thickness evolution indicate that heat transfer during frying depends on gravity level but differently at different potato orientations," write the authors.

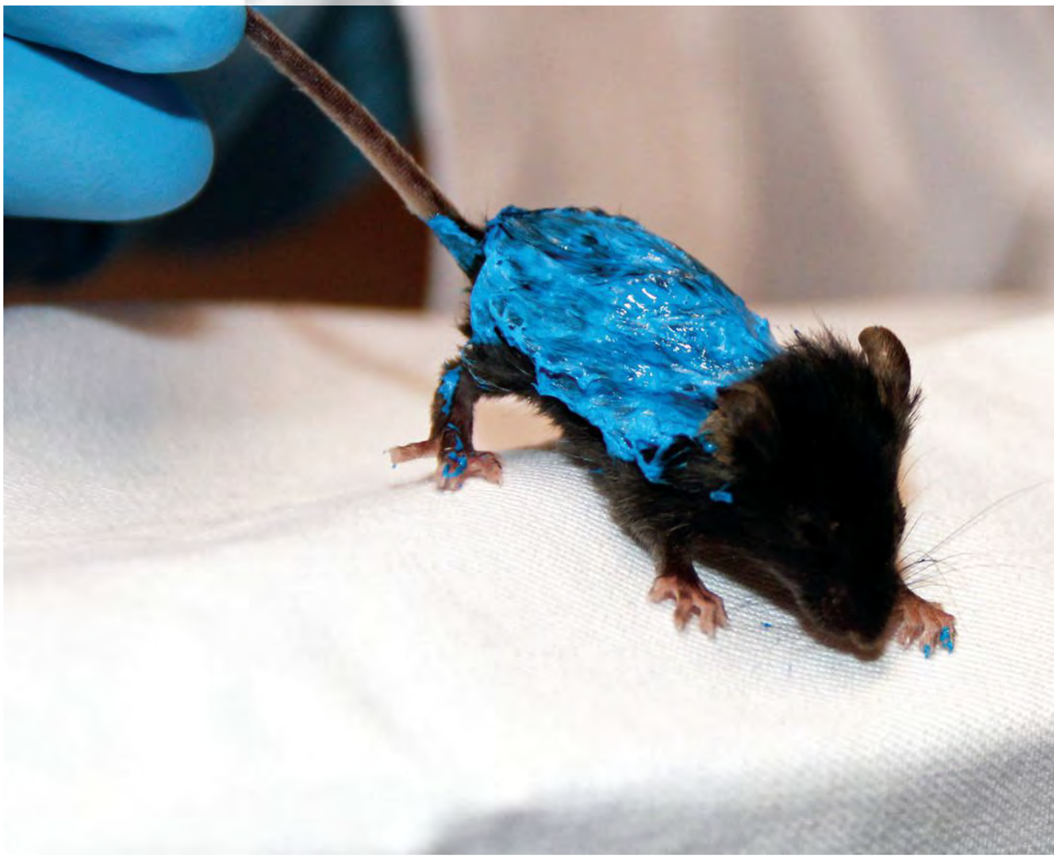
■■■

Is dietary saturated fat associated with elevated blood lipid levels and, consequently, with the risk of chronic diseases, including coronary heart disease? A meta-analysis led by C.B. Dias of the University of Newcastle (Callaghan, New South Wales, Australia) suggests that elevated blood lipids may be due to a lack of omega-3 polyunsaturated fatty acids (n-3 PUFA) rather than a saturated fat-rich diet. The team also suggests that "evidence from animal studies and [a] few clinical trials lead to the hypothesis that there are beneficial or neutral effects of saturated fatty acids when combined with recommended levels of n-3 PUFA in the diet." Their work appears in *Medical Hypothesis* (http://dx.doi.org/10.1016/j.mehy.2013.11.036, 2013).

■■■

The Vitamin D Council—an advocacy group based in San Luis Obispo, California, USA—has created an online resource (http://tinyurl.com/AD-Vit-D) on Alzheimer's disease (AD) in general and the link between AD and vitamin D in particular. "Two large research studies are currently looking at how taking a vitamin D and/or omega-3 supplement affects memory and how well the brain works," the Council notes. "As of now, it is difficult to say what role vitamin D has in treating AD, and more large trials are needed to explore this." ■

FOOD, HEALTH & NUTRITION



Mice insulated with blue latex stopped accumulating fat in the liver. Credit: Birgitte Svennevig/University of Southern Denmark.

Surprising discovery: skin communicates with the liver

Skin talks directly to the liver, according to Danish scientists who think the discovery could help explain how diseases of the skin cascade throughout the entire body.

Two research groups at the University of Southern Denmark led by Susanne Mandrup and Nils Færgeman were actually studying something completely different when they made the discovery that the skin, which is the body's largest organ, can "talk" to the liver.

"We have showed that the skin affects the metabolism in the liver, and that is quite a surprise," said Susanne Mandrup and Ditte Neess, a former student in the Mandrup research group and now laboratory manager in the Færgeman group.

The groups worked with mice lackinga fat-binding protein called acyl CoA. Some of these knock-out mice had atypically greasy fur; they also had difficulties being weaned from their mothers. In the weaning period, they gained less weight and showed a failure to thrive. Analyses also showed that the mice accumulated fat in the liver once they were weaned.

"At first we thought that the fat accumulation in the liver was linked with the fact that the gene was missing in the liver of the knock-out mice. But this was ruled out by a series of studies, and we had to find another explanation," said Neess.

She and her colleagues took another look at the weak knock-out mice. They not only had

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greasy fur, they also had "leaky" skin from which they lost more water than normal mice.

"When they lose water, they also lose heat. We therefore asked ourselves whether this water and heat loss could be the reason why the mice accumulated fat in the liver and became weak when weaned from their mother," noted Neess.

To clarify this, the researchers bioengineered mice that lacked the fat-binding protein only in the skin. Similar to the mice in which the gene was completely blocked, these mice had difficulties after weaning and accumulated fat in the liver. This showed that the lack of the fat-binding protein in the skin was sufficient to induce accumulation of fat in the liver, according to the researchers.

To find the underlying mechanism by which the skin "talked" to the liver in the knockout mice, the researchers decided to cover the mice with a petroleum-based gel (Vaseline™). They hypothesized that this barrier would prevent water evaporating from the skin and thus stop the heat loss. They found that the fat accumulation in the liver did, indeed, disappear. But because Vaseline contains fat that could theoretically be absorbed by the skin or ingested by the mice, the researchers were unsure if the lack of fat accumulation in the liver was actually a side effect from the Vaseline. A student proposed covering the mice with liquid latex, after which the fat accumulation in the liver again disappeared.

"We believe that the leaking of water from the skin makes the mice feel cold, and that this leads to breaking down of fat in their adipose (fat) tissue. The broken-down fat is then moved to the liver," Mandrup and Neess explained.

The study appeared in *Cell Reports* (http://dx.doi.org/10.1016/j.celrep.2013.11.010, 2013).

Meditation changes gene expression

With evidence growing that meditation can have beneficial health effects, scientists have sought to understand how these practices physically affect the body. A new study by researchers in Wisconsin, Spain, and France reports the first evidence of specific molecular changes in the body following a period of mindfulness meditation.

Mindfulness meditation involves maintaining a moment-by-moment awareness of one's thoughts, feelings, bodily sensations, and surrounding environment, without judgment. It has been the subject of increasing research in recent years.

The study investigated the effects of a day of intensive mindfulness practice in a group of experienced meditators, compared to a group of untrained control subjects who engaged in quiet nonmeditative activities. After eight hours of mindfulness practice, the meditators showed a range of genetic and molecular differences, including altered levels of gene-regulating machinery and reduced levels of pro-inflammatory genes, which in turn correlated with faster physical recovery from a stressful situation.

"To the best of our knowledge, this is the first paper that shows rapid alterations in gene expression within subjects associated with mindfulness meditation practice," said co-author Richard J. Davidson, founder of the Center for Investigating Healthy Minds and the William James and Vilas Professor of Psychology and Psychiatry at the University of Wisconsin-Madison (USA).

"Most interestingly, the changes were observed in genes that are the current targets of anti-inflammatory and analgesic drugs," noted Perla Kaliman, first author of the article and a researcher at the Institute of Biomedical Research of Barcelona, Spain, where the molecular analyses were conducted.

Mindfulness-based trainings have shown beneficial effects on inflammatory disorders in prior clinical studies and are endorsed by the American Heart Association as a preventive intervention. The new results provide a possible biological mechanism for therapeutic effects.

The results show a down-regulation of genes that have been implicated in inflammation. The affected genes include the pro-inflammatory genes RIPK2 and COX2 as well as several histone deacetylase (HDAC) genes, which regulate the activity of other genes epigenetically by removing a type of chemical tag. What's more, the extent to which some of those genes were down-regulated was associated with faster cortisol recovery following a social stress test involving an impromptu speech and tasks requiring mental calculations performed in front of an audience and video camera.

Perhaps surprisingly, the researchers say, there was no difference in the tested genes between the two groups of people at the start of the study. The observed effects were seen only in the meditators following mindfulness practice. In addition, several other DNA-modifying genes showed no differences between groups, suggesting that the mindfulness practice specifically affected certain regulatory pathways.

However, the study was not designed to distinguish any effects of long-term meditation training from those of a single day of practice. Instead, the key result is that meditators experienced genetic changes following mindfulness practice that were not seen in the nonmeditating group after other quiet activities—an outcome providing proof of principle that mindfulness practice can lead to epigenetic alterations of the genome.

Previous studies in rodents and in people have shown dynamic epigenetic responses to physical stimuli such as stress, diet, or exercise within just a few hours.

"Our genes are quite dynamic in their expression and these results suggest that the calmness of our mind can actually have a potential influence on their expression," Davidson said.

"The regulation of HDAC and inflammatory pathways may represent some of the mechanisms underlying the therapeutic potential of mindfulness-based interventions," Kaliman noted. "Our findings set the foundation for future studies to further assess meditation strategies for the treatment of chronic inflammatory conditions."

The study was published in the journal *Psychoneuroendocrinology* (http://dx.doi.org/10.1016/j.psyneuen.2013.11.004, 2013).

trans Fats and prostacyclin production

Fred Kummerow, the 99-year-old professor emeritus who filed suit against the US Food and Drug Administration to force action on dietary *trans* fatty acids (TFA), has published almost 500 research papers in his long career. His latest appeared in the December 2013 issue of the *Scandinavian Cardiovascular Journal* (doi:10.3109/14017431.2013.856462; http://tinyurl.com/prostacyclin) and concerns the effects of TFA on prostacyclin production.

As Kummerow and his co-authors—all of whom are at the University of Illinois at Urbana-Champaign (USA)—note in their abstract, prostacyclin is a prostanoid derived from arachidonic acid (ARA) that prevents thrombosis "and is thereby

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expected to protect against heart disease." (The prostanoids are a subclass of eicosanoids, consisting of the prostaglandins, the thromboxanes, and the prostacyclins.)

Because industrially produced TFA in partially hydrogenated vegetable oils (PHVO) have been shown previously to interfere with ARA metabolism, Kummerow and his team wanted to see how fats with different proportions of linoleic acid (LA) and *trans*-18:1 affect prostacyclin released by cultured endothelial cells and to compare these proportions with those found in commercially available foods.

The team mixed soybean oil and hydrogenated soybean oil (coating fat) in different proportions to yield seven fat mixtures with amounts of LA ranging from 5.6% to 54.1% and *trans*-18:1 ranging from 0.4% to 43.9%. They cultured human endothelial cells in each of the mixtures and then separated the phospholipid fractions and characterized the fatty acids by gas chromatography. The prostacyclin released by the cells was measured using radioimmunoassay kits. The team then used "margarines and processed foods . . . purchased from the supermarket for comparison."

Their data revealed that "as the percentage of *trans* fat was increased, the amount of prostacyclin released dose-dependently and significantly ($P < 0.0001$) decreased, the concentration of LA and ARA decreased in the membrane phospholipids while the concentration of *trans*-18:1 increased, the prostacyclin decreased by 35–98%."

The team also found that "supermarket margarines had TFA levels similar to those that suppressed prostacyclin by 35–54%." Further, "most processed foods labeled as *trans*-free contained *trans* fats."

The team concluded that TFA suppress prostacyclin production at levels found in commercial margarines, "and processed foods labeled as *trans*-free could contribute to this effect if consumed in multiple servings or in addition to foods containing larger amounts of *trans* fats." ■

BRIEFS

Biotechnology companies Monsanto (St. Louis, Missouri, USA) and Novozymes (Bagsværd, Denmark) announced in December 2013 that they will partner to create the BioAg Alliance. Its goal will be to research and implement microbial solutions for growers around the world. Microbial-based solutions are derived from various naturally occurring microorganisms (e.g., bacteria and fungi). They can protect crops from pests and diseases and enhance plant productivity and fertility. They can also offer the possibility of sustainainable, cost-effective solutions that can increase yield using less input.

■■■

Demand in Europe for non-genetically modified (non-GM) lecithin has created a supply crisis, and suppliers of the main alternative, non-GM sunflowerseed lecithin, have struggled to meet demand. Europe traditionally imports soy lecithin from the United States or Brazil. However, 94% of US soy and 89% of Brazilian soy is now GM. As a result, Europe has begun to rely on locally grown and processed non-GM sunflower lecithin. Cargill (Minnetonka, Minnesota, USA) introduced a non-GM sunflower lecithin in 2008 for confectionery products, sauces, and instantized foods; the company has said will expand its Ukrainian sunflower lecithin processing facility to produce 100,000 metric tons a year.

■■■

The grocery store chain Whole Foods Market (North American headquarters in Austin, Texas) announced that it will stop selling Chobani (Norwich, New York, USA) brand Greek yogurt by early 2014. The decision came after it was discovered that Chobani uses milk from cows fed feed made containing genetically modified corn and soy.

■■■

China, a major importer of US DDGS (dried distillers grains with solubles, a by-product of ethanol production from corn), rejected two shipments (almost 546,000 metric tons) of this feed ingredient at the end of December 2013 because they contained MIR162, a genetically modified corn produced by Syngenta AG that is not approved by the Chinese government. ■

BIOTECHNOLOGY

Plants shown to make fish oil

Scientists with Rothamsted Research have successfully engineered the metabolic processes in the seed of false flax (*Camelina sativa*) to produce up to 12% eicosapentaenoic acid (EPA) and 14% docosahexaenoic acid (DHA). EPA and DHA are the same long-chain polyunsaturated fatty acids found in oil extracted from marine fishes and marine phytoplankton that have been shown to have multiple benefits to humans and animals, included positive effects on neurological development, inflammation, and heart health.

According to a statement release by Rothamstead, headquartered in Harpenden, UK, Olga Sayanova, one of the scientists working on the project, said: "In this work we used as a starting point a plant [*Camelina sativa*] that is rich in ALA [α-linolenic acid, or all-*cis*-9,12,15-octadecatrienoic acid], which is the building block that is used to produce EPA and DHA omega-3 oils."

Sayanova continued, "Having identified in marine algae and other photosynthetic marine organisms the essential genes required to make these beneficial oils . . . we introduced them to the *Camelina* plant." Starting with five inserted genes, the researchers achieved an average 24% of the total oil content in the *Camelina* seed as EPA.

Following up, the researchers then introduced seven genes. In that case, an average of 8% of the total oil content in the *Camelina* seed was DHA and 11% EPA, which is comparable to values found in fish oil. They had instances were these percentages were as high as 14% and 12%, respectively.

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> "This retraction comes after a thorough and time-consuming analysis of the published article and the data it reports, along with an investigation into the peer-review behind the article."

The scientists also described the distribution of EPA and DHA in the triglycerides of the genetically modified *Camelina* seed lipids, finding, for example that in seeds derived by inserting five genes, the predominant EPA-containing triglycerides (TAG) comprised TAG species containing a single EPA chain.

Johnathan Rapier, lead scientist on the project, was interviewed by NewScientist.com (http://tinyurl.com/Napier-camelina-FishOil). He indicated that, if development of the process proceeds as expected, commercial quantities of *Camelina*-synthesized fish oil could be available within 10 years. The oil could then be consumed by humans in fish oil capsules or by farmed fish.

For further information, see the original paper: N. Ruiz-Lopez, R.P. Haslam, J. Napier, and O. Sayanova, Successful high-level accumulation of fish oil omega-3 long-chain polyunsaturated fatty acids in a transgenic oilseed crop, *The Plant Journal*, http://dx.doi.org/10.1111/tpj.12378, 2013.

GMO paper withdrawn

In a press release dated November 28, 2013, the Elsevier journal *Food and Chemical Toxicology* (*FCT*) announced its retraction of the article "Long term toxicity of a Roundup herbicide and a Roundup-tolerant genetically modified maize," by Gilles-Eric Séralini and coworkers. The article originally appeared online in September 2012 and in print in November [*FCT* *50*(11):4221–4231, 2012].

Elsevier said, in part: "This retraction comes after a thorough and time-consuming analysis of the published article and the data it reports, along with an investigation into the peer-review behind the article. The Editor in-Chief deferred making any public statements regarding this article until this investigation was complete, and the authors were notified of the findings.

"Very shortly after the publication of this article, the journal received Letters to the Editor expressing concerns about the validity of the findings it described, the proper use of animals, and even allegations of fraud. . . . According to the journal's standard practice, these letters, as well as the letters in support of the findings, were published along with a response from the authors" (http://tinyurl.com/16responses; http://tinyurl.com/ResponseSeralini). The statement continued: "The Editor-in-Chief examined all aspects of the peer review process and requested permission from the corresponding author to review the raw data. . . . The corresponding author agreed and supplied all material that was requested by the Editor-in-Chief."

Among the concerns expressed in the letters to the editor were the small number of animals—in this instance, rats—included in each study group and the particular strain selected. The retraction statement continued: "A more in-depth look at the raw data revealed that no definitive conclusions can be reached with this small sample size regarding the role of either NK603 [the genetically modified form of corn fed to rats in the study] or glyphosate in regards to overall mortality or tumor incidence. Given the known high incidence of tumors in the Sprague-Dawley rat, normal variability cannot be excluded as the cause of the higher mortality and incidence observed in the treated groups."

In conclusion, the retraction statement said: "Ultimately, the results presented (while not incorrect) are inconclusive, and therefore do not reach the threshold of publication for *Food and Chemical Toxicology*. . . . The Editor-in-Chief again commends the corresponding author for his willingness and openness in participating in this dialog. The retraction is only on the inconclusiveness of this one paper."

Reactions to the retraction were predictably polarized. According to the journal *Nature* (http://dx.doi.org/10.1038/nature.2013.14268), Seralini and his team alleged that the retraction originated from Richard Goodman (professor at the Food Allergy Research and Resource Program, University of Nebraska, Lincoln, USA), who was appointed associate editor for biotechnology for *FCT* in January 2013 and who worked for Monsanto, the inventors of Roundup herbicide and of NK603, from 1997 to 2004. *Nature* quoted Goodman as saying, "I did not review the data in the Séralini study, nor did I have anything to do with the determination that the paper should be withdrawn from or retained by the journal." *Nature* also pointed out other alleged conflicts of interest that have been mentioned regarding this controversy.

Other representative reactions can be found in an essay by Katherine Rich, chief executive of the New Zealand Food and Grocery Council (http://tinyurl.com/FavoredRetraction), Forbes.com (http://tinyurl.com/Forbes-GMO), and the extended discussions at http://tinyurl.com/Opposition-to-GMO.

Environment Canada approves GE salmon

Environment Canada, a regulatory body of the Canadian government that deals with environmental policies, recently concluded that genetically engineered (GE) Atlantic salmon developed by AquaBounty Technologies (Boston, Massachusetts, USA) present no harm to the environment or human health when produced in contained facilities. The fish include a growth hormone-regulator gene from the faster-growing Pacific chinook salmon that enables them to reach maturity twice as quickly as standard Atlantic salmon, because they can now grow year 'round.

The agency's approval allows the commercial production of salmon eggs at AquaBounty's Prince Edward Island, Canada, facility; it does not allow the sale of either GE salmon or their eggs. AquaBounty has applied to Health Canada and the US Food and Drug Administration (FDA) for regulatory approval to sell the fish. If approved, the company would be the first to introduce a GE animal into the human food supply.

According to company CEO Ron Stotish in an article on FoodNavigator-usa.com (http://tinyurl.com/Stotish-salmon-eggs), AquaBounty plans to produce eggs in Canada and ship them to FDA-approved facilities to grow into fish. Each facility would require FDA approval on a case-by-case-basis to grow the fish. Stotish says several companies are interested in purchasing eggs (http://tinyurl.com/aquabounty). The FDA concluded in 2012 that the GE salmon do not pose a threat to the environment and are as safe as food from conventional salmon (http://tinyurl.com/aquabounty-fda), but it has not approved the sale of the fish yet.

The possibility of the technology's approval has stimulated activity by environmental groups concerned with the safety of GE products. Critics of the technology warn of the potential ramifications were the fish to escape and breed with wild salmon (http://tinyurl.com/aquabounty-post).

Stotish has said that all of AquaBounty's salmon are sterile females and all future facilities would be land-based, reducing the chance of escape.

Several US grocery chains such as Trader Joe's and Whole Foods Market have preemptively agreed to not carry products containing GE salmon even if the FDA ultimately gives its approval. Kroger Co., the nation's largest grocery chain, has made no statement, but spokespersons from Safeway, the second-largest grocery chain, have said the company will not purchase GE salmon.

USDA nears approval of Enlist corn, soybeans

The US Department of Agriculture (USDA) on January 3, 2014, released a statement saying it is likely to approve Dow AgroScience LLC's (Indianapolis, Indiana, USA) Enlist corn and soybeans. The genetically engineered (GE) seeds are resistant to a Dow-produced herbicide that combines glyphosate with 2,4-dichlorophenoxyacetic acid (2,4-D), known for being a component of the defoliant Agent Orange. Dow's products are meant to be an alternative to Monsanto's glyphosate-resistant Roundup Ready seeds.

As part of the process of deregulation, for which Dow applied in 2012, USDA published a draft Environmental Impact Statement (EIS) through the Animal and Plant Health Inspection Service (APHIS) concerning the safety of Dow AgroScience's Enlist Weed and Control System. According to the draft, APHIS found no direct or indirect impacts on the environment from the cultivation of Enlist technology, and it recommends approving it. However, the agency does warn that Dow's technology may increase weed resistance to 2,4-D, which is currently the third-most used herbicide in the United States.

Enlist technology was approved in Canada in October 2013, but it has not been sold there yet. Pending regulatory approvals in the United States, Dow plans to make Enlist soybeans and corn commercially available in 2015. There are also plans to develop Enlist cotton. The Environmental Protection Agency is also reviewing Dow's 2,4-D herbicide and is expected to issue its proposed decision this year.

Monsanto, in conjunction with BASF, is seeking regulatory approval for GE soybeans and cotton seeds that are resistant to a dicamba (3,6-dichloro-2-methoxybenzoic acid)-based herbicide.

North Carolina company developing ricin-free castor

Novo Synthetix, a small biotechnology company founded in 2012 in Research Triangle Park, North Carolina, USA, is reporting progress in its efforts to develop a nontoxic castor oil plant

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AOCS MEETING WATCH

May 4–7, 2014. 105th AOCS Annual Meeting & Expo, Henry B. Gonzalez Convention Center, San Antonio, Texas, USA. http://annualmeeting.aocs.org

October 6–9, 2014. World Conference on Fabric and Home Care—Montreux 2014, Montreux Music & Convention Centre, Montreux, Switzerland. http://montreux.aocs.org

May 3–6, 2015. 106th AOCS Annual Meeting & Industry Showcase. Rosen Shingle Creek, Orlando, Florida, USA

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).

Also, be sure to visit AOCS' online listing of industry events and meetings at http://tinyurl.com/industry-calendar. Sponsoring organizations can submit information about their events to the web-based calendar by clicking a link and completing a web form. Submission is free. No third-party submissions, please. If you have any questions or comments, please contact Valorie Deichman at valoried@aocs.org.

(*Ricinus communis*). The company is using a technology, called Directed Nuclease Editor (DNE), that was developed by Precision Biosciences (Durham, North Carolina, USA) to modify genes. But since DNE does not introduce foreign deoxyribonucleic acid (DNA) into the host plant, the altered plant is not considered a genetically modified organism (GMO). One advantage of this technology is that it minimizes the risk of transferring unwanted traits into the host plant along with the desirable trait(s). Also, because it is a non-GMO, costs engendered by regulations applied to GMOs do not affect the altered castor oil plant.

Experimental plants produce by DNE are presently being grown and tested at North Carolina State University (Raleigh, USA) in the laboratory of Linda Hanley-Bowdoin, a plant virologist. Donald Walters, a biochemist with Novo Synthetix who is working with Hanley-Bowdoin, predicts a prototype plant will become available in the next 6–12 months. Novo Synthetix has two goals: to produce ricin-free castor seeds, and to engineer the castor plant to produce so-called designer oils.

Although the compound ricin, produced in all *R. communis* strains known so far, is highly toxic, the oil from the seeds of this plant is uniquely valuable because of its content of ricinoleic acid, which is both hydroxylated and unsaturated. The oil finds worldwide use in the manufacture of household products, lubricants, paints and dyes, plastics, and pharmaceuticals. It sells for almost three times the price of other seed oils, such as soybeans (http://tinyurl.com/NovoSynthetix-castor).

According to *The Charlotte Observer* newspaper (December 15, 2013), the United States has not produced castor oil since the 1970s, owing to the liability posed by ricin. ■

Disappointment by the financial community over a facility construction delay overshadowed news delivered in November 2013 by renewable oil producer Solazyme regarding its continuing development of a C8–C10-rich algal oil. Solazyme's latest tailored algal oil (known by the company as its Caprylic-Capric Platform) contains a high concentration of C8 and C10 fatty acids, which currently are sourced from coconut and palm kernel oils for a number of applications within the oleochemical, lubricant, personal care, and human nutrition markets. The tailored algal oil, however, contains four times the level of C8–C10 fatty acids in existing sources, according to Solazyme. For more information, see http://tinyurl.com/Solazyme-CCP. Solazyme is based in South San Francisco, California, USA.

■■■

Clariant, the German specialty chemicals company, is for the second time expanding its ethoxylation unit at Clear Lake in Pasadena, Texas. "The expansion includes new reactors and additional storage facilities, bringing the overall ethoxylation capacity to more than 125,000 metric tons from 95,000 metric tons at present," according to www.cosmeticsdesign.com. The new plant will go online in mid-2015.

■■■

The US Environmental Protection Agency (EPA) has updated its online toolbox for exposure assessors. The site (www.epa.gov/risk/expobox/media/cp-gu.htm#!) lists a number of guidance documents to support various aspects of consumer product safety programs at EPA and other agencies.

■■■

The American Cleaning Institute's (ACI; Washington, DC, USA) Board of Directors elected three new members at its meeting in December 2013. They are: Dale Steichen, vice president, Surface Chemistry LLC and director, Business Development, AkzoNobel Specialty Chemicals; Justin Skala, president, North America and Global Sustainability, Colgate-Palmolive Co.; and Mark Miller, senior vice president, Consumer Care, head of global business unit, Lonza Inc. ■

HOME & PERSONAL CARE

FDA demands proof that antibacterial soaps work

The US Food and Drug Administration (FDA) continued cleaning up old business when—on December 16, 2013—it announced a proposed rule on consumer antiseptic washes, including those containing the antibacterial compound triclosan.

FDA first promised a ruling on triclosan in 1978 but never delivered one; the National Resources Defense Council (an environmental group based in New York, New York) sued FDA in 2010 over the lack of action. The agency settled the suit in November 2013, agreeing to act on triclosan by 2016.

In plain English, the proposed rule (see http://tinyurl.com/triclosan-FDA) suggests that antibacterial soaps are no more effective than plain soap and water in preventing illness and may pose health risks. Under the proposal, manufacturers have 181 days to comment (until June 16, 2014) and can provide study data through December 2014; the final rule is scheduled to be released in September 2016.

"To put it simply, we need to collect additional information from the companies that make these products so that consumers can be confident about their effectiveness and about their safety," explained FDA's Sandra Kweder during a telephone press briefing.

"Under the rule, manufacturers would be required to provide additional safety data for these products before they can be recognized as 'generally recognized as safe' for use," she continued. "The proposed rule covers only those consumer antibacterial soaps and body washes that are used with water. It does not apply to hand sanitizers, hand wipes, or antibacterial soaps that are used in health care settings," FDA said in a news release.

FDA cited animal studies that suggest triclosan may disrupt the endocrine system (if they generalize to humans). The agency also noted that laboratory studies have shown that triclosan contributes to producing bacteria that are resistant to antibiotics.

Triclosan is used in 93% of liquid soaps and body washes labeled in the United States as being "antibacterial" or "antimicrobial." The chemical is also used in a number

CONTINUED ON NEXT PAGE

"We intend to file comments to FDA reaffirming that the use of antibacterial wash products in the home environment does not contribute to antibiotic or antibacterial resistance."

of toothpastes; manufacturers can continue using triclosan and other antimicrobial compounds in them, FDA said.

The American Cleaning Institute and the Personal Care Products Council, both of which are trade groups based in Washington, DC, said in a written statement that they were perplexed that FDA would intimate that "there is no evidence that antibacterial soaps are beneficial as industry has long provided data and information about the safety and efficacy of these products. In fact, in 2008, at industry's request, FDA held a public meeting to discuss the data, and industry asked FDA if the agency required any further information. Our industry's Topical Antimicrobial Coalition has submitted to the FDA in-depth data showing that antibacterial soaps are more effective in killing germs when compared with nonantibacterial soap.

"Additionally, a review of two dozen relevant published studies (http://tinyurl.com/ACI-triclosan) analyzing the effectiveness of antibacterial soaps showed that hand washing with these products produces statistically greater reductions in bacteria on the skin than when using nonantibacterial soap.

"We intend to file comments to FDA reaffirming that the use of antibacterial wash products in the home environment does not contribute to antibiotic or antibacterial resistance. The ingredients used in antibacterial soap and washes have been evaluated and regulated by agencies and scientific bodies around the world. In some instances, these products have been found to be critical in the reduction of infection and disease."

AkzoNobel receives DfE label

The Us Environmental Protection Agency recently gave AkzoNobel's Dissolvine GL®, the company's biodegradable and biobased chelate, the right to use the EPA Design for the Environment (DfE; www.epa.gov/dfe) label, which marks the product as being a safer ingredient for consumers and the environment.

EPA awards the DfE designation only to products that pass the DfE criteria after the agency's scientific team screens each ingredient for potential human health and environmental impacts. Dissolvine GL, which AkzoNobel says is derived predominantly from corn and is readily biodegradable, is used as a builder for cleaners and detergents as an alternative to phosphates, nitrilotriacetic acid, and ethylene diamine tetraacetic acid.

Are sustainable cosmetics viable?

Consumer behavior must change in order for the cosmetics industry to be sustainable, according to speakers at the European and Asia-Pacific editions of the Sustainable Cosmetics Summit (www.sustainablecosmeticssummit.com) held in November 2013. More than 150 senior executives convened at each meeting to discuss key sustainability issues affecting the cosmetics industry, according to the meeting organizer, Organic Monitor (OM). OM is a London-based specialist research, consulting, and training company that focuses on the global organic product industries.

A number of speakers suggested that consumer behavior is a major barrier to sustainable development of the cosmetics industry, OM said in a news release. Although operators are implementing a raft of sustainability initiatives, consumer education and recognition of these initiatives remains low. Furthermore, lack of consumer demand for green products and ingredients was discouraging manufacturers from making greater commitments.

In its presentation, the Union for Ethical BioTrade (UEBT; Amsterdam) showed that awareness of biodiversity (and green issues) is rising in Asia. More than 70% of Chinese and Korean consumers state they are aware of such issues, UEBT said; however, awareness has not translated into demand. In fact, consumers in the Asia-Pacific comprise less than 10% of global "green" cosmetic sales, according to OM.

Parabens and phthalate exposure in children

Infants and toddlers in the United States likely are being exposed through lotions, shampoos, and other personal care products (PCP) to the family of preservatives known as parabens at an even higher level than adult women, according to scientists at the State University of New York in Albany (USA). They published their findings on parabens, which have been linked to reproductive and other health issues, in *Environmental Science & Technology* (http://dx.doi.org/10.1021/es4042034, 2013). The team also found that exposure of infants and toddlers to the family of plasticizers known as phthalates likely is lower than the exposure levels for adult females.

Research leaders Kurunthachalam Kannan and Ying Guo point out that phthalates and parabens are used in a wide range of products, from medical devices to children's toys, as well as in PCP. Phthalates hold in moisture; parabens are used as preservatives. Most people are exposed to them every day—for example, data from the US Centers for Disease Control and Prevention suggest that more than 90% of the population is exposed to these substances.

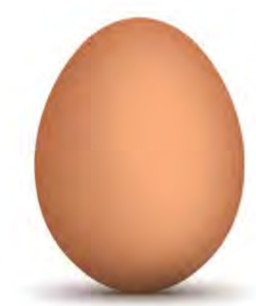
Previous work has shown that the human body breaks these compounds down quickly, but both have been detected in urine, breast milk, and blood. Some research suggests a link between these substances and health issues in animals and people, such as sperm damage, breast cancer, and an increased risk for asthma. Nonetheless, parabens have been found to be "safe as used" by the Cosmetic Ingredient Review, an independent review panel funded by the Personal Care Products Council (Washington, DC, USA). Further, the US Food and Drug Administration states on its website that "FDA believes that at the present time [2007] there is no reason for consumers to be concerned about the use of cosmetics containing parabens. However, the agency will continue to evaluate new data in this area."

In previous studies, Kannan's team found that food and indoor dust contributed to phthalate exposure to varying degrees, but paraben exposure was low. In the new study, they examined at a third route of possible dermal exposure—the use of PCP.

The team collected 170 samples of makeup, lotions, shampoos, and other products, including 20 items for babies, and tested them for nine phthalates and six parabens. Both substances were found in PCP. In baby products, phthalate concentrations were low, but parabens were common. When the researchers calculated possible exposure levels, they estimated that the potential daily skin exposure to parabens by infants and toddlers could be as much as two to three times higher than that for adult women.

Processed foods may be known for having long lists of chemical ingredients, but if we had to list every chemical in an egg, what would the label look like? To answer that question, James Kennedy, a high school chemistry teacher in Melbourne, Australia, created this label for a natural egg. Similar labels for a banana, blueberries, and other natural foods can be viewed at http://io9.com/what-if-natural-products-came-with-a-list-of-ingredient-1503320184.

INGREDIENTS OF AN ALL-NATURAL EGG



INGREDIENTS: AQUA (75.8%), **AMINO ACIDS (12.6%)** (GLUTAMIC ACID (14%), ASPARTIC ACID (11%), VALINE (9%), ARGININE (8%), LEUCINE (8%), LYSINE (7%), SERINE (7%), PHENYLALANINE (6%), ALANINE (5%), ISOLEUCINE (5%), PROLINE (4%), TYROSINE (3%), THREONINE (3%), GLYCINE (3%), HISTIDINE (2%), METHIONINE (3%), CYSTINE (2%), TRYPTOPHAN (1%)); **FATTY ACIDS (9.9%)** (OCTADECENOIC ACID (45%), HEXADECANOIC ACID (32%), OCTADECANOIC ACID (12%), EICOSATETRAENOIC ACID (3%), EICOSANOIC ACID (2%), DOCOSANOIC ACID (1%), TETRACOSANOIC ACID (1%), OCTANOIC ACID (<1%), DECANOIC ACID (<1%), DODECANOIC ACID (<1%), TETRADECANOIC ACID (<1%), PENTADECANOIC ACID (<1%), HEPTADECANOIC ACID (<1%), TETRADECENOIC ACID (<1%), HEXADECENOIC ACID (<1%), EICOSENOIC ACID (<1%), DOCOSENOIC ACID (<1%), OMEGA-6 FATTY ACID: OCTADECADIENOIC ACID (12%), OMEGA-3 FATTY ACID: OCTADECATRIENOIC ACID (<1%), EICOSAPENTAENOIC ACID (EPA) (<1%), OMEGA-3 FATTY ACID: DOCOSAHEXAENOIC ACID (DHA) (<1%)); **SUGARS (0.8%)** (GLUCOSE (30%), SUCROSE (15%), FRUCTOSE (15%), LACTOSE (15%), MALTOSE (15%), GALACTOSE (15%)); **COLOUR** (E160c, E160a), E306, E101; **FLAVOURS** (PHENYLACETALDEHYDE, DODECA-2-ENAL, HEPTA-2-ENAL, HEXADECANAL, OCTADECANAL, PENTAN-2-ONE, BUTAN-2-ONE, ACETALDEHYDE, FORMALDEHYDE, ACETONE); SHELL (E170), ALSO CONTAINS BENZENE & BENZENE DERIVATIVES, ESTERS, FURANS, SULFUR-CONTAINING COMPOUNDS AND TERPENES.

Codexis exits detergent alcohols business

Codexis, a developer of engineered enzymes for pharmaceutical, biofuel, and chemical production, announced at the end of 2013 in its final quarterly report of the year that it is exiting two of its business franchises (see http://tinyurl.com/codexis-exit). The company apparently had stopped further development of its CodeXol® detergent alcohols franchise earlier in 2013 and, as a result, the company said it would also be exiting its CodeXyme® cellulase business. (Cellulase enzymes catalyze the conversion of cellulose into fermentable glucose, which is the feedstock for the CodeXol alcohols.)

According to Codexis, which is based in Redwood City, California, USA, the company began winding down the CodeXyme business after being unable to secure a funding partner for the cellulose business. Codexis also sparred with enzymes producer Dyadic in August 2013 after that company alleged a breach in a license agreement concerning a proprietary fungal expression technology for the production of enzymes. Codexis had been using this license from Dyadic solely in connection with its CodeXyme® cellulase enzyme, according to Doris de Guzman of GreenChemicalsBlog.com.

"LS9 is the only company the blog knows so far that has also been working on fermentation-based fatty alcohols," de Guzman noted. ■

How do you benefit from

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PATENTS

Microemulsion and sub-micron emulsion process and compositions

Larm, M.G., *et al.,* Stiefel Research Australia Pty. Ltd., US8449867, May 28, 2013

An oil-in-water microemulsion or sub-micron emulsion composition for dermal delivery of at least one pharmaceutically active ingredient is provided. The composition includes an oil phase dispersed throughout a water phase, the oil phase including at least one member selected from the group consisting of an animal oil, a mineral oil, a vegetable oil, a silane member, a siloxane, an ester, a fatty acid, a fat, a halogen compound, and an alkoxylated alcohol; and at least one lipophilic surfactant, the water phase including at least one hydrophilic surfactant, water, and optionally a non-surfactant amphiphilic compound, the weight ratio of the at least one hydrophilic surfactant to the at least one lipophilic surfactant being approximately 9.0:1.0 to 2.0:3.0.

Generation of triacylglycerols

Dayton, C., Bunge Oils, Inc., US8541211, September 24, 2013

A method is disclosed for the generation of triacylglycerols from gums that have been separated from an oil product. The gums are treated with an enzyme having PLC [phospholipase C] activity, which results in the formation of diacylglycerols and phosphates, and treated with an enzyme having PLA [phospholipase A] activity, which results in the formation of lyso-phospholipids and free fatty acids (FFA). The diacylglycerols and FFA from these two separate reactions then combine in the presence of the enzymes to generate new triacylglycerol molecules.

Processes for the preparation of phosphatide salts

Rutenberg, D., Lipogen Ltd., US8546104, October 1, 2013

The present invention discloses a process for the preparation of phosphatide-salt complexes, the process including the steps of: using at least one raw material lecithin as a substrate; and enzymatically processing at least one raw material lecithin with phospholipase-D, racemic or enantiomerically pure serine, and/or amine in an aqueous carboxylate-salt-complex solution, wherein the step of processing is performed in a single-phase reaction environment, to produce phosphatide-salt complexes having a structural fatty-acid chain derived from at least one raw material lecithin. Preferably, the step of processing is performed at a pH in the range of about 4.5–8.0 at a temperature in the range of about 25–60°C. Preferably, the aqueous carboxylate–salt-complex solution is formed from an aqueous solution of a carboxylic acid with a chain length of C2–C8 and a salt in an approximately 1:2 (weight per weight) acid-to-salt ratio.

Lipid depot formulations

Thuresson, K., *et al.,* Camarus AB, US8545832, October 1, 2013

The present invention relates to pre-formulations comprising low viscosity, non-liquid crystalline, mixtures of: (i) at least one neutral diacyl lipid and/or at least one tocopherol; (ii) at least one phospholipid; (iii) at least one biocompatible, oxygen-containing, low viscosity organic solvent; wherein at least one bioactive agent is dissolved or dispersed in the low viscosity mixture and wherein the pre-formulation forms, or is capable of forming, at least one liquid crystalline phase structure upon contact with an aqueous fluid. The preformulations are suitable for generating parenteral, non-parenteral, and topical depot compositions for sustained release of active agents. The invention additionally relates to a method of delivery of an active agent comprising administration of a preformulation of the invention, a method of treatment comprising administration of a preformulation of the invention and the use of a preformulation of the invention in a method for the manufacture of a medicament.

GLP-1 analogue formulations

Joabsson, F., *et al,* Camarus AB, US8546326, October 1, 2013

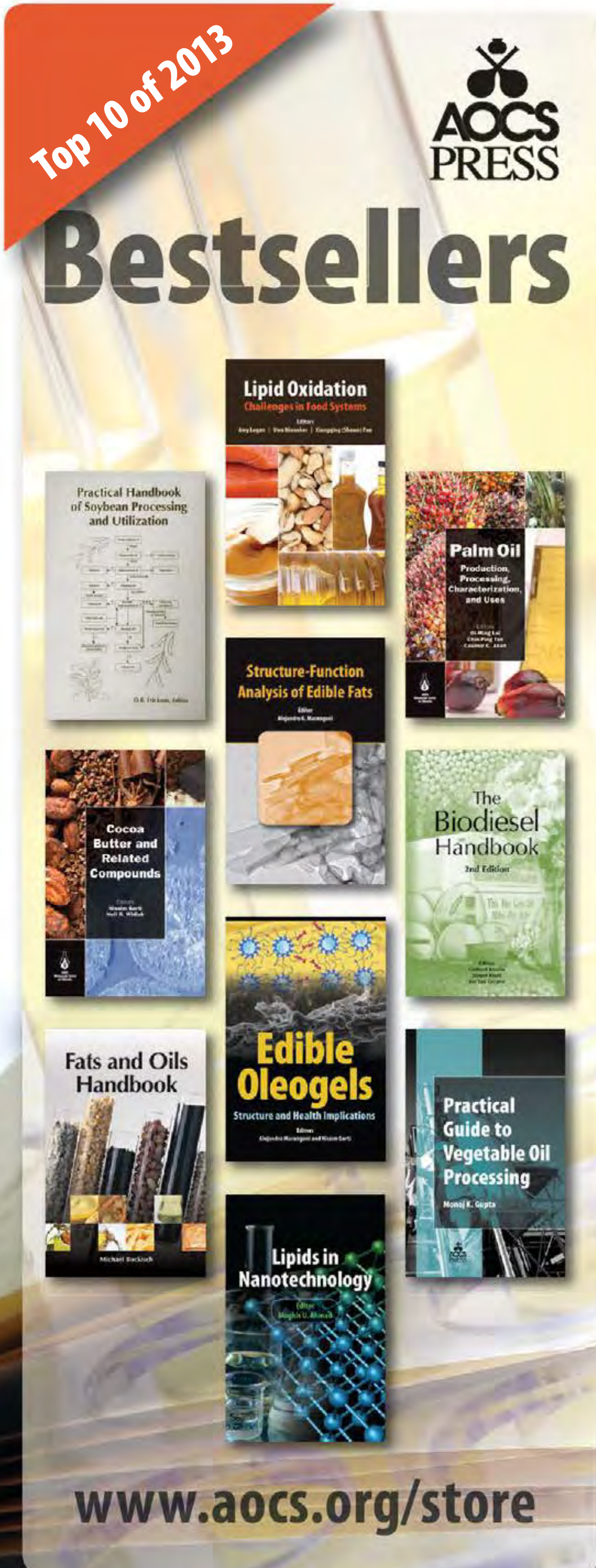
The present invention relates to compositions forming a low viscosity mixture of: (i) at least one neutral diacyl lipid, such as a diacyl glycerol; (ii) at least one phospholipid, such as a phosphatidyl choline; (iii) at least one biotolerable solvent, such as an oxygen-containing solvent; (iv) at least one glucagon-like peptide-1 (GLP-1) analogue; wherein the pre-formulation forms, or is capable of forming, at least one liquid crystalline phase structure upon contact with an aqueous fluid. The invention further relates to methods of treatment comprising administration of such compositions, especially in treating diabetes, and to pre-filled administration devices and kits containing the formulations.

Prilled waxes comprising small particles and smooth-sided compression candles made therefrom

Uptain, K., *et al.,* Elevance Renewable Sciences, Inc., US8551194, October 8, 2013

A candle and process for making it are disclosed. The candle comprises prilled wax particles, comprising hydrogenated natural oil and wherein at least 75% of the prilled wax particles are less than 800 μm in diameter. The candle includes a compressed core and a thermally fused outer layer.

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.



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EXTRACTS & DISTILLATES

Olive (*Olea europaea* L.) tree nitrogen status is a key factor for olive oil quality

Erel, R., *et al.*, *J. Agric. Food Chem. 61*:11261–11272, 2013, http://dx.doi.org/10.1021/jf4031585.

The influence of macronutrient status on olive oil properties was studied for three years. Data were analyzed by a multivariate model considering N, P, K, and fruiting year as explanatory factors. Oil quality parameters were primarily associated with N concentration in leaves and fruits, which increased with N in irrigation solution. The effect of P on oil quality was mainly indirect since increased P availability increased N accumulation. The potassium level had negligible effects. The oil phenolic content decreased linearly as a function of increased leaf N, indicating protein–phenol competition in leaves. The overall saturation level of the fatty acids decreased with fruit N, resulting in increased polyunsaturated fatty acids. Free fatty acids increased with increased levels of fruit N. High fruit load tended to reduce fruit N and subsequently improve oil quality. The effect of N on oil properties depended solely on its concentration in leaves or fruits, regardless of the cause.

Correlation of basic oil quality indices and electrical properties of model vegetable oil systems

Prevc, T., *et al.*, *J. Agric. Food Chem. 61*:11355–11362, 2013, http://dx.doi.org/10.1021/jf402943b.

Model vegetable oil mixtures with significantly different basic oil quality indices (free fatty acid, iodine, and Totox values) were prepared by adding oleic acids, synthetic saturated triglycerides, or oxidized safflower oil (*Carthamus tinctorius*) to the oleic type of sunflower oil. Dielectric constants, dielectric loss factors, quality factors, and electrical conductivities of model lipids were determined at frequencies from 50 Hz to 2 MHz and at temperatures from 293.15 to 323.15 K. The dependence of these dielectric parameters on basic oil quality indices was investigated. Adding oleic acids to sunflower oil resulted in lower dielectric constants and conductivities and higher quality factors. Reduced iodine values resulted in increased dielectric constants and quality factors and decreased conductivities. Higher Totox values resulted in higher dielectric constants and conductivities at high frequencies and lower quality factors. Dielectric constants decreased linearly with temperature, whereas conductivities followed the Arrhenius law.

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Journal of the American Oil Chemists' Society (February)

- Conventional and non-conventional edible oils: an Indian perspective, Choudhary, M., J.K. Sangha, and K. Grover
- The use of FTIR spectroscopy and chemometrics for rapid authentication of extra virgin olive oil, Rohman, A., Y.B. Che Man, and F.M. Yusof
- Identification of vegetable oil or biodiesel added to diesel using fluorescence spectroscopy and principal component analysis, Tomazzoni, G., M. Meira, C.M. Quintella, G.F. Zagonel, B.J. Costa, P.R. de Oliveira, I.M. Pepe., and P.R. da Costa Neto
- Non-destructive determination of high oleic acid content in single soybean seeds by near infrared reflectance spectroscopy, Han, S.-I., J.-H. Chae, K. Bilyeu, J.G. Shannon, and J.-D. Lee
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- Synthesis, purification, and acyl migration kinetics of 2-monoricinoleoylglycerol, Compton, D.L., J.A. Laszlo, M. Appell, K.E. Vermillion, and K.O. Evans
- Evolution of oxidative values during kinetic studies on olive oil oxidation in the Rancimat test, Farhoosh, R,. and S.-Z Hoseini-Yazdi
- Antioxidant property, thymoquinone content and chemical characteristics of different extracts from *Nigella sativa* L. seeds, Solati, Z., B.S. Baharin, and H. Bagheri
- Restricted-range Boraginaceae species constitute potential sources of valuable fatty acids, Guil-Guerrero, J.L., F. Gómez-Mercado, R.P. Ramos-Bueno, M.Á. Rincón-Cervera, and E. Venegas-Venegas
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- Effect of processing parameters on flocculation of *Picochlorum oklahomensis*, Zhu, Y., N.T. Dunford, and C. Goad
- Application of metal triflate catalysts for the *trans*-esterification of *Jatropha curcas* L. oil with methanol and higher alcohols, Daniel, L., C.B. Rasrendra, A. Kloekhorst, A.A. Broekhuis, R. Manurung, and H.J. Heeres
- Photopolymerizable synthons from glycerol derivatives, Mhanna, A., F. Sadaka, G. Boni, C.-H., Brachais, L. Brachais, J.-P. Couvercelle, L. Plasseraud, and L. Lecamp
- Synthesis and characterization of novel diol, diacid and di-isocyanate from oleic acid, Raghunanan, L., J. Yue, and S.S. Narine
- Recovery of sinapic acid from the waste effluent of mustard protein isolation by ion exchange chromatography, Prapakornwiriya, N., and L.L. Diosady

Journal of Surfactants and Detergents (January)

- Flow behavior of oleic acid liposomes in sucrose ester glycolipid oil-in-water emulsions, Chia, S.W., and M. Misran
- Influence of surfactant on the characteristics of $W_1/O/W_2$-microparticles, Benéitez, M.C., J.I. Espada, D. Fernandes, D.H.P. de la Ossa, and M.E. Gil-Alegre
- Effects of surfactant hydrophilicity on the oil solubilization and rheological behavior of a nonionic hexagonal phase, Alam, M.M., Y. Matsumoto, and K. Aramaki
- Removal of copper(II) from a concentrated sulphate medium by cloud point extraction using an *N*,*N*′-bis(salicylaldehyde)ethylenediimine di-Schiff base chelating ligand, Reffas, H., T. Benabdallah, M.H. Youcef, and H. Ilikti
- Aggregation and phase separation phenomenon of amitriptyline hydrochloride under the influence of pharmaceutical excipients, Rub, M.A., A.M. Asiri, M.S. Sheikh, N. Azum, A. Khan, A.A.P. Khan, M.M. Rahman, and Kabir-ud-Din
- Enlargement of nanoemulsion region in pseudo-ternary mixing diagrams for a drug delivery system, Wang, Z., and R. Pal
- Skin penetration of fatty acids from soap surfactants in cleansers dependent on foam bubble size, Sonoda, J., T. Sakai, Y. Inoue, and Y. Inomata
- The irritant effects of pharmaceutically applied surfactants, Erős, G., Z. Kurgyis, I.B. Németh, E. Csizmazi, S. Berkó, P. Szabó-Révész, L. Kemény, and E. Csányi
- Interaction between an ethoxylated alkylphenol polymer with formaldehyde and triblock polyEO–polyPO–polyEO copolymer in aqueous solutions, Xin, X., Y. Zhu, X. Cao, and G. Xu
- Stress-temperature effects on transitions in $PEO_{17}PPO_{60}PEO_{17}$ triblock copolymer micellar solutions, Pérez-García, M.G., G. Landázuri , L.A. Pérez-Carrillo, A. González-Álvarez, J.E. Puig, Y. Rharbi, and J.F.A. Soltero
- Effect of a spacer group on surface activity, salinity and hardness tolerance, mimic oil washing efficiency of monododecyl diaryl disulfonate, Xing, F., J. Niu, X. Liu, and X. Wang
- Synthesis, autoorganization and reactivity of amphiphilic derivatives of 1-aminoisoindole in water and formamide, Levkov, I.V., S. Cassel, Z.V. Voitenko, N. Saffon, A. Lattes, and I. Rico-Lattes
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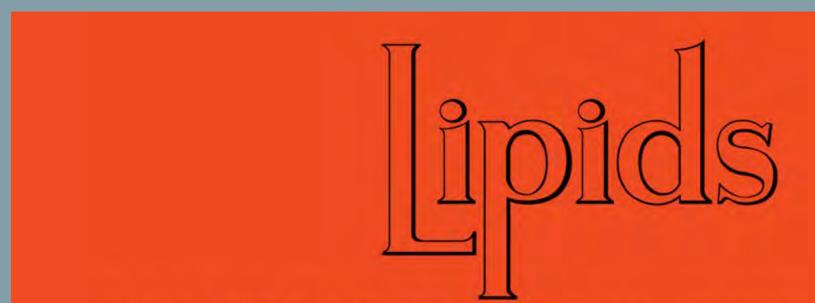
- A comparative study of micellization behavior of an ethoxylated alkylphenol in aqueous solutions of glycine and leucine, Chauhan, S., K. Sharma, K. Kumar, and G. Kumar
- Volumetric, compressibility, and surface tension studies on micellization behavior of SDS in aqueous medium: effect of sugars, Chauhan, S., K. Kumar, K. Singh, and J. Jyoti
- Two spectrophotometric methods for the assay of benzalkonium chloride in bandage samples, Ma, W., X. Ma, O. Sha, and Y. Liu
- Potentiometric determination of alkyl dimethyl hydroxyethyl ammonium surfactant by a new chemically modified carbon paste electrode, Khedr, A.M., H.M. Abu Shawish,M. Gaber, and K.I. Abed Almonem
- Continuous flow methylene blue active substances method for the determination of anionic surfactants in river water and biodegradation test samples, Wyrwas, B., and A. Zgoła-Grześkowiak



Lipids (February)

- PPARα activation induces N^{ε}-Lys-acetylation of rat liver peroxisomal multifunctional enzyme type 1, Contreras, M.A., O. Alzate, A.K. Singh, and I. Singh
- Regulation of polyunsaturated fatty acid biosynthesis by seaweed fucoxanthin and its metabolite in cultured hepatocytes, Aki, T., M. Yamamoto, T. Takahashi, K. Tomita, R. Toyoura, K. Iwashita, S. Kawamoto, M. Hosokawa, K. Miyashita, and K. Ono
- Interaction between VLDL and phosphatidylcholine liposomes generates new γ-LpE-like particles, Ćwiklińska, A., B. Kortas-Stempak, A. Gliwińska, A. Pacanis, A. Kuchta, and M. Wróblewska
- Synbiotic food consumption reduces levels of triacylglycerols and VLDL, but not cholesterol, LDL, or HDL in plasma from pregnant women, Taghizadeh, M., T. Hashemi, H. Shakeri, F. Abedi, S.-S.,Sabihi, S.-A. Alizadeh, and Z. Asemi
- Determination and structural elucidation of triacylglycerols in krill oil by chromatographic techniques, Araujo, P., H. Zhu, J.F. Breivik, J.I. Hjelle, and Y. Zeng
- Kinetics of carnitine palmitoyltransferase I (CPT I) in Chinese sucker (*Myxocyprinus asiaticus*) change with its development, Liu, C.-X., Z. Luo, W. Hu, X.-Y. Tan, J.-L. Zheng, Q.-L. Chen, and Q.-L. Zhu
- Phospholipid transfer protein deficiency decreases the content of S1P in HDL via the loss of its transfer capability, Yu, Y., S. Guo, Y. Feng, L. Feng, Y. Cui, G. Song, T. Luo, K. Zhang, Y. Wang, X.-C. Jiang, and S. Qin
- Exogenous sphingosine 1-phosphate protects murine splenocytes against hypoxia-induced injury, Chawla, S., C. Sahni, R. Tulsawani, M. Singh, D. Saraswat, A. Bansal, and S. Saxena
- The β-subunit of cholera toxin has a high affinity for ganglioside GM1 embedded into solid supported lipid membranes with a lipid raft-like composition, Margheri, G., R. D'Agostino, S. Trigari, S. Sottini, and M. Del Rosso
- Brefeldin A limits *N*-hexanoylsphingosine-induced accumulation of natural ceramide via the salvage pathway by enhancing glucosylation, Spinedi, A.

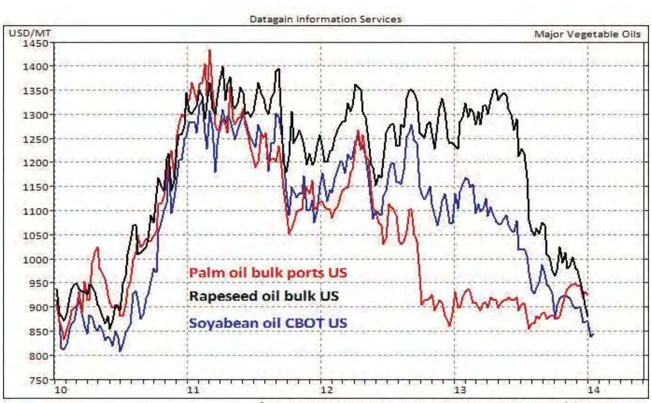
STATISTICAL ANALYSIS FROM MINTEC

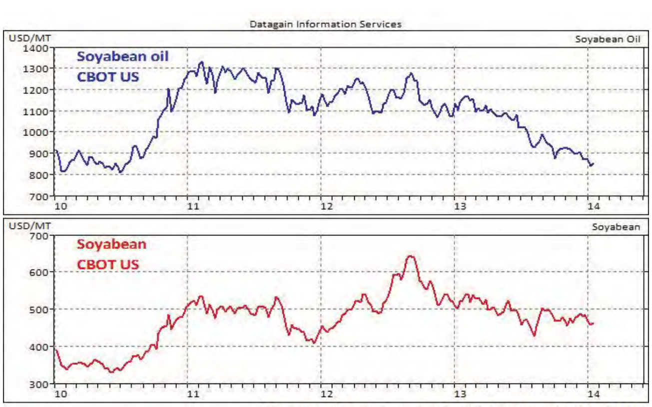
James Hutchings at Mintec

Global soybean production has been revised upward recently to 284.9 million metric tons (MMT), up 6% year-on-year. This upward revision was driven by higher expectations for Argentina, where production is set to reach 54.5 MMT, up 11% year-on-year. This is expected to result in a global production of 44.8 MMT of soybean oil, up 5% year-on-year.

Soybean oil prices have fallen by 20% since May 2013 and have now reached a level last seen in summer 2010. Prices have been affected by both the record soybean harvest seen in 2013/14 and by the weakness seen in other vegetable oil prices due to a plentiful supply of palm oil and a large rapeseed and sunflower seed harvest.

Palm oil prices firmed in the last quarter of 2013 due to strong global demand and concerns that heavy rains will disrupt harvesting in Indonesia and Malaysia, the major producers of palm oil. Global palm oil production is still expected to reach 58.4 MMT, up 5% year-on-year, but palm oil exports from Indonesia and Malaysia will only increase by 1%, reaching 38.8 MMT.





Characterization of phospholipid molecular species and peptide molecules in wheat sprout hydroalcoholic extract

Lucci, P., *et al., J. Agric. Food Chem. 61*:11453–11459, 2013, http://dx.doi.org/10.1021/jf4034392.

The phospholipid molecular species and the main peptide molecules of wheat sprout hydroalcoholic extract have been fully characterized by normal-phase high-performance liquid chromatography coupled online with positive electrospray ionization–tandem mass spectrometry. The extract that resulted was rich in phospholipid molecular species formed by the combination of the two essential fatty acids (α-linoleic and α-linolenic). These species accounted for 51.7% of total phosphatidic acid, 47.3% of total phosphatidylethanolamine, 37.7% of total phosphatidylcholine, and 14.1% of total phosphatidylinositol. The last one showed the highest amounts of species containing palmitic acid, thus representing the most saturated phospholipid class. The extract was also shown to contain several peptide sequences with both potential antioxidant domains and interaction sites for phospholipids (i.e., H-Ala-Gly-Ser-Met-Met-Cys-NH_2, H-Tyr-Met-Thr-Val-Val-Ala-Cys-NH_2, etc.); this latter finding can have a highly positive impact on the poor peptides bioavailability. Because of the presence of essential fatty acids-rich phospholipids and bioactive peptides, wheat sprout hydroalcoholic extract can be considered a potential functional food ingredient.

Oxidative stability of omega-3 polyunsaturated fatty acids enriched eggs

Ren, Y., *et al., J. Agric. Food Chem. 61*:11595–11602, 2013, http://dx.doi.org/10.1021/jf403039m.

Omega-3 polyunsaturated fatty acid (n-3 PUFA)-enriched eggs have a growing market share in the egg industry. This study examined the stability of n-3 PUFA enriched eggs fortified with antioxidants (vitamin E or organic selenium [Sel-Plex] or both) following cooking and storage. The total fat content was not affected by cooking or simulated retail storage conditions, whereas, n-3 fatty acids were reduced. The content of n-3 fatty acids in boiled eggs was higher than in fried eggs. Lipid oxidation was significantly affected by the different cooking methods. Fried eggs contained higher levels of malondialdehyde (MDA, 2.02 μg/kg) and cholesterol oxidation products (COPs, 13.58 μg/g) compared to boiled (1.44 and 10.15 μg/kg) and raw eggs (0.95 and 9.03 μg/kg, respectively, for MDA and COPs). Supplementation of antioxidants reduced the formation of MDA by 40% and COPs by 12% in fried eggs. Although the content of MDA was significantly increased after 28 days of storage, COPs were not affected by storage. Our study indicated that the n-3 PUFA in enriched eggs was relatively stable during storage and home cooking in the presence of antioxidants.

More Extracts & Distillates can be found in this issue's supplement (digital and mobile editions only).

thanks to the editor

Jean-Louis Salager

Jean-Louis Salager has been the editor-in-chief of AOCS' Journal of Surfactants and Detergents (JSD) *since 2008. He is the founder and retired professor of the School of Chemical Engineering at the University of Los Andes in Mérida–Venezuela. He continues to serve as an emeritus researcher at the university in the Laboratory of Formulation, Interfaces, Rheology, and Processes (FIRP), where he is involved with continuing education and consulting activities dealing with surfactants and interfacial phenomena in petroleum engineering, cosmetics, cleaning, and other industrial applications. He was awarded Venezuela's National Scientific Prize, the highest scientific and technological recognition of the country, and the Simón Bolivar Prize, its highest academic award. Under his editorship,* JSD *has gone from publishing quarterly to publishing six times a year and has doubled the number of published articles and performance indices such as the download number and the impact factor.*

Thanks to the Editor is a regular *Inform* column that recognizes those who work on AOCS journals.

In what ways did your previous career and publishing experiences prepare you for the job, and how has being a journal editor shaped your career?
My undergraduate and graduate studies in chemical and petroleum engineering in France and the United States dealt with industrial research and development. This educational background was followed by 40 years of applied research in surfactant science and technology and complemented by 25 years of practice as the Latin American editor of the Journal of Dispersion Science and Technology, a European publication targeted toward industry. My editorship of JSD gave me a wide knowledge and accurate view of industry's significance.

What did you like most about being an editor?
In considering the proposed papers and related readings, I had to assimilate a lot of new information, including scientific and industrial issues that were originally out of my work areas. This widened my scientific and technological appreciation for interfacial phenomena. On the other hand, I really enjoyed the opportunity to lead the complex interactions of many competent people, from AOCS staff, to associate editors and reviewers, to Springer publishing management staff—all of whom demonstrated their willingness to participate in the journal's success.

What did you like the least?
The success of the Journal considerably increased the number of submitted papers and required more of my time every year, while demanding significantly more effort and cooperation from associate editors and reviewers, all without pay—a challenge that was difficult for everybody to satisfy.

In what ways has scientific publishing changed during your editorship, and what changes do you foresee during the next five years?
The scope of JSD has stayed about the same, but more contributions are appearing in the synthesis and use of new surfactants in many applications, particularly enhanced oil recovery. Growing research activities in high-population countries in Asia have led to increased contributions for our journal and motivated the establishment of new publications. This is probably going to continue and will have to be carefully managed to avoid an explosion of information material that would be impossible to handle.

Is there a particular non-scientific interest or activity you enjoy, and what bearing has it had on your life and career?
Aside from out-of-the-office personal distractions such as judo, gardening, and wood working, I have been interested in the psychological factors that influence cooperation among large numbers of competent individuals. Such factors are critical to an academic or industrial research center's success in producing highly effective results through the smart collaboration of all its experts, junior investigators, students, and technological and administrative staff members. Paying attention to such factors has helped me lead a large research laboratory that consistently provides efficient services to industry over many years.

Professional Pathways

Professional Pathways is a regular Inform *column in which AOCS members discuss their professional experiences and share advice with young professionals who are establishing their own careers in oils and fats-related fields.*

Mike Haas is a former AOCS president and recently ended a 15 year stint as Associate Editor and Senior Associate Editor of the Journal of the American Oil Chemists' Society. *He has 32 years of experience in government research, having spent his entire career at the Eastern Regional Research Center of the Agricultural Research Service (ARS), US Department of Agriculture (USDA), in Wyndmoor, Pennsylvania. Haas will retire in early 2014.*

Describe your career path.

I received a Ph.D. in biochemistry from the University of Wisconsin-Madison in 1978. Following a postdoctoral stint, I took a job in 1981 at the Eastern Regional Research Center, one of the handful of large research sites operated by the USDA. I have spent my entire career there and will retire in early 2014.

Why did you join AOCS?

I first joined AOCS because to do so was, basically, an expectation of my job. The better question is why I renew year after year, since it seems that membership is now much less of an expectation. I renew because I have come to view involvement in AOCS as one of the single most useful things I can do to benefit my career.

What do you love about your job?

Successfully solving research problems. Also, I work in the ARS branch of the USDA, its R&D department. The word "Service" in that title conveys something important to me: I appreciate the chance to make a living doing something that could benefit our people.

What is the biggest challenge you have encountered in your career and how did you address it?

I was blindsided in 1997 when I was removed from leadership of a research team with no prior hint that anything was wrong. I felt rejected and marginalized after having given over a decade of high-level productive performance. It fortuitously happened at that time that AOCS began asking me to become more involved in society governance functions. The value, interactions, and contacts that I made through that involvement gave value to the professional side of my life at a time when my day-to-day job was very difficult.

How has your industry changed since you entered the field?

Certainly industrial consolidation has merged or eliminated former entities, and technology has increased the speed and breadth of communication. But good ideas still shine; good research teams still focus on good ideas and turn them into good realities. I believe that timelines have shortened. And even in my organization, which is not sales and profit motivated, there is less value seen in long-term research, less patience for research that is not tightly targeted to near-term, very specific achievement. It is as if the increasing speed of our personal lives has led to a decreased patience with the nature and process of research and has increased focus on the "applied" rather than the "basic" type of work.

What has not changed is the value of interpersonal ties. They may be of even greater value today than they were decades ago. In a world where everyone can know everyone, it is the list of people with whom you have a relationship, the people who will answer the phone when it's you, that can be of great value.

Another perspective on your question is to observe that to some degree my 'industry' is Federal research, with US agriculture and in some ways the US farmer as chief clients of my work. "Utilization Research" is the sign on the bronze plaque at the main entrance to the building in which I work, and the major justification for my job is to conduct research to develop new uses for farm products, to benefit the agricultural community and to generate new products for US citizenry. Because my parents, grandparents, and those before them were farmers, this job has meaning to me. When I began my career, commodity prices were low and US farmers were being squeezed off the land by high equipment and land prices. The justification for value-adding agricultural utilization research was reasonably well understood by many. Today, however, farm commodity prices are at historic highs. (It is personally gratifying that some of this is a result of the wide adoption of newly developed products, among them biodiesel, on which I have worked.) Also, the size of the US farm population has shrunk. An unintended consequence of these changes is that, to some people, they have reduced the impetus for conducting agricultural utilization research. Couple this with a general downturn in federal investment and with a move in some sectors of our country to downplay or dismiss the value of science in even everyday life, and one may begin to feel the government researcher to be an endangered species.

Do you have any advice for those looking to enter your field?

I speak here from my perspective as a US federal researcher. Consider that sequestration [across-the-board spending cuts passed by the US Congress in 2011] may not be a one-time occurrence. Witness the difficulty Washington has in agreeing on a federal budget. The future of federal research seems uncertain. I am strong on research as a profession; I am not as certain that it will continue to be as large a part of the future US government.

How do you see the industry changing in the next five years?

Historically my research funding has been rather stable and secure if one met the prerequisite of coming up with a research project deemed worth funding. As the federal government shrinks, there will be less funding for most types of research. This is already evident, in that of the last seven Ph.D. retirements in my department only two of the vacancies were filled. It will be much more important in the future that a federal researcher augment his or her in-house funding with research funds obtained through competitive grant programs.

Describe a memorable job experience.

It is still most miserable to have a research goal that is bafflingly unattainable; and exceptionally joyful to run down all the possibilities, flukes, misperceptions, artifacts, blind alleys, and misinterpretations and come up with the correct solution to a problem. Also, I have been surprised by how very nice it feels to work with a new researcher who wants to win, wants to do good work, who is interested in learning the system of a place. It is nice to find someone who seems to want a mentor.

Please describe a course, seminar, book, mentor, or speaker that has inspired you in ways that have helped you advance your career.

I don't know that anyone consciously mentored me during my career. You find your mentors by watching everyone you run across, seeing the example each person sets, learning from their example.

There are many opportunities to see the dark side of a situation, any situation. There will always be deadlines, funding shortages, bad lab days, difficult employees, cold water in the showers, or a freezer that melted down and took your samples with it. I have been fortunate to know people who focused on the positive in spite of the never-ending existence of the negative, people who focused on getting the job done in spite of the system. Professor Julian Davies, my thesis advisor in graduate school, was one of these men. He may not have dreamed up the mantra "When there is no wind, row," but he subscribed to it, lived it, and expected his people to do the same. Similarly, one of my supervisors, Steve Feairheller, was attracted not by title, or power, or size of budget and staff, but by ideas. He would support a good, innovative scientific idea and figure out how to muster the resources to make good science happen. People like these helped me see the value of focusing on the positives and the targets, and of minimizing the energy spent focusing on unalterable difficulties. They were refreshing.

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Do you have any advice for young professionals who are trying to develop an effective network of other professionals?

Nothing I have done in my career was of greater value in the context of network than my involvement in AOCS. I used to think it would be enough to do good work, and people would find me and form contacts. To some extent network does develop that way. But let's face it, few of us are so brilliant as to have that be our path to success. Of far greater value for me have been the interpersonal contacts I have made in this Society. By being involved in such things as Division leadership, Governing Board membership, journal editorship, and elected society officership I have met and worked shoulder-to-shoulder with a multitude of really fine, energetic, and intelligent people to whom it matters to be professional and productive. These people are my network, and many are my personal friends. People in that group have positions of authority and knowledge around the world, and it seems that they DO pick up the phone when I call, just as I do for them. I was also fortunate in that my employer saw value in this involvement and gave me authorization and time to pursue it.

What are the opportunities for advancement in your career/field and how can someone qualify for such advancements?

Again as a researcher in the US federal system: "advancement" means going from being in a research group, to leading one, to leading a department or facility. Good ideas, good initiative, and good research productivity will get you the first parts of the way, just as they long have in this and other research environments, and will qualify you for further advancement. The USDA-ARS research workforce is age heavy and shrinking due to retirements. This creates opportunities for the earlier career professional to fill vacancy in upper level management positions. An individual in the federal system who is interested in "advancing" to positions of greater responsibility—in research or program management, for example—may well find numerous opportunities and a system that supports you as you go for them.

If you were starting your career again, what would you do differently?

Pay more attention to the literature. I enjoy doing science and being active in the lab more than sitting at my desk reading of other people's discoveries. However, there is great value in the ability of other people's discoveries to enlighten one's own work, or at least keep you from reinventing a wheel already invented. You ignore the literature at your own expense.

How would you describe the culture in your field and how has it developed.

I presently find most research scientists to be affiliative, inclusive, and welcoming as opposed to cutthroat, competitive, exclusive, and arrogant. This is particularly evident and refreshing in the case of the biodiesel research community in which I work. Either the world has changed in 40 years or I am spending time in a different portion of it these days.

In your area/field and considering today's market, is it more important to be well-rounded or a specialist?

I would suggest that it is best to be a specialist with a diverse toolkit—that is, don't just conduct organic chemistry; do so with many different catalytic approaches, multiple analytical skills, and some molecular genetics thrown in to modify a biocatalyst here and there. Or, as a further example, don't just make an organic chemical; rather, gain the skills to test its performance in the context of some imagined or desired application.

An employer may well expect you to be diverse down the road, to be able to be transferred into completely new areas and still function well. But in the first analysis they will, I believe, value someone who has demonstrated broad proficiency in a specialized topic. People most often hire early career professionals to specific job descriptions, not general ones.

What is your opinion toward the value of obtaining or possessing a graduate degree during a challenging economy?

I would never advise choosing one's degree level or field of specialization based on the economy. Go for what calls you, what you think you will love. It seems to me that if you choose your educational level and area of specialization based on the economy rather than on what interests you and energizes you, you might just be lucky enough to make enough money to buy a really good therapist to help you work out the anxieties generated in your job, if you are smart enough to use it for that.

In the federal system, and I believe in most research organizations, it is primarily the B.S. and M.S. people who are in the labs doing hands-on research. Their foci and day-to-day assignments are dictated by the goals of their directors. A Ph.D. degree gives you the ability to be the director, to call more of the shots of your day-to-day existence. But the Ph.D.s, those directors, who might get an office rather than a cubicle, have the responsibility to write all the reports, proposals, performance appraisals, papers and patent applications. They are at the keyboard a lot more than they are at the bench. Decide what field calls you. Decide what level you want to be at—the hands-on doer or the planner/writer/director. It will be easier to live with whatever salary you get if you like the field and position you are in. End up in a poor-fit position Monday through Friday and beyond, and there may not be enough money, however much you bring home, to make life bearable, let alone enjoyable. Thirty or 40 career years is a huge chunk of a person's life. And I am pretty sure that this is your one chance on earth; it's not a rehearsal. ■

Surface-active free fatty acids promote oxidation in water-in-walnut oil emulsions

Jianhua Yi, David Julian McClements, and Eric Andrew Decker

All food fats and oils contain free fatty acids (FFA). These FFA are undesirable because they produce off-flavors, foam during mixing and heating, and decrease the smoke/flash point of the oil. Due to these adverse effects on oil quality, FFA concentrations are lowered in many oils during the neutralization step of refining. Neutralization decreases FFA concentration to 0.05–0.70% of refined oil (Chen *et al*., 2011). However, oils that are not refined, such as olive oil, can have FFA concentrations up to 1.5%.

Besides negatively affecting flavor, foaming, and smoke point, FFA are also well documented to promote lipid oxidation both in bulk oils and in O/W emulsions (Waraho *et al*., 2009, 2011; Aubourg, 2001). While a great deal of research has focused on the prooxidant activity of FFA in bulk oil and oil-in-water (O/W) emulsions, there are few studies on the impact FFA have on lipid in bulk oils because the surface of the lipid phase exposed directly to air would be the same in oxidation in water-in-oil (W/O) emulsions. The possible reasons for this lack of research include: (i) bulk oil and O/W emulsions are more commonly encountered in food products than W/O emulsions; (ii) it is very hard to make stable W/O emulsion model systems for research studies; and (iii) Fritsch has stated that the rate of lipid oxidation in W/O emulsions will be similar to that both systems. This latter assumption is based on the hypothesis that the most important interface in oxidation chemistry would be the air-oil interface.

On the other hand, it is possible that lipid oxidation mechanisms in heterogenous systems are not the same as they are in bulk oils since W/O emulsions have a water-oil interface

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- **Free fatty acids (FFA) are widely known to promote lipid oxidation in bulk oils and oil-in-water (O/W) emulsions, but few studies have looked at the impact of FFA on lipid oxidation in water-in-oil (W/O) emulsions.**
- **Recent investigations of the impact of FFA on lipid oxidation in walnut O/W emulsions demonstrated that FFA promoted oxidation in a dose-dependent manner.**
- **The prooxidative activity of the FFA was also influenced by their chain length, degree of unsaturation, and shape.**

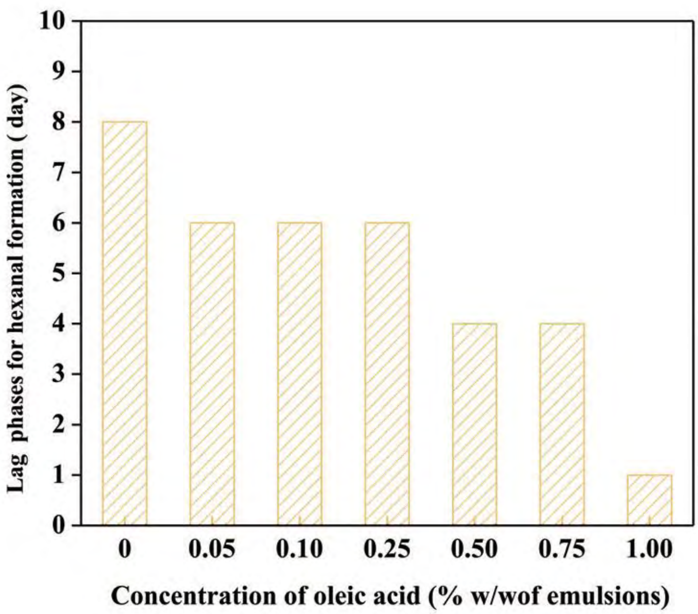

FIG. 1. Lag phases of hexanal formation in 2% water-in-stripped walnut oil emulsions with addition of different concentrations of oleic acid during storage at 45°C in the dark for 12 days. Oxidation lag phases were defined as the first data point significantly greater than the zero time value at the level of $p < 0.05$.

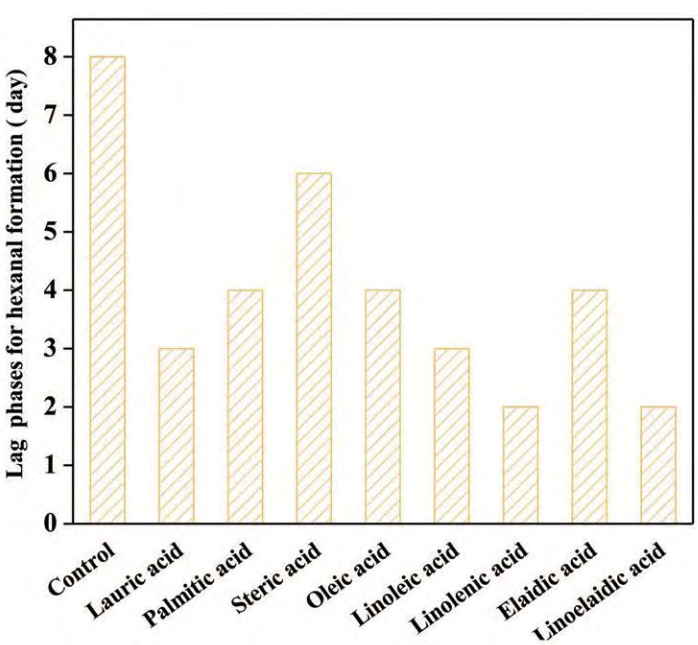

FIG.2. Lag phases of hexanal formation in 2% water-in-stripped walnut oil emulsions without (control) and with addition of different type of FFA (0.50% w/w of emulsions) during storage at 45°C in the dark for 12 days. Oxidation lag phases were defined as the first data point significantly greater than the zero time value at the level of $p < 0.05$.

that could have more impact on lipid oxidation than the oil-air interface. This is because both prooxidants and antioxidants can concentrate at water-oil interfaces, thus having a large effect on lipid oxidation kinetics. The study described below was conducted to investigate how FFA actually influence lipid oxidation in W/O emulsions given that FFA are surface active and could concentrate at the oil-water interface. Walnut oil was used because it contains 70% polyunsaturated fatty acids, which have been shown to be important for the maintenance of good health and for the potential alleviation of a range of human diseases and disorders (Oliveira *et al.*, 2002). The W/O emulsion in this study was stabilized with polyglycerol polyricinoleate (PGPR), a lipophilic emulsifier that is used to stabilize W/O emulsions such as spreads and margarines.

FFA PROMOTE OXIDATION IN WATER-IN-WALNUT OIL EMULSIONS IN A DOSE-DEPENDENT MANNER

The ability of FFA to impact lipid oxidation in W/O emulsions was evaluated by adding oleic acid (0.05–1.0% w/w of emulsions) to the PGPR-stabilized 2% water-in-stripped walnut oil emulsions with an aqueous phase of pH 7.0 (Yi *et al.*, 2013). The impact of FFA in this and subsequent studies was determined by measuring the lag phase of oxidation.

Lag phase is an important determinant of oil quality, because once oxidation reaches the exponential phase the oil is rancid. Many studies measure differences in lipid oxidation after the lag phase to determine differences in oil quality (e.g., effectiveness of antioxidants). However, these comparisons are not relevant indices as they are a comparison of which oil is the most rancid whereas the goal of improving oil quality is to increase the time before the oil becomes rancid (e.g., lag phase).

One should understand that determination of lag phase with chemical markers as a measurement of oil quality also has limitations since sensory detection of rancidity can be more sensitive than chemical techniques especially for oils high in n-3 fatty acids. However, even in these cases lag phase can still be useful as one can determine factors that increase or decrease the shelf life of the oil.

In the water-in-walnut oil emulsion used in this study, oleic acid was prooxidative at concentrations as low as 0.05% as indicated by the lag phase of both lipid hydroperoxides and hexanal formation (Fig. 1).

The ability of oleic acid to be prooxidative at these low concentrations suggested that FFA would be important in the oxidative stability of W/O emulsions prepared with either refined or unrefined oils. Similar prooxidative trends of FFA have also been reported in bulk oils and O/W emulsions, but the concentration of FFA needed to promote oxidation was generally greater (Aubourg, 2001; Waraho *et al.*, 2011).

In an attempt to understand how FFA where increasing lipid oxidation rates in water-in-walnut oil emulsions, EDTA was added to the aqueous phase. In all cases, EDTA strongly inhibited oxidation indicating that transition metals were important prooxidants. Previous work on the effect of FFA on lipid oxidation in O/W emulsions and bulk oils with associated colloids showed that FFA are surface active and thus are able to concentrate at oil-water interfaces. By concentrating at the interface, the FFA make the interface more negative thereby allowing cationic metals to bind at the interface. Since lipid hydroperoxides are also surface active, these results suggests that the FFA could concentrate metals at the same location as the hydroperoxides, thus increasing metal-promoted peroxide decomposition into free radicals and lipid oxidation rates.

FFA CHAIN LENGTH, UNSATURATION, AND SHAPE ALL INFLUENCE PROOXIDATIVE ACTIVITY

The prooxidant activity of FFA with different chain lengths was in the order of lauric > palmitic > stearic acid (Fig. 2).

The effect of level of unsaturation was also tested, and prooxidant activity was in the order of linolenic > linoleic > oleic acid. Finally, the influence of geometric shape on the prooxidant activity of FFA was tested. In this case, elaidic and oleic acids had similar prooxidant activities whereas linoelaidic was more prooxidative than linoleic acid.

There are several possible reasons why the structures of fatty acids could impact their prooxidant activity. First, structure could affect the solubility of fatty acids. As FFA chain length increases, melting point increases, meaning that the potential for the FFA to crystallize increases. Therefore, it is possible that stearic acid would be (i) more crystalline than lauric acid, (ii) less likely to partition at the oil-water interface, and therefore (iii) less prooxidative. Second, level of unsaturation could impact prooxidative activity if the FFA itself was prone to oxidation. Thus, linolenic acid would be the most susceptible to oxidation, and its oxidation would produce free radicals that could increase the oxidation of other fatty acids in the walnut oil. Third, shape could affect prooxidative activity because *trans* fatty acids are more linear than *cis* fatty acids, which could influence the ability of the fatty acids to pack closely and concentrate at the oil-water interface. While all of these hypotheses can be justified based on differences in the physical properties of the fatty acids, more work is needed to determine differences in their partitioning behavior in W/O emulsions.

FFA are important prooxidants in W/O emulsions as they are in other lipid systems. In water-in-walnut oil emulsions, FFA were able to promote oxidation at the concentrations found in both refined and unrefined oils. Prooxidant activity increased with decreasing chain length and with increasing unsaturation. While more work is needed to determine exactly how fatty acid type affects oxidation, it is clear that (i) all fatty acid types are potential prooxidants and (ii) producing produce oils with FFA concentrations low enough to stop their prooxidant activity will be very difficult. To control the prooxidant activity of FFA, it will be important to find novel methods to inhibit their ability to bind metals or to find free radical scavengers that will partition in the same location as the FFA. Development of such technologies could help increase the use of highly unsaturated healthful oils such as walnut oil.

Jianhua Yi is an associate professor at College of Life Science and Engineering, Shaanxi University of Science and Technology (China). She was a visiting scholar in the Department of Food Science, University of Massachusetts (UMASS), Amherst (USA) in 2011–2012. She can be reached at yijianhua@sust.edu.cn.

David Julian McClements is a professor and colloidal chemist at UMASS. He is one of the most highly published agricultural scientists, with over 525 refereed publications and over 13,500 citations.

Eric Andrew Decker is a professor and department head at UMASS Food Science. He is the director of the UMass Industrial Strategic Research Alliance and has over 300 publications in the areas of lipid stability, functionality, and nutritional attributes. He can be reached at edecker@foodsci.umass.edu.

INFORMATION

- Aubourg, S.P., Fluorescence study of the prooxidant effect of free fatty acids on marine lipids, *J. Sci. Food Agri. 81*:385–390 (2001).
- Chen, B.C., D.J. McClements, and E.A. Decker, Minor components in food oils: a critical review of their roles on lipid oxidation chemistry in bulk oils and emulsions, *Crit. Rev. Food Sci. Nutr. 51*:901–916 (2011).
- Fritsch, C.W. Lipid oxidation–the other dimensions, *Inform. 5*: 423-436(1994).
- Oliveira, R., M. Fátima Rodrigues, and M. Gabriela Bernardo-Gil, Characterization and supercritical carbon dioxide extraction of walnut oil, *J. Am. Oil Chem. Soc. 79*:225–230 (2002).
- Waraho, T., V. Cardenia, T.M. Rodriguez-Estrada, D.J. McClements, and E. A. Decker, Prooxidant mechanisms of free fatty acids in stripped soybean oil-in-water emulsions, *J. Agric. Food Chem. 57*:7112–7117 (2009).
- Waraho, T., D.J. McClements, and E.A. Decker, Impact of free fatty acid concentration and structure on lipid oxidation in oil-in-water emulsions, *Food Chem. 129*:854–859 (2011).
- Yi, J.H.,Z.B. Zhu, W.B. Dong, D.J. McClements, and E.A. Decker, Influence of free fatty acids on oxidative stability in water-in-walnut oil emulsions, *Eur. J. Lipid Sci. Technol. 115*:1013–1020 (2013).
- Yoshida, H., I. Kondo, and G. Kajimoto, Participation of free fatty acids in the oxidation of purified soybean oil during microwave heating, *J. Am. Oil Chem. Soc. 69*:1136–1140 (1992).

Cold-pressed canola oil turns commodity into innovative consumer product

Heather Burson

Every farmer and rancher in the state of Oregon (USA) is driven by a great purpose: to produce quality commodities that serve and feed their local communities and the world. Most send theirs off to various places to be processed or added into foods and sold elsewhere, some may get to produce and sell it themselves, but few get to do what Family Generation Foods is doing. Family Generation Foods is giving local multigenerational farm families a unique opportunity to take their commodity, turn it into an innovative food product, and sell it directly to consumers. Some might call that "living the dream." For Madison Ranches' Kent and Laura Madison, that dream has become a reality.

- **In 1990, Kent Madison planted canola to conserve water.**
- **During the 2000s, when biofuels were hot, he and his wife, Laura, started crushing the canola to produce biofuel.**
- **When producing biofuel became too expensive for the economy to support, they converted their crushing plant to a food-grade oil production plant and turned their commodity crop into an innovative food product that is sold directly to consumers.**

Family Generation Foods started at Madison Ranches, Kent and Laura's own multigenerational farm. The farm started with Gaylord Madison who, after several years of drought in Iowa, made a fresh start in eastern Oregon in 1914, taking advantage of the Water Reclamation Act. Purchasing dry desert land outside of Echo, he raised sheep and feed crops to provide for his flock and horsepower. Eventually the farm passed to his son, John Madison, who expanded the farm by adding an irrigation system to raise commodity crops such as wheat and alfalfa. He also replaced the sheep with cattle before transitioning the farm to his son Kent Madison in the early 1980s. Kent expanded the farm even further, utilizing the newest computer technology to plant crops, apply fertilizers, and conserve water.

Conserving water involved a transition to deficit irrigation, which requires crop diversity, with each crop using water at a different time and at a lesser rate. Out of this practice, and the need for better crop rotation, canola entered the picture. "We started raising canola in 1990 and also raised it in rotation with alfalfa, corn, and other crops," says Kent. Canola uses less water than other crops, especially as it matures. When water is no longer

Madison Ranches' canola oil was recently put to the test in at the Potato Champion food cart in Portland, Oregon, USA. Using a centrifuge to remove the solid particulates preserves the savory flavor of the oil while allowing it to achieve a high temperature without giving off excessive amounts of smoke. Photo: courtesy of Madison Ranches/Family Generation Foods.

needed it is shut off and used for other crops, allowing the canola to dry before harvest. Once the canola is harvested, it can be crushed into oil.

In the early 2000s, when there was interest in biofuels, Kent and Laura decided to crush canola oil themselves to make biofuel for SeQuential Pacific Biodiesel. For this they installed their own canola crushing system and biodiesel production plant on-site at Madison Ranches. Eventually, the process became too expensive for the economy to support, and that's when Kent and Laura made an exciting discovery. "We realized the canola oil we were pressing was of incredible quality, golden in color, almost like an olive oil, and started playing with that," says Kent. The results carried over to the kitchen, as Laura started cooking with the oil, and that was when they decided to start producing food-grade oil. In 2012 they converted the canola crushing plant to a food-grade oil production plant, and Family Generation Foods was born.

The canola seed is harvested through a combine and, as it's needed for crushing, it's dry cleaned through a rotary cleaner and fed into crushers that press the oil from the seed. This occurs at the food-grade production plant, which is on-site at Madison Ranches.

The name honors the many generational farming families in Oregon, as 98% of Oregon's farms and ranches are family farms and ranches. Kent and Laura were amazed, in claiming such an appropriate name, that it had not already been taken. "It was surprising . . . when you do a Google search there are a lot of family genealogy sites that come up, but that's about it," says Laura. Although Oregon farm and ranch families have been serving and feeding their communities, and the world, for many generations, this is the first venture of its kind to bring them all together. "The concept of Family Generation Foods is generational farming families providing generational family food," says Laura. A simple and important concept for a company in its early stages that's starting to take off.

Madison Ranches' canola oil is the first product and has already evolved into seven flavors: Original, Lemon, Dill Weed, Basil, Roasted Garlic, Adobo Spice, and Habañero. All of them are pure, unique oils that stand out in a variety of foods, but they especially enhance presentation and the taste of homemade breads. "It has a beautiful color, and if you're into presentation, and into

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Phospholipids: natural functional ingredients and actives for cosmetic products

Peter van Hoogevest, Beate Prusseit, Rudi Wajda

In cosmetic products phospholipids are popular as biodegradable natural ingredients. The phospholipid molecule comprises a glycerol backbone which is esterified in positions 1 and 2 with fatty acids and in position 3 with phosphate. The systematic designation of e.g. phosphatidic acid (PA) is 1,2-diacyl-sn-glycero-3-phosphate (where sn means stereo- specific numbering). The specific and non- random distribution of substituents over the positions 1,2 and 3 of the glycerol molecule introduces chirality. In typical membrane phospholipids, the phosphate group is further esterified with an ad- ditional alcohol, for instance in phosphatidylcholine (PC) with choline (Fig. 1), in phosphatidylethanolamine (PE) with ethanolamine and in phosphatidylglycerol (PG) with glycerol. Depending upon the structure of the polar region and pH of the medium, PE and PC are zwitterionic and have a neutral charge at pH values of about 7, whereas e.g. PG is negatively charged.

Due to the molecular structure which is comprised of a hydrophilic part and a lipophilic part, phospholipids have a special amphiphilic character. When mixed with water, they form various structures depending on the number of fatty acids esterified to the glycerol backbone and the resulting geometry of the molecule. When only one fatty acid is esterified (monoacyl phospholipids/lysophospholipids) to the glycerol backbone, the mole- cules are cone shaped and they are able to form micelles. Di-acylphospholipids with cylindrical shape are organized as lipid bilayers (lamellarphase) with the hydrophobic tails lined up against one another and the hydrophilic head-group facing the water on both sides (Fig. 2).

The latter structures formed are called liposomes. The membrane of such a liposome resembles the basic structures of cellular membranes. It is therefore obvious that such structures will have a bene- ficial interaction with skin cells.

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- **As cosmetic actives, natural phospholipids isolated from soybeans provide the essential fatty acids linoleic acid and linolenic acid. Such phospholipids are renowned for their ability to maintain the skin in healthy condition and to ameliorate skin disorders like acne vulgaris and neurodermitis, or slow down skin aging.**

- **Recent comparisons of the characterisitcs of soybean phosphatidylcholine (SPC) and hydrogenated soybean phosphatidylcholine (HSPC) for use in cosmetics indicated that SPC plays a role in liquefying the stratum corneum and enhancing penetration, while HSPC helps strengthen the skin barrier function (HSPC).**

- **The availability of multifunctional natural phospholipids in various grades and modifications with controlled quality provide the formulator a valuable tool box for designing optimal cosmetic products.**

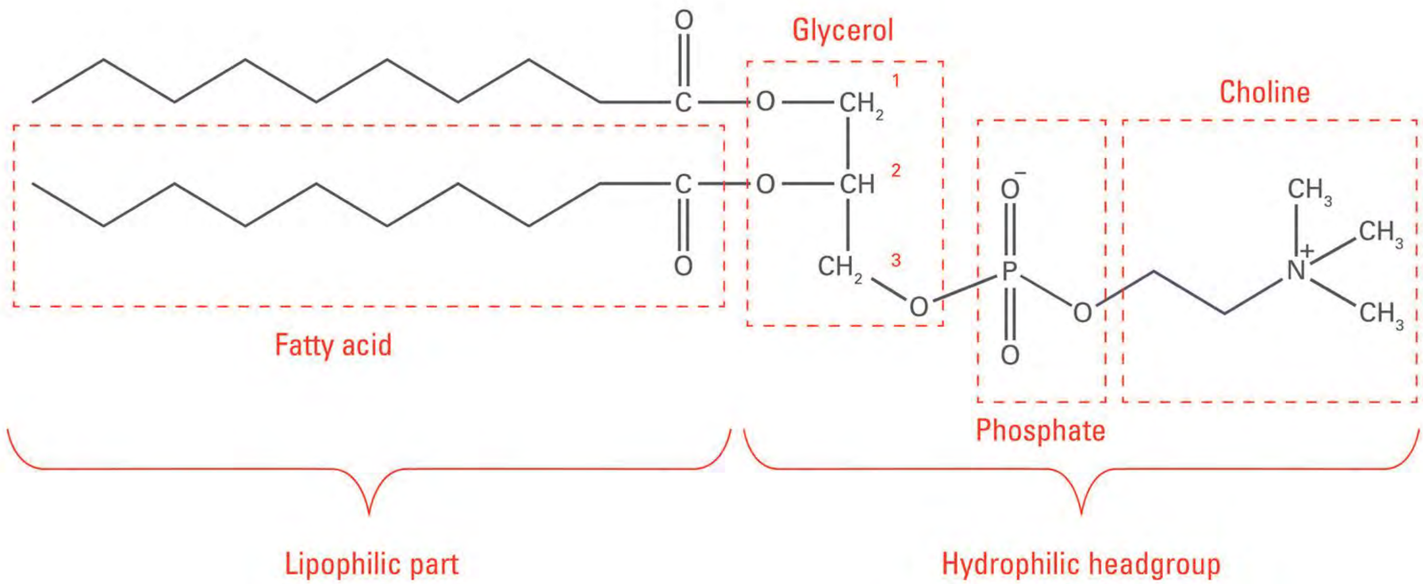

Fig. 1. Molecular structure of phosphatidylcholine

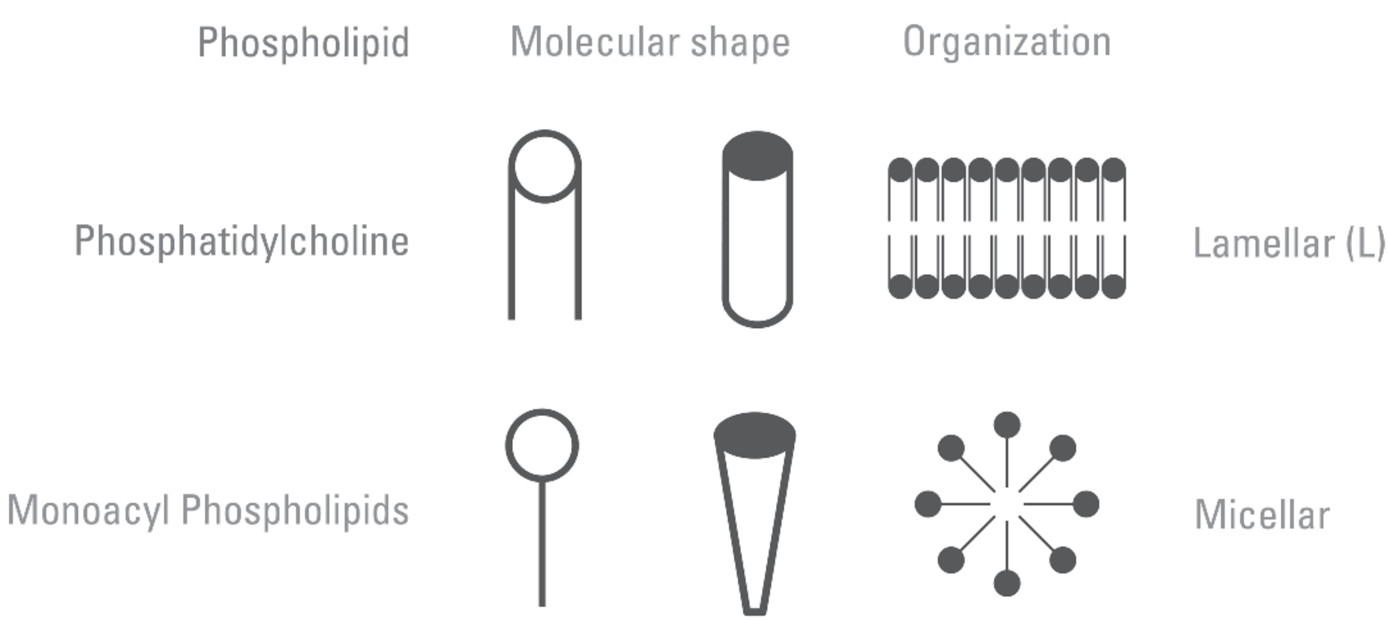

Fig. 2. Shape of phospholipid molecules dependent on polar head group and fatty acid composition and resulting aggregate organization upon hydration.

Table 1. Fatty acid composition (mole %) of SPC determined by enzymatic hydrolysis followed by gas-chromatography (1)

Fatty acid	In 1-position (%)	In 2-position (%)	Total (%)
C16:0 palmitic acid	24.0	1.7	12.9
C18:0 stearic acid	7.9	1.0	4.4
C18:1 oleic acid	10.9	10.0	10.5
C18:2 linoleic acid	52.4	80.6	66.5
C18:3 linolenic acid	4.7	6.7	5.7

In cosmetic formulations di-acylphosphatidylcholines are the main phospholipids used. In the literature lecithin is sometimes used as a synonym for phosphatidylcholine; the EU directive 2006/ 257/EC and CAS define lecithin as a phospholipid mixture containing besides mainly phosphatidylcholine other phospholipids and components such as fatty acids, triglycerides, sterols, carbohydrates and glycolipids. These lecithins can be fractionated with respect to their phosphatidylcholine content. In this way several grades can be produced starting from crude lecithin with ca. 15% PC still containing substantial amounts of the plant oil from which it has been isolated, and de-oiled or fractionated lecithin to obtain contents from 25-96% PC. Phospholipids are essential natural components of the membrane of all living cells; they are non-toxic and possess very high skin tolerability. For cosmetic use mainly phospholipids isolated from natural vegetable sources like soy beans, rapeseed (canola seed) and sunflower seed are used. The isolated phospholipids have a fatty acid composition typical for the plant source used. The fatty acid composition of soybean phosphatidylcholine (SPC) is provided in Table 1.

Typical for these soybean phospholipids is the high total content of the omega-3 18:3 linolenic acid and omega-6 18:2 linoleic acid, which are essential fatty acids, and oleic acid. The fatty acid composition of phospholipids determines the temperature at which the fatty acids change their mobility. Below this so-called 'gel state to liquid crystalline state phase transition temperature' the fatty acids are rigid (gel state), whereas above this temperature the fatty acids are mobile (liquid crystalline or fluid state). Phospholipids containing polyunsaturated fatty acids have very low (below 0 °C) transition temperatures. This means that these lipids at skin temperatures of around 22°C are in the liquid crystalline state and form, upon hydration, very flexible structures/liposomes. Phospholipids containing unsaturated fatty acids can be converted to phospholipids with saturated fatty acids by means of hydrogenation. The resulting phospholipids are in the gel state at skin temperature and tend to form more rigid and stable membrane structures.

PHOSPHOLIPIDS: MULTIFUNCTIONAL COSMETIC INGREDIENTS AND ACTIVES

Because of their chemical structure and physicochemical properties, the use of phospholipids in cosmetic formulations has several unique aspects. In the following, it will be apparent that

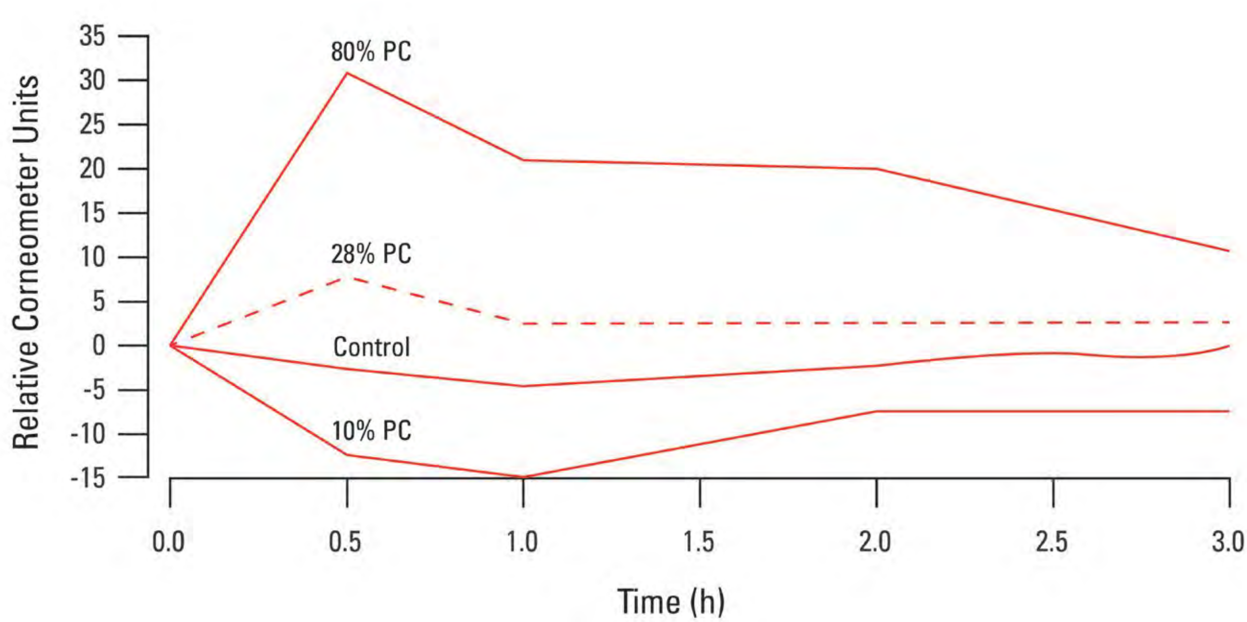

Fig. 3. Influence of SPC concentration in topical formulations on the humidity of the human skin after single application to ten health volunteers

phospholipids are not only technically useful ingredients but support the barrier function of the skin as well. Hence Phospholipids will keep the skin in healthy condition and can therefore be considered as cosmetic actives. These functional properties of phospholipids are the basis for the excellent skin tolerability of phospholipids (2,3).

TECHNICAL INGREDIENTS

Di-acylphospholipids are very mild detergents (4,5). After hydration di-acyl-phospholipids with cylindrical shape do not form micelles like strong detergents but lamellar structures. For these reasons they are not able to emulsify oil with water spontaneously. However, when applying high pressure homogenization to make oil-in-water emulsions, they are excellent emulsifiers yielding very stable emulsions. Without oils, di-acylphospholipids form liposomes/lamellar structures similar to the skin spontaneously, simp-ly by hydrating the phospholipids. The formed lamellar structures (liposomes) or emulsified oils are able to incorporate lipophilic compounds in formulations. Liposomes further allow the (simultaneous) encapsulation of water soluble cosmetic components in their aqueous core. Phospholipids can also be used as wetting agents to disperse water insoluble compounds in aqueous vehicles.

COSMETIC ACTIVES

Upon application to the skin, unsaturated di-acylphospholipids like SPC act as a source of linoleic- and linolenic acid (Table 1). The fraction of administered phospholipids containing linoleic acid reaching metabolic active skin cells may also strengthen the natural barrier function of the skin through incorporation into skin ceramides I. In addition, these phospholipids may play a role in the suppression of acne (6, 9), neurodermitis and psoriasis (10,11). The linolenic acid bound to phosphatidylcholine can be eventually converted to the omega-3 fatty acids docosahexaenoic acid (DHA, 22:6n-3) and eicosapentaenoic acid (EPA, 20:5n-3).

Dependent on their fatty acid composition, di-acylphosphatidylcholines, have a different interaction with the skin. In the following, this is described for (unsaturated) SPC and (saturated) hydrogenated soybean phosphatidylcholine (HSPC) (5)(12).

SOYBEAN PHOSPHATIDYLCHOLINE (SPC)

The influence of the SPC concentration on skin humidity was tested after single skin application of formulations containing 0% (control), 10%, 28% and 80% PC to ten volunteers.

The results obtained (Fig. 3) demonstrate an acute and significant increase in skin humidity for the formulation with 80% PC. The formulation with 28% exhibited a weaker effect, whereas the formulation with 10% PC showed a reduction in skin humidity. Since the only difference between these formulations is the PC content, it can be concluded that PC provides a

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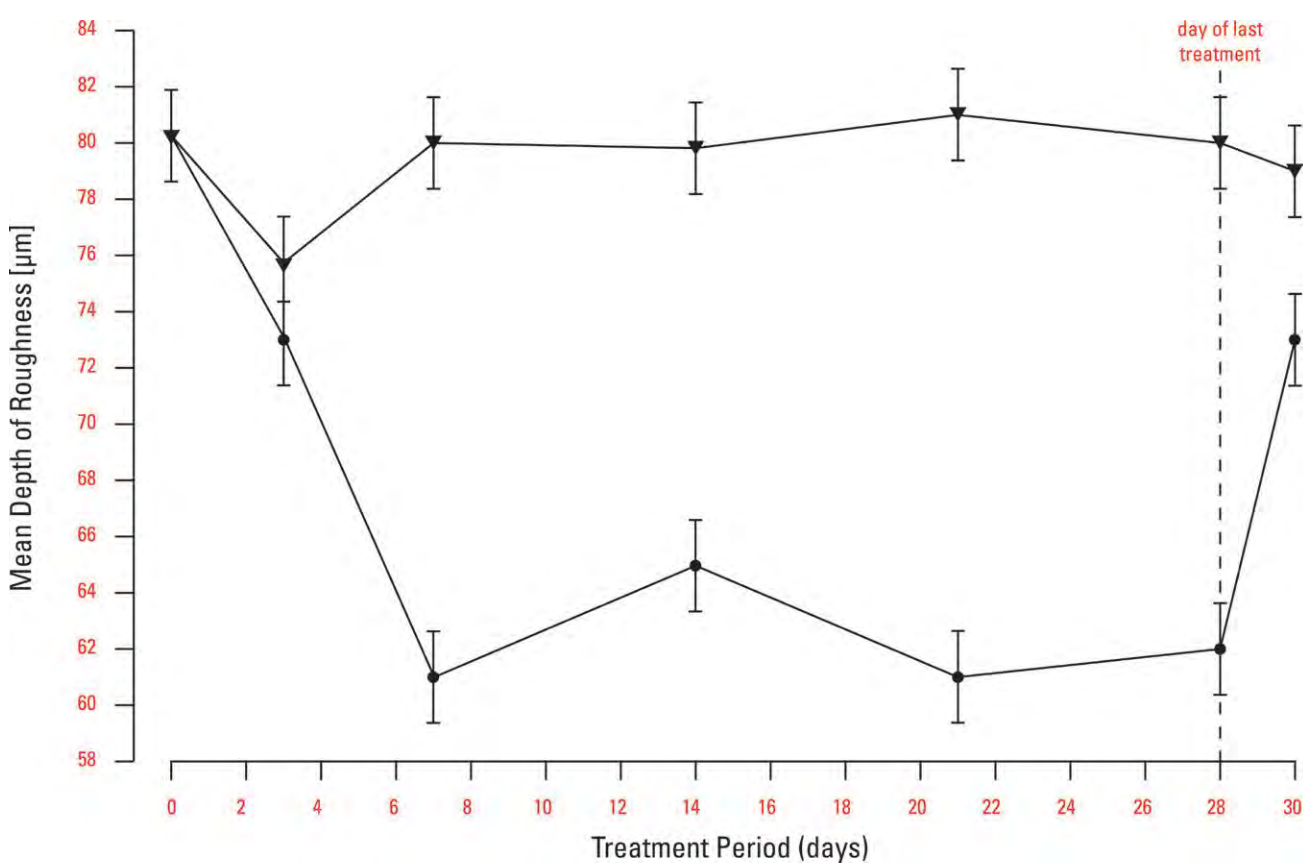

Fig. 4. Effect of a 20.6% SPC-containing formulation on the roughness of the human skin after multiple application to health volunteers (n=20).

Table 2. Penetration of ^3H labeled liposomes into porcine skin after three hours after single application at 1 mg phospholipid/cm^2 skin

Skin Strips/Cuts	Skin Section	µg Liposomal Phospholipid/g Tissue
20 strips	Stratum corneum	100 000
1 mm	Epidermis	500
2 mm	Dermis	20
3 mm	Subcutis	8
4 mm	Subcutaneous fat	8
5 mm	Subcutaneous fat	12

moisturizing effect to the stratum corneum. This conclusion was confirmed by a second multiple application study, which showed an increase of skin humidity to steady state levels.

The influence of SPC on the skin roughness was studied by comparing an aqueous SPC liposome dispersion comprising of 20.6% w/v SPC (with 93% PC) and ca. 16% ethanol with an oil-in-water emulsion after multiple applications to 20 volunteers (Fig. 4, page 185). The skin roughness was significantly decreased in the group treated with the SPC containing formulation.

In order to assess the degree of skin penetration of SPC liposomes, 3H labeled (in fatty acid) liposomes were applied to porcine skin non-occlusively at 1 mg phospholipid/cm2 skin. After 30, 60 and 180 min the phospholipid concentration in the stratum corneum and underlying skin layers was determined using liquid scintillation counting on samples obtained by 20-fold stripping and subsequent tissue sampling (13, 14). The results provided in Table 2, show that more than 99% of the applied PC accumulates in the stratum corneum, suggesting that the liposomes strongly interact with the stratum corneum lipids. It is assumed that the ceramides, which are the main components of stratum corneum lipids, are diluted after a treatment with SPC liposomes, with the PC molecules by means of a fusion process of the liposomes with the membranes of the stratum corneum. The fluidity of the lipid barrier is thereby increased. The depth of modification is strongly dependent on the concentration of PC.

An SPC based product for cosmetic use from Lipoid Kosmetik AG is Natipide® II. It consists of densely packed multilamellar liposomes with a mean particle size in the range of 200-250 nm (15, 16).

HYDROGENATED SOYBEAN PHOSPHATIDYL-CHOLINE (HSPC) (16)

In contrast to the fluid-state SPC, HSPC contains mainly saturated fatty acids at amounts of approximately 85% stearic acid, 14% palmitic acid, and 1% other fatty acids. These fatty acids have a high melting point and induce a high transition temperature of approximately 55 °C. At skin temperatures, hydrated dispersions of the lipids are therefore in the gel state and rigid in nature.

COMPARISON SPC AND HSPC (14)

The different kinetics of the interaction between the native skin lipids and the fluid-state PC and/or HSPC were determined by several in vivo and in vitro penetration studies. Fluorescent labeled liposomes made from fluid-state PC penetrate significantly deeper into the rat skin than those composed of HSPC (18). The penetration of liposomes with encapsulated fluorescent dye carboxyfluorescein into the human abdomen skin studied by fluorescence microscopy showed that liposomes made from fluid-state PC compared to liposomes composed of HSPC are taken up by the skin more readily, permeate faster, and penetrate beyond the stratum corneum (19). These findings suggest that HSPC, and most probably also the accompanying water, is taken up by the stratum corneum but not by the deeper layers of the skin. In addition, HSPC does not seem to perturb the lipid barrier.

Topical formulations comprising of HSPC possess a skin protective function. They restore and stabilize the skin barrier layers. Measurement of the TEWL (transepidermal water loss) showed that formulations with HSPC do not influence the natural TEWL level. Formulations with HSPC comprise lamellar structures, which are layered on top of each other very similar to the skin structures (20).

A product which contains high concentrations of HSPC is Skin Lipid Matrix (SLM) from Lipoid Kosmetik AG **.

SPC, i.e. phosphatidylcholines with unsaturated fatty acids, form flexible liposomes which are able to penetrate more deeply into the skin compared to rigid liposomes/lamellar phases comprising of HSPC which for these reasons reside predominantly in the upper layers of the skin. SPCs are therefore more suitable as penetration enhancers / transportation vehicles enhancers to carry co-encapsulated compounds more deeply into the skin whereas formulations comprising of HSPC are more suitable to stabilize the barrier function of the skin.

Relevant parameters for the design of cosmetic formulations using both classes of phosphatidylcholines are provided in Table 3 (21).

Phospholipids are unique compounds for formulators of cosmetic products. This is owed to their multifunctional properties as a technical ingredient and cosmetic active in combination with their high degree of tolerability. The availabili-ty of these natural compounds with controlled quality in various grades and modifications provide the formulator with a valuable tool box for designing optimal cosmetic formulations.

Peter van Hoogevest is head of the scientific department at Lipoid, GmbH in Ludwigshafen, Germany. He can be con-

Table 3. Relevant characteristics of SPC and HSPC for cosmetic products

Parameter	SPC	HSPC
Fatty acid composition	Unsaturated fatty acids;	Saturated fatty acids;
	linoleic, linolenic and oleic acid	stearic and palmitic acid
Phase transition temperature (°C)	Below 0	50-60
Structures upon hydration	Liposomes and lamellar structures dependent on process conditions	Liposomes and lamellar structures dependent on process conditions
Technical Ingredient		
Emulsifier	Yes	Yes
Dispersing and solubilizing ability	Hydrophilic, amphiphilic and lipophilic compounds	Hydrophilic, amphiphilic and lipophilic compounds
Cosmetic Active		
Skin barrier function	Penetration enhancement; conditioning the SC*	Stabilizing the barrier function; conditioning the SC
	Penetrates into layers below SC	Penetrates only into SC and not below
Barrier compatibility	Yes, slightly enhancing TEWL**	Yes, stabilizing normal TEWL
Supply of linoleic and linolenic acid	Yes; beneficial effects of phospholipids containing omega-3 and omega-6 fatty acids on acne vulgaris, psoriasis, neurodermitis	No
Tolerability	Very high: CIR*** report	Very high: CIR report

* SC: Stratum corneum, ** TEWL: Transepidermal water loss, *** CIR: Cosmetic Ingredient Review

tacted at van.hoogevest@lipoid.com. Coauthors Beate Prusseit and Rudi Wajda are also at Lipoid, where Prusseit is head of marketing and Wadja is a chemist.

This article was reprinted with permission from the August 2013 issue of *SOFW Journal*, which tracks developments in the soap, detergent, perfume, personal care, and cosmetics industries.

Further reading

1. LeKim D, Betzing H (1974) Einbau von EPL-Substanz in Organe von gesunden und durch Galaktosamin geschädigten Ratten (metabolism). Drug Res 24(8):1217-1221
2. Ghyczy M, Vasata V (1999) Concept for topi-cal formulations adjusted to the structure of the skin. Chimica OGGI, Chem Today 9: 17-20
3. Fiume Z (2001) Final Report on the safety assessment of lecithin and hydrogenated lecithin. Int J Tox 20 (Suppl. 1): 21-45
4. Ghyczy M (1999) Die Hautstruktur und adä-quate Kosmetika - Beeinflussung der Permeabilitätsbarriere der Haut mittels Struktur der Kosmetika. Kosm. Med. 20(4): 192-195
5. Ghyczy M, Vasata V (2002) Phosphatidylcholine and skin hydration; Skin Moisturization, (Eds.) Leyden JJ; Rawlings AV, Marcel Dekker Inc., NY/ Basel Chapter 15:303-321

CONTINUED ON NEXT PAGE

6. Ghyczy M, Nissen HP, Biltz H (1996) The treatment of acne vulgaris by phosphatidylcholine from soybeans, with a high content of linoleic acid. J Appl Cosmetol 14: 137-145
7. Fabrizi G, Randazzo SD, Cardillo A, Tiberi L, Morganti P (1999) Safety and efficacy of lamellar phosphatidylcholine emulsion to treat mild-to-moderate inflammatory acne. SOFW-Journal 125(6): 12-14
8. Kutz G, Biehl P, Waldmann-Laue M (1997) Zur Auswahl von O/W Emulgatoren für dem Einsatz in Hautpflegeprodukte bei sensibler Haut. SOFW Journal 123: 145-149
9. Kutz G (1997) Galenische Charakterisierung ausgewählter Hautpflegeprodukte. PZ 142 (45): 11-15
10. Morck H (1993) Liposomen bei Neurodermitis und Psoriasis. PZ 128(12): 50-51
11. Lautenschläger H (2003) Starke Wirkung-Phospholipide in Kosmetika, Kosmetik International 2: 38-40
12. Ghyczy M, Gareiss J; Kovats Th (1994) Liposomes from vegetable phosphatidylcholine; Their production and effect on the skin Cosmetics &Toiletries magazine 109(7): 75-80
13. Röding J, Artmann C (1992) The fate of liposomes in animal skin. In: Liposome Dermatics, Eds: Braun-Falco O; Korting HC; Maibach HI, Springer Verlag, Heidelberg Berlin 185-194
14. Röding J (1992) Properties and characterization of preliposome systems. In: Liposome Dermatics Eds.: Braun-Falco O; Korting HC; Maibach HI, Springer Verlag, Heidelberg Berlin 110-117
15. Röding J (1990) Liposomes – Liposomen – Natipide II: new easy liposome system. SOFW Journal 14: 509-515
16. Morsy E (1992) Applied Liposomology Natipide II. F2CO 149-151
17. Ghyczy M, Albrecht M, Vacata V (2006) Phospholipids, metabolites, and skin hydration. In:Dry Skin and Moisturizers Chemistry and Functions 6, 2nd Ed Editors: Loden M; Maibach HI CRC Press Taylor & Francis Group, Boca Raton 299-308
18. Van Kuijk-Meuwissen ME, Mougin L, Junginger GE, Bouwstra JA (1998) Application of vesicles to rat skin in vivo: a confocal laser scanning microscopy study. J. Control Rel. 56: 189-196
19. Fahr A, Schäfer U, Verma DD, Blume G (2000) Skin permeation enhancement of substance by a novel type of liposomes. SOFW-Journal 126(9): 49-53
20. Lautenschläger H (2003) Starke Wirkung-Phospholipide in Kosmetika, Kosmetik International 2: 38-40
21. Lautenschläger H (2006) Liposomes. In: Cosmetics, Science and Technology, Eds. A.O. Barel AO; Payne M; Maybach HI, CRC Press Taylor & Francis Group, Boca Raton 155-163

Canola (cont. from page 181)

Can it stand in for olive oil?

Refined canola oil is favored by restaurants and consumers because of its tendency to give off very little smoke when heated, but the refining process also has the tendency to remove the savory natural flavor of the oil.

Removing particulates is what allows canola oil to achieve a high temperature without giving off excessive amounts of smoke. Conventional refining uses chemicals to remove the solids, but Madison Farm's cold-pressing process uses a centrifuge system, similar to the centrifuge systems used in refining olive oil and avocado oil (*Inform 24*:558–560, 2013). This retains the color and savory flavor of the oil while allowing it to be heated without producing a lot of smoke.

Although refined canola oil is generally used for deep-frying, the Madisons' cold-pressed version can be used in a variety of culinary applications. Madison reports that some chefs are opening up to the idea of using the canola oil in place of olive oil.

"Some of the chefs that have tried it were skeptical at first," Madison said. "The restaurants that we have given samples to have all become customers because they really notice the difference after they've had a chance to play with it."

food looking pretty, it's appealing on the plate as well," says Laura. "The lemon oil is great in cornbread and cinnamon rolls, the flavored oils really stand out in breads." A few places carry these oils already, including Bennesere Olive Oils and Vinegar, which sells in bulk in Portland; Provvista, a premier specialty foods importer and wholesale distributor in Portland; and Bellinger Farms and Gourmet Shoppe in Hermiston. The oils are hitting their mark, striking a chord with fine shops, hotels, and restaurants alike. "Our target audience is the Portland, Eugene, Seattle market, people who enjoy good quality food," says Kent. They are also sold on Family Generation Foods' website.

Pleased with the success of their canola oil, Kent and Laura are already working with other growers on potential expansions. Potatoes, Wagyu beef, and blueberries in unique refillable containers are just some of the possibilities for the future of Family Generation Foods; and expanding it will fulfill an exciting purpose. In an age where consumers are far removed from the farm, Family Generation Foods seeks to close the gap, telling Oregon agriculture's story and connecting the consumer back to the source. "It gets the story out on these farms, each of these commodities will tell their stories, and it brings agriculture back to the forefront where food and fiber comes from," says Laura. Madison Ranches has recently transitioned to their son Jake, and Family Generation Foods could become an employee-owned company someday. Yet, each will continue to fulfill the rich tradition of generational farm and ranch families that have come before them, sharing wholesome, natural food and feeding their communities and the world.

Heather Burson is a communications professional with the Agri-Business Council of Oregon.

Biodegradable lamellar systems in skin care, skin protection, and dermatology

Hans Lautenschläger

In the context of the revision of the European Cosmetic Directive, the particle size of carriers is being discussed. However, in terms of the risk assessment of biodegradable liposomes and nanoparticles, no higher standards have been set, since small intact particles will not merge into the human body even in the case of skin barrier disorders. That's why these systems, which temporarily seemed to be old hat, became attractive again overnight. The most important ingredient of these particles is the naturally occurring phosphatidylcholine (PC).

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- **There have been many reviews of publications and patents on liposomes and related nanodispersions—particularly with respect to their chemical components, various preparations, and use in skin care products.**
- **Rarely are the more general questions addressed of why these lamellar particles should be used in cosmetics, what functionalities are expected from them, and what advantages they provide compared with alternative formulations.**
- **The following review comprises background, literature and applications of biodegradable lamellar systems, their characteristics and limitations, with an emphasis on phosphatidylcholine-containing preparations such as liposomes, nanodispersions, and derma membrane structure.**

Publications and patents on liposomes and related nanodispersions, along with their different chemical components, preparations, and use in skin care products, have often been reviewed (1–6). (A complete set of references is available in this issue's Supplement—digital and mobile editions only.).The reviews do not need any additional comments. Of interest are general questions, such as why these lamellar particles should be used in cosmetics, what functionalities are expected from them, and what advantages they provide compared with alternative formulations.

The relationship of the lamellar structures of liposomes and nanodispersions with lamellar creams based on phospholipids (5) allows a smooth transition from an active agent-dominated skin care (7) to skin protection. As regards skin care, the skin barrier can be opened for the penetration of active agents and then closed again without the risk of counterproductive occlusive conditions. This specific technique is rather significant for professional treatments (8).

NATIVE PC

In looking at the horny layer, whose structure (9) protects the skin from external materials, phospholipids and PC in particular play a minor role. The lipid bilayers contain only traces of phospholipids, and the main components are free fatty acids, cholesterol, triglycerides, hydrocarbons, and ceramides. But deeper in the living part of the epidermis, PC is usually found as the most important constituent of all biological membranes, especially of plasma cell membranes. Over and above that, PC is the source of phosphocholine to transform ceramides into sphingomyelins. In this context, PC stands for living tissues, whereas the increase of ceramides in the cells means that their death by apoptosis is imminent.

PC of both human and vegetable origin shows a fatty acid composition that is dominated by unsaturated fatty acids. The fatty acid content of soy PC, which is readily available and mostly used in cosmetic formulas, is characterized by a proportion of linoleic acid up to 70% of the total fatty acids. Consequently, soy PC has a low phase-transition temperature of below 0°C in water-containing systems. This explains its ability to fluidize the lipid bilayers of the horny layer, which can be determined by measuring the increase of the transepidermal water loss (TEWL) after application for a short while. The slight increase of TEWL coincides with the penetration of PC and active agents, which are co-formulated with PC. Because of its high content of linoleic acid and penetration capability, soy PC delivers linoleic acid very effectively into the skin, resulting in anti-acne properties (10). By adhering very strongly to surfaces containing proteins such as keratin, PC shows conditioning and softening effects.

When native PC is dispersed in water, it is practically inevitable that lamellar systems such as liposomes will occur, because this is the most natural form of the material. For example, PC swollen by water transforms spontaneously into liposomes when "disturbed" by small amounts of salts or water-soluble organic compounds such as urea. In contrast, it has been known for a long time that the horny layer pretreated by PC can be penetrated much more easily by nonencapsulated materials. So liposomes are not really needed to bring out the functionalities of PC, but they are very convenient, because the handling of pure PC requires a lot of experience and sometimes patience as well.

PC is known as a penetration enhancer. This property is usually associated with liposomes. Liposomes are the vesicles said to transport cosmetic agents better into the horny layer. That is true and, moreover, the conditioning effect causes the horny layer to become a depot for these agents. Measurements of systemically active pharmaceuticals revealed that an increase of penetration is not synonymous with an increase of permeation. Actually, permeation of active agents is often slowed by PC in such a way that a high permeation peak in the beginning of the application is prevented. Instead, a more continuous permeation takes place outside the horny layer depot into the living part of the body over a longer period of time. This property makes PC and liposomes very attractive for the application of vitamins, provitamins, and other substances influencing the regenerating ability of the living epidermis.

HYDROGENATED PC

Liposomes consisting of unsaturated PC do not strengthen the natural barrier function of the skin in the short term, with the exception of its indirect effect of supporting the formation of ceramide I in the long term. Ceramide I is known for containing linoleic acid and for being one of the most important barrier-activating substances. Instead of unsaturated PC, a fully saturated PC should be selected for products designed for skin protection. Saturated PC stabilizes the normal TEWL, similar to ceramides, when the horny layer is attacked by hydrophilic or lipophilic chemicals (11–14). Saturated PC is synonymous with hydrogenated soy PC, which contains mainly stearic and palmitic acids. On the other hand, semisynthetic compounds such as dipalmitoyl-phosphatidylcholine (DPPC) and distearoyl- phosphatidylcholine are available.

The multifunctional properties of PC lead to a number of different applications. Formulations with unsaturated PC are preferred to support skin regeneration, anti-aging, acne prevention, and penetration of other active agents such as vitamins and their derivatives into the skin. Formulations with hydrogenated PC may be used for skin and sun protection. Because of their special properties, it can make sense to combine unsaturated with saturated PC in one and the same cosmetic or dermatological product (7).

LIPOSOMES

Liposomes are spherical vesicles with membranes consisting of one (unilamellar) or more (oligolamellar, multilamellar) bilayers of PC. Sometimes, especially in patents, reference is made not to liposomes but to "vesicles with an internal aqueous phase." The vesicles can differ in size (diameter about 15–3,500 nm) and shape (single and fused particles). At a given chemical composition, these parameters strongly depend on the process of preparation. Very often the preparations are metastable. That means the state of free enthalpy is not in equilibrium with the environment. As a result, the vesicles change their lamellarity, size, size distribution, and shape with time. For example, small vesicles tend to form larger ones and large vesicles smaller ones. Fortunately this is mostly not critical for quality, because the properties of the PC, on which the vesicles are based, remain unchanged as a rule. Nevertheless, the stability seems to be the best in a range of about 100–300 nm. That is the case for pure aqueous dispersions of highly enriched (80–100%) soy PC.

Once in a while it is discussed that multilamellar liposomes (multiple-shell, onion-shaped vesicles) can transport higher amounts of active agents than unilamellar ones (one-shell vesicles).

This, however, rather seems to be a pseudodiscussion since cosmetic liposomes on the whole represent a potpourri of one-shell and multiple-shell vesicles, which is due to the manufacturing process. The manufacturing of unilamellar liposomes would be far too expensive. On top of that, the number of shells (membranes) has no impact on the above-described "transport mechanism." Only the low or high dosage of the fluidizing membrane component (PC) influences the efficacy of liposomes.

In a complete formulation together with further ingredients, other influences such as compatibility, concentration of salts, amphiphilics, and lipophilics play an important role. Therefore, it is often very difficult to prove the existence of liposomes, for example, in a gel phase (15) or a creamy matrix. However, this is more a marketing problem than a problem of effectiveness of the formulation. Today, we can assume that the effectiveness of PC is based more on the total chemical composition of the cosmetic product and less on the existence or nonexistence of the added liposomes.

Of course, formulations are very effective in particular when consisting of pure liposomal dispersions bearing lipophilic additives in the membrane spheres and/or hydrophilics in the internal and external aqueous phases within the range of their bearing capacity. In this respect, there has been an intensive search to increase the encapsulation capacity of liposomes for lipids because consumers are used to applying lipid-rich formulations. Efforts were made to add emulsifier to the liposomal dispersions to stabilize higher amounts of lipids. Formulators now know that the compatibility of liposomes with regard to emulsifiers is generally limited. In contrast, additional emulsifiers have a weakening effect on the barrier affinity of PC. They cause the PC and lipids to be more easily removed from the skin while washing. In this respect there is only one rational consideration: to make use of nanodispersions consisting of PC and lipids instead of liposomes.

Liposomal dispersions have proved not only to be innovative and effective cosmetic ingredients but also to be a very convenient form to work with PC. In dermatology, they are used as such with success for preventing and treating several skin diseases.

Liposomal formulations may have a totally different functional quality. Just to mention an example: Free vitamin C (ascorbic acid) in high concentrations has the same keratolytic effect as a fruit acid and hence can scale off the cells of the horny layer. Even so, it has little impact on collagen synthesis owing to the fact that the acid remains on the skin surface. However, if low concentrations of ascorbic acid esters of phosphoric, stearic, or palmitic acid are encapsulated into liposomes (water-soluble esters) or in biodegradable nanoparticles (fat-soluble esters), the ascorbic acid can be transported to the areas where it is actually needed. The esters are far more resistant to oxidation than free ascorbic acid. The carrier bodies have the size of about 50–200 nm. After the "transport" into the skin, the esters are enzymatically hydrolyzed into substances that are identical to the natural substances of the body and, in the present case, into free ascorbic acid and phosphoric acid, stearic acid, or palmitic acid. At this point, the ascorbic acid can take full effect.

NANODISPERSIONS—BIODEGRADABLE NANOPARTICLES (5,16)

Biodegradable nanoparticles are a consequence of the observation that oil droplets can fuse with liposomes when the capacity of bilayers for lipids is exhausted (17). Further increasing the lipid/PC ratio and using high-pressure homogenizers lead to nanoparticles. Nanoparticles consist of emulsion-like oil droplets surrounded by a monolayer of PC. The advantage of nanoparticles is that they allow formulations to tolerate more lipids and remain stable. Additional emulsifiers are not needed.

Further functions of nanoparticles are the protection of the encapsulated material against oxidation or against the impact of other substances, providing a convenient application of active agents, conditioning the skin, and improving the bioavailability of active agents. Conditioning the skin implies the reaction of the capsule material with the skin barrier. Like the PC-containing membranes of liposomes, the membranes of nanoparticles analogously merge with the membranes of the skin barrier and make them more fluid and permeable. Thus, the encapsulated active agents can pass the skin barrier. The original membrane completely dissolves, and the different ingredients slowly permeate into the skin in the form of molecules.

The increased dermal bioavailability of lipophilic active agents in nanodispersions allows reducing the concentration of lipophilic active agents. Not only is this a very interesting economic aspect, it can also improve the tolerance and, as far as pharmaceutical active agents are concerned, it can reduce the side effects too.

Liquid, biodegradable nanoparticles based on PC can be used as a medium for vitamins A, E, and their esters (e.g., tocopheryl acetate and retinyl acetate). A wide range of applications are vegetable oils with their triglycerides whose acid components are long-chained and polyunsaturated (omega-3 and omega-6 fatty acids). These emulsifier-free dispersions can be applied like water; they are nongreasy, penetrate instantly, and show a high anti-inflammatory potential due to the metabolites of essential fatty acids formed in the skin (18). A typical field of application is the care of sun-damaged and atopic skin (19).

DERMA MEMBRANE STRUCTURE

An interesting field of lamellar cosmetic compositions with hydrogenated soy PC is the derma membrane structure (DMS) (20) technology (21). DMS stands for lamellar cream bases containing hydrogenated soy PC, sebum-compatible medium-chain triglycerides, phytosterols, and squalane. In addition to liposomal dispersions and nanoparticles, DMS is a third way to formulate PC with hydrophilic and lipophilic compounds free of further emulsifiers. DMS is waterproof and sweat proof and therefore suitable for skin protection and sun protection creams without using silicones or mineral oil additives. It can easily be transformed into other final products by stirring at room temperature together with liquid lipids and/or hydrophilic active agents dissolved in water.

Lamellar cream bases are appropriate formulations for skin care and also for skin protection purposes due to their chemical composition and their physical characteristics (22–24). Professional associations recommend the preparations for occupational skin protection, in particular for contact with different working substances (11) and for recovery purposes; meanwhile, skin protection and skin recovery are rated equally (12).

The washout effect of lamellar cream bases in comparison to typical oil-in-water emulsions is negligible with the result that the natural barrier structure with its characteristic conformation

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is largely maintained, a fact that is particularly important for problem skin. Hence, they are appropriate formulations for the treatment of barrier disorders. As far as supportive prevention is concerned, individual cosmetic formulations in strict accordance with the German Cosmetic Directive (KVO) can be prepared in the pharmacy. Regarding dermatological prescriptions (25–27), the German Ordinance on the Operation of Pharmacies as to the definition of additives (cream bases) and pharmaceutical active agents has to be considered (28,29). A number of active agents serve for dermatological as well as for cosmetic preparations (30); in these cases the respective regulation regarding the claims should be observed.

Topical treatments can be realized either on a modular base by preparing individual formulations or alternatively by applying finished lamellar products. In the foreground are preparations for the care of barrier, cornification, and connective tissue disorders as well as sun protection preparations. The transition of dermatological therapy to a cosmetic prevention can easily be realized.

MODULAR USE OF LAMELLAR SYSTEMS

As mentioned, DMS is predestined for skin protection, but by addition of nanoparticles and/or liposomal dispersions it can easily be enriched by unsaturated PC containing esterified linoleic acid. The resulting products are creamy, stable, and anticomedogenic. The effect of pure DMS basic creams on skin moisturizing, smoothing ,and tightening is still significant several days after finishing the application. A comparison of cosmetic and dermatological formulations based on medical indications shows that various skin disorders already can be cured by applying appropriate skin care preparations (31–33). A characteristic is the release of active agents from lamellar preparations: Liposomes with polar active agents, such as azelaic acid, help avoid high initial dosages. Vitamin A derivatives from phospholipidic nanodispersions show typical vitamin A acid effects already in low concentrations (34). Depot effects can be observed with cream, which allow time-dependent dosage reductions (35). The current state of knowledge on lamellar formulations has been reviewed (36).

The improved permeability of the skin barrier based on the use of PC-containing liposomes and nanoparticles is particularly advantageous for the application of masks. If the permeability is to be reversed after the mask, a DMS cream can be applied.

STABILITY AND LIMITS OF LAMELLAR SYSTEMS

Like linoleic esters and linoleic glycerides, liposomal dispersions based on unsaturated PC dispersions have to be stabilized by antioxidants. By thinking naturally, a complex of vitamins C and E can be used with success. In some cases PC and urea seem to stabilize each other (37,38). Moreover, agents that are able to mask traces of radical-forming ions of heavy metals, such as iron, can be added. Such additives are chelators like citrates, phosphonates, or ethylene diamine tetraacetic acid (EDTA). Alternatively, the unsaturated PC can be substituted by a saturated one such as DPPC or hydrogenated soy PC, which should be favored for its price. Because of the higher phase-transition temperature, liposomal dispersions based on hydrogenated material are more sophisticated in their preparation and are reserved for pharmacological applications as a rule.

Liposomes, nanoparticles, and DMS have to be microbiologically stabilized. This may be a problem, because PC, like lecithin, inactivates most of the conventional preservatives (39). In contrast, preservatives should not penetrate into the skin to avoid irritation and sensitization. Therefore, glycols such as propylene glycol, glycerol, butylene glycol, pentylene glycol, hexylene glycol, sorbitol, and their mixtures are the compounds of choice. In contrast to ethanol, which can also be applied up to a certain extent, these polyols show a moisturizing effect at the same time.

One of the reasons to substitute PC by polyglycerols and other synthetic derivatives at the beginning of the liposomal developments is its hydrolytic instability in aqueous preparations for longer periods of time and at higher temperatures. In fact PC, like other glycerides, is attacked by water to form lysophosphatidylcholine and free fatty acids. But the cleavage of the glyceride bond occurs mainly at a pH > 7; so formulations in the range of pH 5.5–7 are sufficiently stable for most purposes. It is possible that hydrolysis depends on the amount of additional surface-active compounds. This is another reason to use liposomal dispersions without additional emulsifiers.

Liposomes and nanoparticles based on PC are incompatible with a series of substances commonly used in cosmetic preparations. They are sensitive to emulsifiers, surfactants, and solvents above all—like the skin after dissolving the lamellar structures.

As far as encapsulating is concerned, the molecular weight of the active agents is of significance. Macromolecules such as hyaluronic acid, polysaccharides, and proteins only form physical mixtures with PC-containing carriers. These physical mixtures, however, also are beneficial owing to the above-described reactions of the carriers. With regard to skin hydration and skin smoothing, for instance, they can complement each other very well.

In addition, it has been observed that added, nonencapsulated low-molecular-weight substances also benefit from the fluidization of the skin barrier and that their dermal bioavailability increases. Even highly polar substances such as amino acids, azelaic acid, fumaric acid, and caffeine as well as hydrophilic vegetable extracts such as green tea, eyebright [*Euphrasia*], or butcher's broom [*Ruscus aculeatus*] can pass through the skin barrier.

Generally, members of the lamellar family such as liposomes, nanoparticles, and DMS are more compatible with the skin structure than usually applied conventional emulsions. "Compatible" means that formulations are physiologic, do not disturb the integrity of the skin lipid bilayers, and are not washed out when the skin is cleansed. In the sense of modern strategies of cosmetics, these formulations get by with a minimum of auxiliary compounds, which put only a strain on the skin. Moreover, compatibility means embedding lipids and hydrophilic agents in the horny layer and being in line with the natural situation.

Remarkably, PC need not be applied in high concentrations, because experience shows that formulations are physically stable at lower amounts. Also, there is a cumulative effect in the horny layer with repeated application of PC. In many cases liposomes, nanoparticles, and DMS are compatible with each other in the sense that they can be used as a modular system.

Hans Lautenschläger is managing director and shareholder of KOKO Kosmetikvertrieb GmbH & Co. KG in Leichlingen, Germany. He can be contacted at koko@dermaviduals.de.

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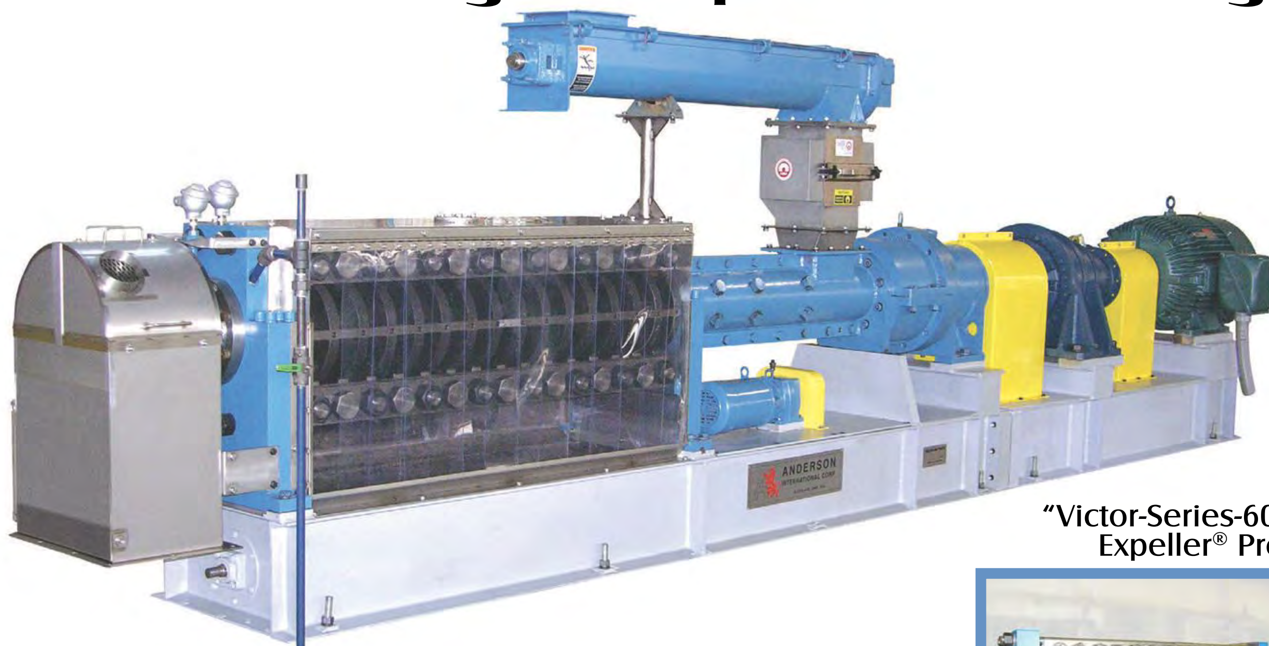

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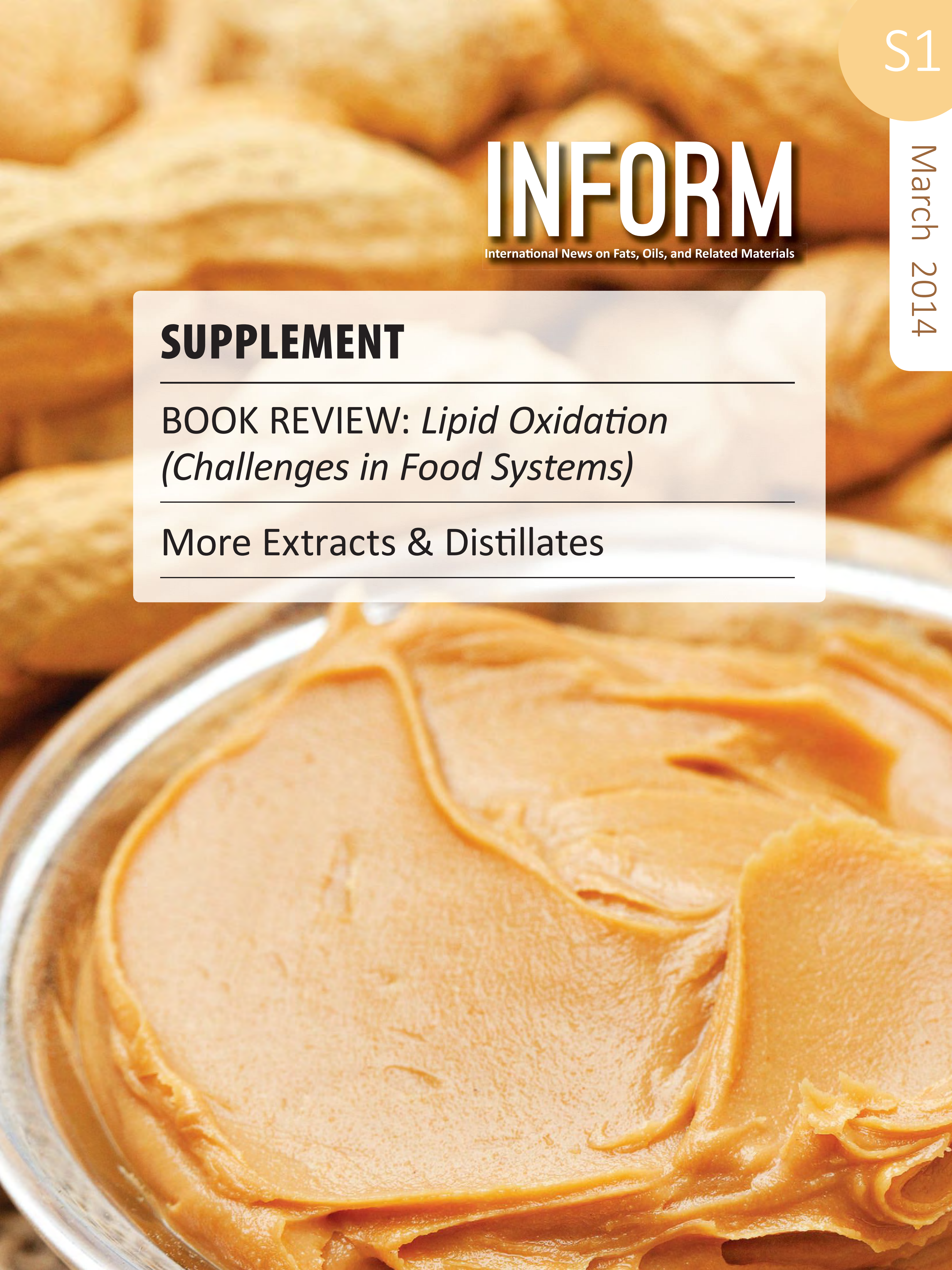

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INFORM

International News on Fats, Oils, and Related Materials

March 2014

SUPPLEMENT

BOOK REVIEW: *Lipid Oxidation (Challenges in Food Systems)*

More Extracts & Distillates

BOOK REVIEW:
LIPID OXIDATION (CHALLENGES IN FOOD SYSTEMS)

Editors: Amy Logan, Uwe Nienaber, Xiangquing (Shawn) Pan
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Review by Laurence Eyres

This 15-chapter, 500-page book with 35 editors and authors covers entirely new ground. Some of the authors are well-known and have years of experience in the field of oils and fats. However, more than a dozen new authors present fresh perspectives that are not covered in other books, published by AOCS and other publishers,that cover lipid oxidation in full. Consequently, Lipid Oxidation (Challenges in Food Systems) adds to the sum total of knowledge with new science and without much duplication. Even the book's subtitle, as one of the authors in chapter 2 points out, indicates a novel shift from the traditional focus on the oils themselves to a focus on oils within foods.

The control of lipid oxidation remains an ongoing challenge, as most foods constitute very complex matrices. Lipids are primarily incorporated as emulsions, and chemical reactions occur at various interfaces throughout the food matrix. Recently, incorporating healthful lipids into food systems is becoming a popular way for food manufacturers to deliver products with desired nutrients. Many food ingredients contain a vast array of components, some of which may be unknown or constitute diverse or undefined molecular structures. Hence, mitigating lipid oxidation in such food systems requires new approaches.

The first two chapters by Schaich cover oxidation mechanisms and also the main issues in analysing the products of lipid oxidation. I found these two chapters absorbing in their detail. The first challenge is to extract quantitatively all the lipids from the foodstuffs, whilst ensuring that the lipids that are being extracted are not oxidized in the process. It is a common problem in food analysis that the extraction is either incomplete or the technique used extracts too much non-lipid material. The use of ASE (accelerated solvent extraction) is fully discussed. The sound and comprehensive discussions in these first two chapters will assist practioners in sorting out these common issues. There is a wealth of useful information gathered in these two initial chapters, such as the difference in using nitrogen or argon for sparging oils. (Argon is more soluble in lipids and solvents than nitrogen.) Oxygen and water permeability for the plastic materials that are normally used to store samples are also listed and discussed.

One of the basic and commonly used analyses for lipid oxidation is the peroxide value. This analysis was first developed in the 1930s (Wheeler and Lea), but continues to be subject to error due to several factors listed in the chapter on analysis. Schaich proposes using a variety of approved methods to evaluate foodstuffs for oxidative status and referencing the most useful ones. This reviewer would have liked to have seen a discussion and comparison of the early benzidine method, subsequent anisidine value, and the controversy over using thibarbituric acid-reactive substances. Chapters 3-5 focus on emulsion systems which are very susceptible to oxidation. Chapter 6 examines the stability of enzymatically modified fats, a technique that has replaced hydrogenation.

Chapters 7 and 8 review the antioxidant "polar paradox," look at studies that contradict the current understanding, and introduce the concept of the "cut-off theory." Testing out patterns from volumes of confusing data is one method scientists have traditionally used to form testable hypotheses. This is what one scientist did whilst sorting through confusing and apparently contradictory data on the performance of antioxidants in various food systems. Patterns found suggested that, all other factors being equal, polar or hydrophilic antioxidants were more effective in the type of low surface-to-volume situations that occur in bulk oils. In contrast non-polar or hydrophilic antioxidants were more effective in high surface-to-volume situations such as occur in emulsions. Polar materials work best in non-polar matrices; non-polar antioxidants work best in polar systems. This is known as the "polar paradox." These authors review Rancimat results on oil blends using different antioxidant systems. Results for olive oil were interesting, comparing tyrosol with hydroxytyrosol. The stabilisation of the complex lipid systems that occur in infant formulae could be improved by applying some of the science discussed in these chapters.

Chapters 9 and 10 look at antioxidant evaluations and at assays, such as oxygen radical absorbance capacity and others, which are being used to promote antioxidants in food even though many of these analyses have no direct correlation with health benefits. These authors point out that in complex food systems, the phase distribution of antioxidants such as polyphenols with starches, proteins, and other lipids may alter the ability to neutralise radicals. This does not seem an issue when antioxidant capacity evaluations are carried out on homogenous systems such as oils. So, as they point out, it is not surprising that there is poor correlation between the antioxidant capacity of a sample using chemical reactions and the antioxidant behaviour in food or biological systems.

Chapters 11-15 discuss the important subjects of natural antioxidants, such as green tea and rosemary extracts, with a focus on their utilisation in food systems. This is extremely important, as there are global initiatives aimed at totally removing synthetic antioxidants such as *tert*-butyl hydroquinone from food due to toxicity concerns. There is an intriguing section on ergothioneine, extracted from ergot or mushrooms, in Chapter 12.

The last chapter is co-authored by the editor Dr. Amy Logan, who has been well known for her lipid work in Australasia. Her work at the CSIRO, co-authored by Dr. Peter Fagan, provides excellent insight into the stabilisation of oil-in-water emulsions and the novel use of canola-based phenolic compounds.

Few errors were found in the book. The index is adequate but not comprehensive, and a commonly used modern and innovative touch is to include the pictures and brief biographies of the authors and editors at the back of the book.

I would recommend this book as an extension to existing literature for all technical personnel in the food and natural health products industry.

Some useful references on determination of peroxide value by iodometry:

- Lea, C.H., The effect of light on the oxidation of fats, *Proc. R. Soc. Lond. B 108*:175–189 (1931). http://dx.doi.org/10.1098/rspb.1931.0030.
- Wheeler, D.H., Peroxide formation as a measure of autooxidative deterioration, *Oil Soap 9*:89–97 (1932).
- AOCS Method number Cd 8b-90: Peroxide value acetic acid–isooctane method
- AOCS Method number Cd 8-53: Peroxide value acetic acid–chloroform method

I would recommend this book as an extension to existing literature for all technical personnel in the food and natural health products industry.

Laurence Eyres is a consultant with Food Inc. in Aukland, New Zealand.

EXTRACTS & DISTILLATES

Identification of native catechin fatty acid esters in green tea (*Camellia sinensis*)

Myers, R.A., *et al.*, *J. Agric. Food Chem. 61*:11484–11493, 2013, http://dx.doi.org/10.1021/jf403620f.

Catechins are potent antioxidants and make up the primary class of polyphenols present in tea (*Camellia sinensis*). They are especially abundant in the less-fermented green teas that have been employed in various foods to enhance shelf life stability (Namal Senanayake, S.P.J., *J. Funct. Foods 5*:1529–1541, 2013; Gramza, A., and J. Korczak, *Trends Food Sci. Technol. 16*:351–358, 2005). The antioxidative activity of native (polar) catechins has proven to be useful in foods of relatively high polarity, while mixed results have been achieved in high-fat foods. However, the polarity of catechins can be attenuated by esterification with fatty acids, producing adducts that effectively partition into lipids and protect against rancidity even in high-fat foods (Cutler, S.; E. Fuller, I. Rotberg, C. Wray, M. Troung, and M.; Poss, International Patent WO 2013/036934 A1, March 14, 2013; Zhong, Y., and F.J. Shahidi, *J. Agric. Food Chem. 59*:6526–6533, 2011). In this work, a search for the presence of naturally occurring lipid-conjugated catechins was undertaken in various green tea varieties. Rather than the traditional aqueous infusion, dried tea leaves were extracted with organic solvents followed by analysis for catechin adducts with both lower polarities and increased molecular weights as monitored by liquid chromatography and tandem mass spectrometry. Native catechin palmitates were identified and indirectly confirmed by synthesis and nuclear magnetic resonance as natural components of several Chinese green teas. Evidence of other fatty catechin esters was also observed.

Online LC-GC-based analysis of minor lipids in various tree nuts and peanuts

Esche, R., *et al.*, *J. Agric. Food Chem. 61*:11636–11644, 2013. http://dx.doi.org/10.1021/jf403900q.

As information on free sterols/stanols and steryl/stanyl esters in nuts is lacking, the compositions and contents of these lipid constituents in 10 different nut types were analyzed. The applied approach was based on online liquid chromatography-gas chromatography and enabled the simultaneous analysis of free sterols/stanols and individual steryl/stanyl fatty acid esters, and additionally of tocopherols and squalene. Total contents of free sterols/stanols ranged from 0.62 mg/g nut in hazelnuts to 1.61 mg/g nut in pistachios, with sitosterol as the predominant compound. Total contents of steryl/stanyl fatty acid esters were in the range of 0.11–1.26 mg/g nut, being lowest in Brazil nuts and highest in pistachios. There were considerable differences between the various nut types not only regarding the contents but also the compositions of both classes. The levels of tocopherols were highest in pine nuts (0.33 mg/g nut); those of squalene were remarkably high in Brazil nuts (1.11 mg/g nut).

Effect of olive leaf (*Olea europea* L.) extracts on protein and lipid oxidation in cooked pork meat patties enriched with n-3 fatty acids

Botsoglou, E., *et al.*, *J. Sci. Food Agric. 94*:227–234, 2014, http://dx.doi.org/10.1002/jsfa.6236.

The effect of olive leaf extracts on lipid and protein oxidation of cooked pork patties refrigerated stored for 9 days was evaluated. Patties were prepared from *longissimus dorsi* muscle of pigs, and dietary supplemented with linseed oil. Results showed that dietary linseed oil modified the fatty acid composition of pork patties by increasing ($P \leq 0.05$) n-3 (α-linolenic acid) and decreasing ($P \leq 0.05$) n-6 (linoleic acid) fatty acids. Olive leaf extracts at supplementation levels of 200 and, especially, of 300 mg gallic acid equivalents kg^{-1} meat delayed lipid oxidation by reducing ($P \geq 0.05$) both primary (conjugated dienes and hydroperoxides) and secondary (malondialdehyde) oxidation products. They also inhibited protein oxidation in a concentration-dependent manner by reducing ($P \leq 0.05$) protein carbonyls and increasing ($P \leq 0.05$) protein sulfhydryls. In addition, they improved sensory attributes of the n-3 enriched patties.

HDL and cholesterol: life after the divorce?

Vickers, K.C., and A.T. Remaley, *J. Lipid Res. 55*: 4–12, 2014, http://dx.doi.org/10.1194/jlr.R035964

For decades, HDL and HDL-cholesterol (HDL-C) levels were viewed as synonymous, and modulation of HDL-C levels by drug therapy held great promise for the prevention and treatment of cardiovascular disease. Nevertheless, recent failures of drugs that raise HDL-C to reduce cardiovascular risk and the now greater understanding of the complexity of HDL composition and biology have prompted researchers in the field to redefine HDL. As such, the focus of HDL has now started to shift away from a cholesterol-centric view toward HDL particle number, subclasses, and other alternative metrics of HDL. Many of the recently discovered functions of HDL are, in fact, not strictly conferred by its ability to promote cholesterol flux but by the other molecules it transports, including a diverse set of proteins, small RNAs, hormones, carotenoids, vitamins, and bioactive lipids. Based on

HDL's ability to interact with almost all cells and transport and deliver fat-soluble cargo, HDL has the remarkable capacity to affect a wide variety of endocrine-like systems. In this review, we characterize HDL's unique cargo and address the functional relevance and consequences of HDL transport and delivery of non-cholesterol molecules to recipient cells and tissues.

Locating double bonds in lipids—New approaches to the use of ozonolysis

Sun, C., and J.M. Curtis, *Lipid Technol. 25*:279–282, 2013, http://dx.doi.org/10.1002/lite.201300312.

Since the location of double bonds within a lipid molecule is critical to its biological function, methods that reveal details of this structural arrangement are of importance. Ozone can react with double bonds resulting in ozonolysis products that have masses characteristic of the exact location of these double bonds within fatty acid residues. This paper describes the use of the ozonolysis reaction for the assignment of double bond positions, with a focus on the recent developments in coupling ozonolysis reactions *in-situ* and in-line with mass spectrometry, even for use with complex lipid samples.

Omega-3 fatty acids and sickle cell disease: Intriguing association and promising therapeutic effect

Daak, A.A., and K. Ghebremeskel, *Lipid Technol. 25*:275–277, 2013, http://dx.doi.org/10.1002/lite.201300308.

The therapeutic effects of omega-3 fatty acids on inflammatory disorders and cardiovascular diseases are well known. The current consensus considers sickle cell disease (SCD) as a chronic inflammatory state with significant membrane fatty acids perturbation. This new paradigm toward the pathophysiology of the disease paved the way for novel anti-inflammatory and anti-aggregatory therapeutic agents. The clinical trials that investigated the role of omega-3 fatty acid in SCD showed good evidence that omega-3 fatty acids are safe and effective treatment.

Unintended compositional changes in genetically modified (GM) crops: 20 years of research

Herman, R.A., and W.D. Price, *J. Agric. Food Chem. 61*:11695–11701, 2013, http://dx.doi.org/10.1021/jf400135r.

The compositional equivalency between genetically modified (GM) crops and nontransgenic comparators has been a fundamental component of human health safety assessment for 20 years. During this time, a large amount of information has been amassed on the compositional changes that accompany both the transgenesis process and traditional breeding methods; additionally, the genetic mechanisms behind these changes have been elucidated. After two decades, scientists are encouraged to objectively assess this body of literature and determine if sufficient scientific uncertainty still exists to continue the general requirement for these studies to support the safety assessment of transgenic crops. It is concluded that suspect unintended compositional effects that could be caused by genetic modification have not materialized on the basis of this substantial literature. Hence, compositional equivalence studies uniquely required for GM crops may no longer be justified on the basis of scientific uncertainty.

Enhancing the release of the antioxidant tocopherol from polypropylene films by incorporating the natural plasticizers lecithin, olive oil, or sunflower oil

López de Dicastillo, C., *et al., J. Agric. Food Chem. 61*:11848–11857, 2013, http://dx.doi.org/10.1021/jf404283q.

In this work, natural plasticizers-modified polypropylenes intended for food active packaging were developed. Sunflower oil, olive oil, and soy lecithin, without any known harmful effects or toxicity, were employed as natural plasticizers, also implementing the attractiveness of using synthetic plastics on active packaging developments. Their incorporation during the extrusion of polypropylene was tried as a means to obtain polymers with improved diffusion paths, allowing differences in antioxidant release rates for active packaging materials. Thermal and rheological characterization of the films showed that blending natural plasticizers does not significantly modify their thermal properties; however, small variations of viscoelastic properties were observed. Furthermore, the resulting release of tocopherol was highly dependent on the polymer formulation. Furthermore, it was clearly time controlled by using those natural plasticizers, especially olive oil. Antioxidant activity results also showed that packaged foods are protected against oxidative degradation over time, resulting from the improved release of the antioxidants.

Transgenic soybeans and soybean protein analysis: an overview

Natarajan, S., *et al., J. Agric. Food Chem. 61*:11736–11743, 2013, http://dx.doi.org/10.1021/jf402148e.

To meet the increasing global demand for soybeans for food and feed consumption, new high-yield varieties with improved quality traits are needed. To ensure the safety of the crop, it is important to determine the variation in seed proteins along with unintended changes that may occur in the crop as a result various stress stimuli, breeding, and genetic modification. Understanding

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the variation of seed proteins in the wild and cultivated soybean cultivars is useful for determining unintended protein expression in new varieties of soybeans. Proteomic technology is useful to analyze protein variation due to various stimuli. This short review discusses transgenic soybeans, different soybean proteins, and the approaches used for protein analysis. The characterization of soybean protein will be useful for researchers, nutrition professionals, and regulatory agencies dealing with soy-derived food products.

Medium-chain sugar amphiphiles: a new family of healthy vegetable oil structuring agents

Jadhav, S.R., *et al.*, *J. Agric. Food Chem. 61*:12005–12011, 2013, http://dx.doi.org/10.1021/jf401987a.

Vegetable oils are frequently structured to enhance their organoleptic and mechanical properties. This is usually achieved by increasing the net amount of saturated and/or trans fatty acids in the oil. With the risk of coronary heart diseases associated with these fatty acids, the food industry is looking for better alternatives. In this context, the medium-chain dialkanoates of low-calorie sugars (sugar alcohol dioctanoates) are investigated as a healthy alternative structuring agent. Precursors of sugar amphiphiles, being US Food and Drug Administration-approved GRAS [generally regarded as safe] materials, exhibited high cell viability at a concentration ~50 μg/mL. They readily formed nanoscale multilayered structures in an oil matrix to form a coherent network at low concentrations (1–3 wt%/vol), which immobilized a wide range of oils (canola, soybean, and grapeseed oils). The structuring efficiency of sugar amphiphiles was computed in terms of mechanical, thermal, and structural properties and found to be a function of its type and concentration.

Bioactive properties of the main triterpenes found in olives, virgin olive oil, and leaves of *Olea europaea*

Sánchez-Quesada, C., *et al.*, *J. Agric. Food Chem. 61*:12173–12182, 2013, http://dx.doi.org/10.1021/jf403154e.

Oleanolic acid, maslinic acid, uvaol, and erythrodiol are the main triterpenes present in olives, olive tree leaves, and virgin olive oil. Their concentration in virgin olive oil depends on the quality of the olive oil and the variety of the olive tree. These triterpenes are described to present different properties, such as antitumoral activity, cardioprotective activity, anti-inflammatory activity, and antioxidant protection. Olive oil triterpenes are a natural source of antioxidants that could be useful compounds for the prevention of multiple diseases related to cell oxidative damage. However, special attention has to be paid to the concentrations used, because higher concentration may lead to cytotoxic or biphasic effects. This work explores all of the bioactive properties so far described for the main triterpenes present in virgin olive oil.

Ultrahigh performance liquid chromatography analysis of volatile carbonyl compounds in virgin olive oils

Zhu, H., *et al.*, *J. Agric. Food Chem. 61*:12253–12259, 2013, http://dx.doi.org/10.1021/jf404368m.

The enzymatic and chemical oxidation reaction in olive oil produces many volatile carbonyl compounds that contribute to the complex flavor of olive oil. A novel ultrahigh performance liquid chromatography (UHPLC) method with dynamic headspace sampling and 2,4-dinitrophenylhydrazine (DNPH) derivatization were established to determine the volatile carbonyls in virgin olive oil (VOO). Quantification of nine characteristic carbonyls (acetone, hexanal, *E*-2-hexenal, octanal, *E*-2-octenal, nonanal, *E*-2-nonenal, *E,E*-2,4-nonadienal, and *E,E*-2,4-decadienal) was achieved using cyclopentanal as an internal standard. This method provides comparable linearity ($R^2 = 0.9917–1.0000$) and repeatability [less than 7.6% relative standard deviations (RSD)] with solid phase microextraction gas chromatography (SPME-GC). The %RSD of all applied carbonyl standards were lower than 7.6%. The limits of detection (LOD) and quantification (LOQ) were in the ranges of 1.6–150.1 and 4.8–906.1 μg/kg. The recoveries obtained for olive oil samples were in the range of 81.0–115.3%. To show the potential of this method on the quantification of other volatile carbonyls that were not included in this study, GC–electron ionization mass spectrometry (GC–EI/MS) was employed to identify the derivatized carbonyls [carbonyl (2,4-DNPH) hydrazones] while peak assignments were made on the basis of elution sequences and peak areas. This method provided feasibility of using LC to determine volatile carbonyls in oil matrices, which can be applied to examine the degree of lipid oxidation and evaluate the sensory properties of VOO and other edible oils.

Controlling lipid oxidation via a biomimetic iron chelating active packaging material

Tian, F., *et al.*, *J. Agric. Food Chem. 61*:12397–12404, 2013, http://dx.doi.org/10.1021/jf4041832.

Previously, a siderophore-mimetic metal chelating active packaging film was developed by grafting poly(hydroxamic acid) (PHA) from the surface of polypropylene (PP) films. The objective of the current work was to demonstrate the potential applicability of this PP-*g*-PHA film to control iron-promoted lipid oxidation in food emulsions. The iron chelating activity of this film was investigated, and the surface chemistry and color intensity of films were also analyzed after iron chelation. In comparison to the iron chelating activity in the free Fe^{3+} solution, the PP-*g*-PHA film retained approximately 50 and 30% of its activity in nitrilotriacetic acid (NTA)/Fe^{3+} and citric acid/Fe^{3+} solutions, respectively (pH 5.0), indicating a strong chelating strength for iron. The ability of PP-*g*-PHA films to control lipid oxidation was demonstrated in a model emulsion system (pH 3.0). PP-*g*-PHA films performed even better than ethylenediaminetetraacetic acid (EDTA) in preventing the formation of volatile oxidation products. The particle size and ζ potential results of emulsions indicated that PP-*g*-PHA films had no adverse effects on the stability of the emulsion system. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analysis suggested a non-migratory nature of the PP-*g*-PHA film surface. These results suggest that such biomimetic, non-migratory metal chelating active packaging films have commercial potential in protecting foods against iron-promoted lipid oxidation.

Changes of tocopherols, tocotrienols, γ-oryzanol, and γ-aminobutyric acid levels in the germinated brown rice of pigmented and nonpigmented cultivars

Ng, L-T., *et al., J. Agric. Food Chem. 61*:12604–12611, 2013, http://dx.doi.org/10.1021/jf403703t.

This study examined the changes of tocopherols (Toc), tocotrienols (T3), γ-oryzanol (GO), and γ-aminobutyric acid (GABA) contents in germinated brown rice (GBR) of pigmented and nonpigmented cultivars under different germination conditions. Results showed that the Toc and T3 contents in GBR were significantly different between treatments in both rice cultivars. The pigmented GBR possessed higher total vitamin E, total Toc, total T3, and GO contents than the nonpigmented GBR; however, its level of GABA was lower. The order of the three highest vitamin E homologs in pigmented and nonpigmented GBR was γ-T3 > γ-Toc > α-Toc and α-Toc > γ-T3 > α-T3, respectively; β-Toc, β-T3, δ-Toc, and δ-T3 were present in only small amounts (≤1.0 mg/kg) in GBR of both cultivars. Although both cultivars showed an increase in GABA contents with increasing germination time, the GABA content in nonpigmented GBR was higher.

Phytochemicals in sweet sorghum (*Dura*) and their antioxidant capabilities against lipid oxidation

Shen, X., *et al., J. Agric. Food Chem. 61*:12620–12624, 2013, http://dx.doi.org/10.1021/jf4040157.

Hydrophilic (HPE) and lipophilic (LPE) extracts were obtained from the Louisiana sweet sorghum millets. Nine major hydrophilic phytochemicals were quantified at levels of 8.9 μg/g for cinnamic acid to 1570.0 μg/g for apigeninidin. Lipophilic phytochemicals (α- and γ-tocopherol, lutein, and β-carotene) were quantified at levels of 7.7, 145.7, 4.8, and 18.8 μg/g, respectively. The total phenolic contents of HPE and LPE were 768.9 and 97.6 μg of catechin equivalent/g, respectively, while DPPH [2,2-diphenyl-1-picrylhydrazyl] activities were 6.5 and 0.8 μmol of Trolox equivalent/g for HPE and LPE, respectively. In an emulsion model, HPE exhibited higher capability of inhibiting cholesterol oxidation and stabilizing linoleic acid than LPE. Inhibition rates of cholesterol oxidation for HPE and LPE at 40 μg/mL were 92.2% and 65.4%, respectively. Retention rates of linoleic acid were 70.4% for HPE and 33.6% for LPE at a given concentration. Thus, HPE of sweet sorghum millet has potential in functional food applications.

Effect of cyclolinopeptides on the oxidative stability of flaxseed oil

Sharav, O., *et al., J. Agric. Food Chem. 62*:88–96, 2014, http://dx.doi.org/10.1021/jf4037744.

Polar compounds present in flaxseed oil increase its oxidative stability. Flaxseed oil becomes less stable to oxidation when filtered with silica. This observation may be linked to antioxidant compounds present in flaxseed oil. Flaxseed oil was passed over a silica adsorbent column to remove polar compounds. The polar compounds were then eluted from the silica absorbent using a series of increasingly polar solvents. The polar fractions from flaxseed oil were then added back to silica-treated flaxseed oil to determine the impact of fractions containing polar compounds on oxidative stability (induction time) at 100°C. A polar fraction containing mainly cyclolinopeptide A (CLA, **1**), but also containing β-/γ- and δ-tocopherol increased the induction time of silica-treated flaxseed oil from 2.36 ± 0.28 to 3.20 ± 0.41 h. When oxidative stability was determined immediately after addition of the polar fractions other flaxseed fractions and solvent controls did not affect oil stability. However, when the oxidative stability index (OSI) test was delayed for three days and oil samples were held at room temperature after the addition of the polar fractions to the flaxseed oil, it was observed that the control oil treated with silica had become highly sensitive to oxidation. A polar fraction containing a mixture of CLs (**1, 5, 7, 9, 11**) improved the oxidative stability of peptide-free oil with respect to the control when the OSI measurement was made three days after adding the fraction. In addition, effects of **1** on the oxidative stability of peptide-free oil containing divalent metal cations was investigated.

Oxidative stability of functional phytosterol-enriched dark chocolate

Borges Botelhoa, P., *et al., LWT–Food Sci. Technol.* 55:444–451, 2014, http://dx.doi.org/10.1016/j.lwt.2013.09.002.

A dark chocolate containing phytosterol (PS) esters was developed to reduce cholesterol in individuals. However, oxidative instability during chocolate processing and storage could reduce the PS bioactivity. Chocolate bars were prepared containing palm oil (CONT) or 2.2 g of PS (PHYT). All samples were stored at 20°C and 30°C during five months. A peak of hydroperoxide formation was observed after 60 days at 20°C and after 30 days at 30°C. PS-enriched samples presented higher values of hydroperoxides than

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control samples, which could be attributed to the higher level of α-linolenic acid present in the PHYT samples. All chocolate bars became lighter and softer after 90 days of storage. However, these physical changes did not reduce their sensory acceptability. In addition, PS bioactivity was kept during the storage, since no significant alterations in the PS esters were observed up to five months. However, some PS oxidation occurred in the PHYT bars, being sitostanetriol, 6-ketositosterol, 6β-hydroxycampesterol, and 7-ketocampesterol the major phytosterol oxidation products (POPs). The POPs/PS ratio was low (0.001). Therefore, the dark chocolate bars developed in this study kept their potential functionality after five months of storage at room temperature, representing an option as a functional food.

Removal and isolation of germ-rich fractions from hull-less barley using a Fitzpatrick comminuting mill and sieves

Moreau, R.A., and K.B. Hicks, *Cereal Chem. 90*:546–551, 2013, http://dx.doi.org/10.1094/CCHEM-09-12-0118-R.

A process was developed to produce a germ-enriched fraction from hull-less barley using a Fitzpatrick comminuting mill (FitzMilling) followed by sieving. Hulled and hull-less barleys contain 1.5–2.5% oil and, like wheat kernels, which contain wheat germ oil, much of the oil in barley kernels is in the germ fraction. A process that combined FitzMilling and sieving produced a germ-enriched fraction with an oil content of ≈15% and a yield of ≈1.1%. For comparison, this is higher than the levels of oil in most samples of commercial wheat germ. Experimental conditions were also described to produce a germ-enriched fraction with a higher yield (2.16%), but it would have lower oil content (10.24%). Germination and compositional analysis studies suggested that FitzMilling hull-less barley for 2 min or longer reduced germination rates to 1% or less, which was interpreted to mean that almost the entire viable germ was removed. In contrast, FitzMilling conventional hulled barley for 4 min had no effect on germination, and milling for 6 and 8 min resulted in germination rates of 36 and 12%, respectively. The oil extracted from germ-enriched fractions was rich in free phytosterols (≈1%), phytosterol esters (3–7%), and free fatty acids (2–10%). These germ-enriched fractions and the extracted oil they contain may have value as nutraceuticals or premium edible oils.

The purification of edible oils and fats

Dijkstra, A.J., *Lipid Technol. 25*:271–273, 2013, http://dx.doi.org/10.1002/lite.201300316.

Originally, oils were not refined; but with the introduction of solvent extraction, refining became necessary. Crude cottonseed oil was refined by treating the oil with caustic soda, and the same process was used for all other oils that needed refining. The subsequent introduction of centrifugal separators converted the original batch process into a continuous process. Degumming was introduced to obtain lecithin but limited to soybean oil. Physical refining was introduced for high-acidity oils such as palm oil after the oil had been degummed to low residual phosphorus levels in the dry degumming process, in which the oil is first of all treated with an acid and then with bleaching earth. In Europe, further degumming processes were developed that allowed seed oil to be physically refined, and later phospholipase enzymes were introduced to reduce oil retention by the gums and improve oil yield. Given these various oil purification processes, the refiner must decide which process to use for which oil in which circumstances. The paper provides a survey of what to do and when. It also discusses several topics that require further investigation and development.

Specific plasma lipid classes and phospholipid fatty acids indicative of dairy food consumption associate with insulin sensitivity

Nestel, P.J., *et al.*, *Am. J. Clin. Nutr. 99*:46–53, 2014, http://dx.doi.org/10.3945/ajcn.113.071712.

Reports have suggested that the consumption of dairy foods may reduce risk of type 2 diabetes on the basis of evidence of raised circulating ruminant fatty acids. We determined whether certain phospholipid species and fatty acids that are associated with full-fat dairy consumption may also be linked to diminished insulin resistance. Four variables of insulin resistance and sensitivity were defined from oral-glucose-tolerance tests in 86 overweight and obese subjects with metabolic syndrome. Plasma phospholipids, sphingolipids, and fatty acids were determined by using a lipidomic analysis and gas chromatography–mass spectrometry to provide objective markers of dairy consumption. Food records provided information on dairy products. Associations were determined by using linear regression analyses adjusted for potential confounders age, sex, systolic blood pressure, waist/hip ratio, or body mass index (BMI) and corrected for multiple comparisons. Lysophosphatidylcholine, lyso-platelet-activating factor, and several phospholipid fatty acids correlated directly with the number of servings of full-fat dairy foods. Lysophosphatidylcholine and lyso-platelet-activating factor were also associated directly with insulin sensitivity when accounting for the waist/hip ratio (Matsuda index unadjusted, $P < 0.001$ for both; adjusted for multiple comparisons, $P < 0.02$ for both) and inversely with insulin resistance (fasting insulin unadjusted, $P < 0.001$ for both; adjusted, $P = 0.04$ and $P < 0.05$, respectively; homeostasis model assessment of insulin resistance adjusted, $P = 0.04$ for both; post-glucose insulin area under the plasma insulin curve during the 120 min of the test adjusted, $P < 0.01$ for both). The substitution of BMI for the waist/hip ratio attenuated associations modestly. Phospholipid fatty acid 17:0 also tended to be associated directly with insulin sensitivity and inversely with resistance. Variables of insulin resistance were lower at higher concentrations of specific plasma phospholipids that were also indicators of full-fat dairy consumption. This trial was registered at clinicaltrials.gov as NCT00163943. ■