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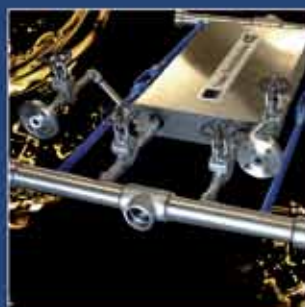
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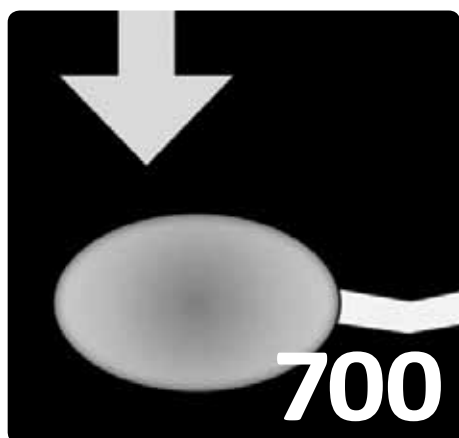


Credit: Adam Cuerden

CONTENTS

694 Surfactants and Skin

Soap is irritating, but synthetic surfactants, hydrophobically modified polymers, and other ingredients have enabled the formulation of increasingly mild cleansers.



700 Are emerging deep eutectic solvents (DES) relevant for lipase-catalyzed lipophilizations?

Learn why this new subfamily of low-transition-temperature mixtures is emerging as a serious green alternative for conventional organic solvents during chemical or enzyme-catalyzed reactions.

706 FT-NIR analysis of lecithin

Researchers describe a fully automated near-infrared method of analysis for phospholipids in fluid lecithins.

708 Organogels of vegetable oil with plant wax

Organogels made from 12 different vegetable oils and five plant waxes are compared.

DEPARTMENTS

- 693 Index to Advertisers
- 736 Classified Advertising
- 733 AOCS Meeting Watch

Briefs

- 734 News from Inform SmartBrief
- 734 AOCS Member News

Analysis/commentary

- 712 Olio
- 726 Latin America Update
- 716 Regulatory Review
- 728 Formulation Science
- 732 Statistical Analysis from Mintec

Publications and more

- 718 Patents
- 720 Extracts & Distillates
- 714 Lipid Snippets
- 717 Tips from inform|connect

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INDEX TO ADVERTISERS

Avanti Polar Lipids Inc.....	705
Crown Iron Works Company.....	C3
Desmet Ballestra Engineering NA.....	C2
GEA Westfalia Separator Group GmbH	733
Sharplex Filters (India) Pvt. Ltd.	731

Surfactants and Skin

Laura Cassiday

A popular legend traces the origins of soap to Mount Sapo near ancient Rome, where ashes and animal fats from Roman sacrifices mingled and washed into a nearby stream, helping local women get their laundry cleaner. Although this colorful account is likely fictitious, historical records indicate that soap has indeed been in use for thousands of years. But only in the past century have scientists begun to understand the molecular interactions of surfactants (the active ingredients in soap) with human skin, allowing formulators to concoct effective, yet gentle, cleansers.

- Early soaps were harsh and irritating toward the skin.
- In the past century, synthetic surfactants, hydrophobically modified polymers, and other ingredients have enabled the formulation of increasingly mild cleansers.
- This article reviews the progress that has been made and the challenges that remain.

A CLEAN HISTORY


Early soap-making involved heating animal fats or vegetable oils with a strong base, for example, lye derived from wood ashes. In a process called saponification, triglycerides from the fats are cleaved by base to release fatty acid salts (anionic surfactants) and glycerol (a byproduct). The glycerol may be removed to produce an opaque bar of soap, or retained in the formula to yield a transparent bar. Prior to the 19th century, soaps were mainly homemade or produced in small batches.

With the Industrial Revolution, new manufacturing processes enabled the production of large quantities of pure soap (Walters, R. M., *et al.*, *Cosmetics & Toiletries*, 2008). In 1879, Procter & Gamble (Cincinnati, Ohio, USA) introduced Ivory soap, a bar that contained sodium tallowate (derived from rendered beef fat) and sodium cocoate (from coconut oil) as surfactants (Fig. 1).

Early commercial soaps had a high pH (typically greater than 10) and harsh surfactants that made them potentially irritating to the skin. In the 1940s, manufacturers added glycerin to soaps in an attempt to increase mildness. However, the glycerin could not be effectively delivered to the skin, limiting its benefit as a moisturizing agent.



FIG. 1. Ivory soap advertising poster from 1898. Credit: Adam Cuerden



A major breakthrough in soap mildness came in the 1950s with the introduction of synthetic detergent (“syndet”) bars, for example, the Dove bar (Unilever; London, UK). With surfactants derived from petroleum, rather than more costly plant or animal oils, syndet bars had a neutral pH that was more compatible with human skin. In addition, synthetic surfactants such as sodium isethionate are generally milder than the harsh anionic surfactants found in soaps. In 1953, Johnson & Johnson (New Brunswick, New Jersey, USA) introduced the first liquid baby shampoo, which was formulated with synthetic nonionic surfactants designed to get babies clean without irritating their sensitive skin and eyes.

THE DIRTY TRUTH ABOUT SURFACTANTS

The purpose of cleansing is to remove dirt, oils, and other contaminants from the surface of the skin. Surfactants have a hydrophilic polar head group and a lipophilic nonpolar tail that allow them to bind oily soils and solubilize them, so that the dirt can be more easily rinsed away. Above a certain concentration, called the critical micelle concentration (CMC), surfactant monomers assemble into micelles—spherical aggregates in which the hydrophilic head groups contact the polar solvent (water), and the hydrophobic tails extend into the center of the micelle. Dirt and oils get trapped in the hydrophobic core, while the hydrophilic outer surface dissolves the soil in the wash water.

Surfactants are classified mainly by the nature of their polar head group. Cationic surfactants have a positively charged polar head group, while anionic surfactants bear a negatively charged group. Nonionic surfactants have uncharged head groups. Amphoteric surfactants have both a positive and negative charge. The hydrophobic tails of surfactants vary in length and composition, depending on the fatty acid from which they were derived. In general, anionic surfactants offer the best cleansing and foaming properties; however, they are also the harshest toward skin.

“Surfactants remove oily sebum, sweat, and dirt, which is good for the skin. They also may help in the exfoliation process,” says Kavserri Ananthapadmanabhan, senior principal research scientist at Unilever’s research and development center in Trumbull, Connecticut, USA. “But often the surfactant does not know when to stop. If the interaction goes beyond these unwanted materials and extends to skin proteins and lipids, surfactants can be detrimental to skin.”

HOW SURFACTANTS INTERACT WITH SKIN

Surfactants interact primarily with the outermost layer of the epidermis, called the stratum corneum (SC). Composed of about 10–15 layers of dead cells called corneocytes embedded in a lipid matrix, the SC is the main barrier that keeps contaminants from entering the skin and water from diffusing out (Wickett, R. R., and Visscher, M. O., <http://dx.doi.org/10.1016/j.ajic.2006.05.295>, 2006). Corneocytes form when skin cells called keratinocytes in deeper layers of the epidermis lose their nucleus and cytoplasm. During this transformation, the cells release lipids into the extracellular space. The permeable cell membrane of the keratinocyte gets replaced by a tough cell envelope made of cross-linked protein with covalently attached lipids. Within corneocytes, keratin filaments aggregate to form microfibrils, which align parallel to the skin surface and structurally reinforce the corneocytes. Natural moisturizing factor (NMF), a complex of lactate, amino acids, and amino acid derivatives, binds water within corneocytes to help maintain proper SC hydration. Each day, an average of one layer of corneocytes is shed from the skin’s surface and replaced by a new layer of keratinocytes from below the SC.

Once dismissed as merely a layer of dead cells, the SC is now recognized as a highly ordered, biochemically active component of the epidermis. The SC is commonly described as having a “brick and mortar” structure, with flattened corneocytes embedded in a lipid matrix. Enzymes in the lower SC process lipids to form a matrix of approximately 50% cerami-

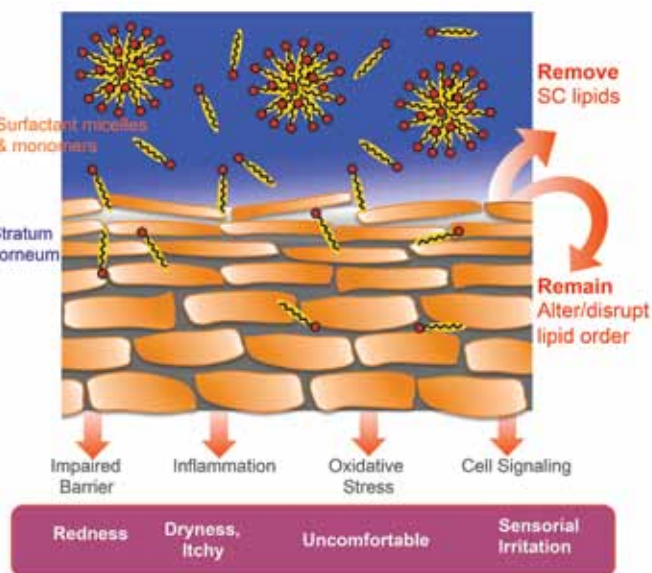
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des, 25% cholesterol, 15% free fatty acids, and 10% cholesterol esters (Ananthapadmanabhan, K. P., *et al.*, <http://dx.doi.org/10.1111/ics.12042>, 2013). Between corneocytes, lipids spontaneously organize into multiple bilayers, which interact with lipids attached to the envelopes of corneocytes. In deeper layers of the SC, lipids are densely packed into what is known as an orthorhombic phase, which acts as a tight barrier to liquid transport. Closer to the surface, the lipids form a looser hexagonal phase that allows more liquid to pass through.

Surfactants can interact with proteins and lipids in the SC, causing the barrier to break down. Redness (erythema), irritation, dryness, and itching may ensue. Early studies focused on the interaction of surfactants with proteins. Surfactants can bind nonspecifically to SC proteins such as keratin, causing the proteins to swell (Ananthapadmanabhan, K. P., *et al.*, <http://dx.doi.org/10.1111/j.1396-0296.2004.0451002.x>, 2004). As a result, excess water enters the corneocytes—a condition known as hyperhydration. After cleansing, the water rapidly evaporates, leading to drying stresses that may cause structural damage to the SC. Five to ten minutes after washing, this rapid water loss may cause the consumer to feel after-wash tightness in their skin. Surfactants can also remove NMF and denature enzymes involved in lipid modification, further affecting the structure and composition of the SC.

In recent years, the potential of surfactants to damage lipid components of the SC has been increasingly recognized (Fig. 2).

FIG. 2. Mechanisms by which surfactants can disrupt lipids in the stratum corneum. Credit: Russell Walters



Just as surfactants can extract and solubilize oils from the surface of the skin, they may also remove lipids from the SC when the surfactant is present at concentrations at or above the CMC. For example, a 2% solution of sodium lauryl sulfate (SLS) can remove up to 7% of the total lipid content in the SC within 20 minutes (reviewed in Ananthapadmanabhan, K. P., *et al.*, <http://dx.doi.org/10.1111/ics.12042>, 2013). Among SC lipids, fatty acids appear to be the most susceptible to removal. Lipid extraction (also known as delipidation) can cause corneocytes to clump,

leading to the shedding of large flakes of dry skin rather than individual cells.

In addition to delipidation, surfactants can damage SC lipids by intercalating into the lipid bilayers and disrupting their structure. Some studies suggest that this undesirable effect of surfactants occurs earlier and is longer-lasting than either protein damage or lipid extraction. Breaching of the SC barrier by surfactants causes cells in the epidermis to release inflammatory cytokines such as IL-1 α and TNF- α . These cytokines may signal the epidermis to become inflamed and hyperproliferate, resulting in an abnormal SC structure with flaking or cracking. Cracks in the skin allow surfactants to penetrate farther into living layers of the epidermis, increasing irritation.

Russel Walters, a research fellow at Johnson & Johnson Consumer Companies in Skillman, New Jersey, USA, and his colleagues recently examined the distribution of sodium dodecyl sulfate, a harsh anionic surfactant, in human skin by confocal Raman and infrared microspectroscopy (Saad, P., *et al.*, <http://dx.doi.org/10.1111/j.1468-2494.2011.00678.x>, 2012; Mao, G., *et al.*, <http://dx.doi.org/10.1007/s11095-012-0748-y>, 2012). The researchers exposed excised skin samples to a 40 mM SDS solution—a concentration similar to that found in personal care cleansers. In the SC, SDS accumulated to a concentration of up to 1000 mM, whereas in the dermis, the SDS concentration reached only 32 mM. This result demonstrates the vital barrier function provided by the SC. The intercalated SDS increased the amount of SC lipids in the hexagonal phase compared with the orthorhombic phase, loosening the structure of the lipid “mortar.” As a result, transepidermal water loss (TEWL) increased following SDS treatment. The disruption to SC lipids increased with increasing time and temperature. In contrast, SDS had little or no effect on keratin protein structure in the SC.

OCCUPATIONAL HAZARDS

Surfactant-induced skin irritation is a particular concern for people in professions that require extensive hand washing, such as health care. To minimize the spread of infection, health care workers are required to wash their hands before and after patient contact. However, compliance rates are only 30–61%, primarily because of skin irritation (Visscher, M. O., and Wickett, R. R., <http://dx.doi.org/10.1111/j.1468-2494.2012.00733.x>, 2012). In one study, 55% of inpatient nurses and 65% of intensive care nurses had observable hand dermatitis (inflammation and redness of the skin).

In addition, genetic factors may make some people more susceptible to surfactant-induced irritation. Fifty percent of people with atopic dermatitis, or chronic eczema, have a loss-of-function mutation in the filaggrin gene, which encodes a protein that helps keratin microfibrils assemble. Individuals with a G-to-A polymorphism within the promoter region (position -308) of the TNF- α gene, which apparently increases production of the inflammatory cytokine, experience more skin irritation than those with the wild-type G allele. On the other hand, people with the IL-1 α -889T polymorphism produce less of cytokine IL- α and, correspondingly, have lower levels of occupational dermatitis than those with a C at position 889.

“There’s tremendous variability among individuals in skin response to surfactants,” says Randall Wickett, emeritus profes-

sor of pharmaceuticals and cosmetics science at the University of Cincinnati, in Ohio, USA. In 2010, Wickett and his colleagues investigated the influence of the TNF- α polymorphism-308 on irritant contact dermatitis in health care workers (Davis, J. A., *et al*, <http://dx.doi.org/10.1111/j.1600-0536.2010.01778.x>). The study included 68 nurses and respiratory therapists in a newborn intensive care unit. The participants worked 2–3 consecutive 12-hour shifts within a 2-week period and washed their hands at least 20 times in an 8-hour period.

When the researchers analyzed the genotypes of the nurses, they found that 42 had the wild-type TNF- α -308G polymorphism (GG genotype), whereas 26 nurses had either one or two copies of TNF- α -308A (GA/AA genotypes). Wickett and his colleagues examined erythema (redness) on the hands of the workers at the beginning and end of their work shifts, as well as after their time off from work. The researchers found that the GG genotype recovers from skin irritation more quickly during time off than the GA/AA genotypes. In addition, the GA/AA genotypes experienced more erythema and TEWL when upper arm skin was exposed repetitively to a 0.1% SLS solution in a patch test.

NOT JUST CLEANSERS

Matthew Zirwas, a dermatologist and associate professor at Ohio State University, in Columbus, Ohio, USA, says that he sees a lot of skin issues caused by surfactants, and personal care cleansers are not the only culprits. Some patients with rashes suspect allergies to laundry detergents, but in most cases not enough residual allergens, such as fragrances, remain in clothing to cause a reaction. “Almost no one is allergic to laundry detergent,” says Zirwas. “However, in many instances there is enough residual surfactant in clothing that people can wear the clothing, and then if they sweat a little bit, the surfactant can transfer onto the skin and cause irritation.”

In one test, 100 g of cotton fabric retained 125 mg of laundry detergent after a cold-water rinse (reviewed in Crawford, C., and Zirwas, M. J., *Skinmed*, 2014). The amount of residual detergent left in clothes depends on factors such as the wash water temperature, the number of rinses, the fabric, the washing machine, and the amount of detergent added. Researchers have estimated that 2.5% of detergent remains on fabric for a wash that consumes 60 L of water and has an intermediate spin cycle between the first and second rinse.

“Although we don’t have any good statistics, it seems like skin irritation from residual laundry detergent has become more common in recent years because of the shift toward energy- and water-conserving washing protocols,” says Zirwas. Cold-water rinses, combined with the lower water usage of many modern washing machines, leave more residual surfactant in clothing.

GENTLE YET EFFECTIVE

Whether the surfactant-containing product is a personal care cleanser or laundry detergent, the formulator’s challenge is to minimize skin irritancy while maintaining an effective, aesthetically pleasing product. Initial efforts focused on lowering pH. With a pH closer to the SC value of pH 5.5, syndet bars are typi-

cally less damaging to skin than alkaline soaps. In one study, a single wash with a soap bar raised the pH of the SC to about 7.5, whereas washing with a syndet bar did not have this effect (Wickett, R. R., and Visscher, M. O., <http://dx.doi.org/10.1016/j.ajic.2006.05.295>, 2006). The slightly acidic pH of the SC helps prevent colonization of the skin by pathogenic bacteria. Disruption of this so-called “acid mantle” may alter the skin microbiome.

For many years, scientists believed that only surfactant monomers could penetrate skin and were, therefore, the only species that need be considered. The “surfactant monomer skin penetration model” was based on the observation that, in general, skin irritation correlates with the CMC of the surfactant. In other words, surfactants with a high CMC are likely to have more free monomer, and they are also more likely to irritate skin. Surfactant micelles were thought to be too large to penetrate skin.

The surfactant monomer skin penetration model drove efforts to develop surfactant systems with lower CMCs. However, in recent years problems with this model have surfaced (Walters, R. M., *et al*, <http://dx.doi.org/10.1155/2012/495917>, 2012). For example, even at surfactant concentrations above the CMC, skin irritation increases with increasing surfactant concentration. Moreover, typical exposure levels of surfactants in personal care products are two or three orders of magnitude above the CMC, so that only around 0.1% of surfactant exists as monomers. Also, some research suggests that SDS micelles can penetrate skin through aqueous pores.

Formulators now recognize that both surfactant monomers and micelles contribute to the irritancy of surfactants. Even if micelles do not enter the SC, they are highly dynamic structures that undergo rapid exchanges with monomers in solution. “Surfactant that was recently in a micelle can rapidly become a monomer and get into the skin as a monomer,” says Walters. “Micelles will fall apart and reform in tenths of a second.”

Anionic surfactants, although very effective, generally cause more skin irritation than other surfactant classes because of their potential to damage SC proteins. “In the mid-1980s and early 1990s, scientists realized that adding amphoteric surfactants at about 20–30% of the concentration of the anionic surfactant can significantly reduce protein damage and irritation of cleansing surfactants,” says Ananthapadmanabhan. As a result, most modern cleansers contain blends of anionic surfactants, such as sodium laureth sulfate, with amphoteric co-surfactants, for example, cocamidopropyl betaine.

According to Walters, all of the surfactants in a cleanser assemble together into mixed micelles. Adding an amphoteric or nonionic surfactant lowers the charge density, and thereby stabilizes, micelles of anionic surfactants. Because the mixed micelles are less likely to fall apart, less surfactant monomer is able to enter the SC and damage lipids and proteins.

Another approach to stabilizing surfactant micelles is to add certain polymers to the formulation, such as hydrophobically modified polymers (HMPs). HMPs have multiple hydrophobic groups that bind to surfactants at their hydrophobic tails. Through these contacts, HMPs stabilize the micelle core and increase its size. HMPs can also improve foaming by stabilizing the air-water interface of bubbles.

CONTINUED ON NEXT PAGE

Walters and his colleagues compared the tolerability and efficacy of a foaming liquid facial cleanser containing HMPs with a nonfoaming cleanser in 40 women with sensitive skin (Draelos, Z., *et al.*, <http://dx.doi.org/10.1111/jocd.12061>, 2013). Both cleansers were marketed as being gentle, with blends of amphoteric and nonionic surfactants. The study participants used the cleansers daily for 3 weeks, and then they answered questions about the cleanser, and their skin condition was evaluated by a dermatologist. Both cleansers were effective at cleaning skin, including removing makeup, and both were well tolerated by the women. However, the cleanser containing HMPs caused less irritation and erythema. In addition to increasing mildness, the HMPs increased lathering—a cleansing attribute preferred by most consumers.

Another type of polymer, polyethylene oxide, has been used for decades to increase the mildness of baby shampoo. Compared with adult skin, the SC in baby skin is thinner and much more vulnerable to irritation (Walters, R. M. *et al.*, *Cosmetics & Toiletries*, 2008). As a result, baby shampoos typically contain lower total surfactant concentrations, and they utilize blends of amphoteric and nonionic surfactants, rather than the anionic and amphoteric surfactants commonly used in adult shampoos (Table 1).

PEG-80 sorbitan laurate, used in Johnson's Baby Shampoo, is a nonionic surfactant and polyethylene oxide polymer that forms mixed micelles about twice the size of those present in a typical adult shampoo. "Each micelle has about three of these polymers," says Walters. "The hydrophobic domain anchors the polymer in the micelle, and the PEG chains sort of reach across the surface. This makes the micelle more stable." As a result, the baby shampoo is much milder and less irritating than adult shampoo, but it foams less than half as much.

Although adding amphoteric surfactants to anionic surfactants generally improves mildness, there are exceptions. "In some cases, surfactants that are milder to proteins are harsher to lipids," says Ananthapadmanabhan. "For example, nonionic

and amphoteric surfactants are generally harsher to lipids than to proteins." Anionic surfactants are known to bind and damage proteins; however, amphoteric and nonionic surfactants can better solubilize SC lipids such as stearic acid (Ananthapadmanabhan, K. P. *et al.*, <http://dx.doi.org/10.1111/j.1396-0296.2004.0451002.x>, 2004). As a result, formulators must consider the potential of a surfactant to damage both SC protein and lipids.

In a recent study, Ananthapadmanabhan and his colleagues used two *in vitro* assays to compare the protein-damage and lipid-extraction potentials of several surfactants (*Cosmet. Dermatol.*, 2009). The Zein protein solubility test measures the ability of surfactants to denature and solubilize a model protein from corn. This test is commonly used to gauge the skin irritation potential of surfactants. The second *in vitro* test, a lipid extraction assay, measures the ability of surfactants to solubilize stearic acid.

In one experiment, the researchers tested a blend of an anionic surfactant, sodium laureth sulfate, with an amphoteric surfactant, cocamidopropyl betaine (Fig. 3).

As expected, the protein damage potential of the surfactant blend decreased with an increasing proportion of amphoteric surfactant. However, the lipid damage potential increased as more amphoteric surfactant was included. The lipid-damage potential of various surfactants correlated with *in vivo* clinical dryness experienced by volunteers in a forearm controlled application test. Therefore, when formulating a new body wash, the researchers chose a primary surfactant (sodium cocyl isethionate; SCI) that caused minimal damage to both proteins and lipids.

In the same study, Ananthapadmanabhan and his colleagues found that the addition of C16 and C18 fatty acids to the SCI-based body wash reduced both protein and lipid damage in the *in vitro* tests. The fatty-acid-containing body wash also caused less skin dryness and TEWL in human volunteers.

TABLE 1. Typical formulations for adult shampoo and baby cleanser

Ingredient	Function	Adult Level (% w/w active)	Baby Level (% w/w active)	Examples
Surfactants				
Anionic	Provide detergency and foaming	5.0–15.0	0.0–4.0	Sodium laureth sulfate, disodium laureth sulfosuccinat
Amphoteric	Improve mildness, foaming, detergency	0.0–5.0	2.0–5.0	Cocamidopropyl betaine, disodium lauroamphodiacetate
Nonionic	Improve mildness; solubilize hydrophobic	0.0–2.0	2.5–7.5	PEG-80 sorbitan laurate, polysorbate 20, decyl glucoside
Other				
Thickeners	Build viscosity; modify rheology	0.0–2.0	0.1–2.0	PEG-150 distearate acrylates copolymer
Preservatives	Prevent microbial contamination	0.05–1.0	0.05–1.0	Methylparaben, quaternium-15
Conditioning polymers	Condition hair/skin; enhance aesthetics	0.0–0.5	0.0–0.5	Polyquaternium-7 or -10
Humectants/emollients	Enhance moisturization and skin feel	0.0–10.0	0.0–10.0	Glycerin, glyceryl oleate, di-PPG-2 myreth-10 adipate
Fragrance, dyes/opacifiers	Modify scent, appearance, consumer appeal	0.0–3.0	0.0–1.0	Fragrances, Yellow 10, Orange 4 glycol distearate

Adapted from Walters, R. M., Fevola, M. J., LiBrizzi, J. J., and Martin, K. (2008) "Designing cleansers for the unique needs of baby skin." *Cosmetics & Toiletries* 123: 53–60.

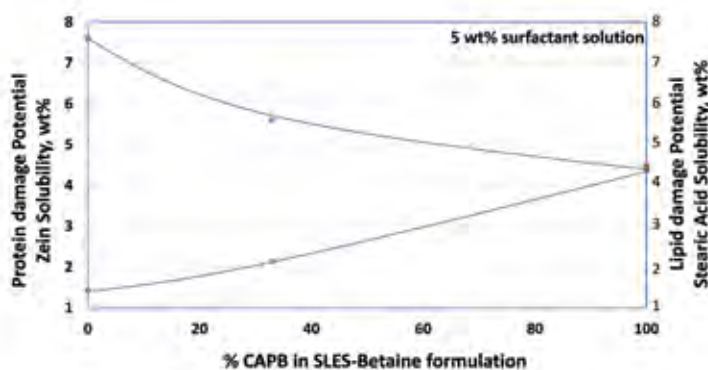


FIG. 3. Lipid vs. protein damage for an anionic/surfactant blend Credit: Adapted from Ananthapadmanabhan, K. P., *et al.*, *Cosmet. Dermatol.* 22: 307–316 (2009).

The researchers think that the fatty acids may presaturate surfactant micelles to help prevent lipid extraction (in other words, act as “sacrificial lipids”), or they may replenish lipids extracted during cleansing. Stearic acid deposited by the cleanser penetrated 10 layers into the SC and replaced a quantity of fatty acid similar to that removed during a typical wash (Ananthapadmanabhan, K. P., <http://dx.doi.org/10.1111/ics.12042>, 2013).

Other additives can also help prevent or repair damage caused by surfactants. Petrolatum forms an occlusive barrier on skin, reducing water evaporation. Liquid triglyceride oils, such as sunflower or soybean oil, can penetrate cracks in skin and moisturize to deeper layers. In addition, triglyceride oils may bind to SC proteins and protect them from surfactant-induced damage. Glycerol is a humectant that can help skin retain moisture, but because of its high water solubility, deposition and retention on the skin are challenging.

Cleansers have come a long way since the days of boiling animal fat with ashes to produce a foul-smelling, skin-irritating slurry. Formulators now have an increasingly sophisticated toolbox of surfactants, polymers, and other additives to produce milder soaps without sacrificing effectiveness or aesthetics. Yet much remains to be learned about the structure and function of the SC, the nonliving yet incredibly complex barrier that helps keep surfactants and other contaminants from contacting living cells. Such knowledge will undoubtedly aid the development of even milder cleansers for those who still struggle with surfactant-induced irritation.

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Are emerging deep eutectic solvents (DES) relevant for lipase-catalyzed lipophilizations?

Erwann Durand, Jérôme Lecomte, and Pierre Villeneuve

- Ionic liquids (IL) were among the first low-transition-temperature mixtures (LTTM) to be considered as potential “green” substitutes for conventional organic solvents during chemical or enzyme-catalyzed reactions.
- Although IL are non-volatile, thermally stable, and able to solubilize a wide range of molecules, their complex preparation is very expensive and their implementation beyond laboratory scale is rather poor. The non-toxicity put forward to justify their use has also been questioned.
- More recently, a new subfamily of LTTM called “deep eutectic solvents (DES)” is emerging as a serious alternative that offers more realistic and economical features. This article looks at recent studies of lipase-catalyzed reactions in DES, and reviews strengths and weaknesses of this medium.

The majority of solvents emerging from the green chemistry concept are almost exclusively composed of at least two molecules. The unique common property of these new multimolecular-based solvents is their low-transition-temperature (solid-liquid) compared to that of their constituents. These new green media are formed by the association of two or more components that can self-associate through intermolecular interactions (mainly Van der Waals interactions, hydrogen bonding, or ionic forces) to form a mixture with a solid-liquid transition temperature significantly lower than that of each individual component. That is why they are called “low-transition-temperature mixtures (LTTM).” The two most widespread subfamilies of LTTM are deep eutectic solvents (DES) and ionic liquids (IL).

IL are multi-component liquid salts that differ from the molten salts because their melting point is below 100 °C (arbitrarily set in reference to the boiling point of water), but a large number of them are liquid at about 25 °C. IL are constituted of a cation (usually organic) combined with an organic or inorganic anion. The cations are quaternary phosphoniums or ammonium salts (tetraalkylammoniums, tetraalkylphosphoniums, alkylpyridiniums, triazoliums, pyrrolidiniums, or imidazoliums). These are generally large, asymmetric, and may be functionalized with amines, alcohols, ethers, carboxylic acids, esters, thiols, vinyls, allyls, alkynes, or nitriles. The anions may be organic or inorganic with different sizes, electronegativities, or polarizabilities. Thus, the huge choice of combinations anions/cations (>106) offers the possibility to adjust the physicochemical characteristics of the medium. Consequently, IL are capable of dissolving a wide range of organic and inorganic compounds with very different polarities.



Their application as reaction solvents has many advantages due to their wide range of thermal and chemical stability, high conductivity (0.01 to 1.5 S/m), non-volatility (decomposition temperature typically over 300 °C), and non-flammability. Nevertheless, the use of IL as reaction media for chemical or enzymatic synthesis faces many problems. Their controversial ecotoxicological data and environmental safety (Ranke, *et al.*, 2004; Stolte, *et al.*, 2006), associated with their high costs, difficult synthesis, and tedious purification, considerably limit their implementation on an industrial scale. Consequently, the widespread use of IL is deeply affected by economic and environmental imperatives, and we believe that the use of such solvents is currently only realistic for low productions of specific and very high-value molecules.

As researchers attempt to overcome IL's drawbacks while maintaining their advantages, the use of DES is now rapidly emerging in the literature. These solvents were initially described by Abbott and co-workers as any mixture characterized by a significant ("deep") decrease in the melting point compared to its individual counterpart (Abbott, *et al.*, 2004, 2003). Most of these mixtures are actually obtained by mixing an ammonium or phosphonium salt with a hydrogen-bond donor such as acids, amides, amines, and alcohols, among others. The flexibility to choose the components offers numerous opportunities to prepare DES (Kareem, *et al.*, 2010).

DES display many advantages over IL, including a low price and a very easy preparation without any purification steps (DES are simply prepared by mixing the components). Most DES are also biodegradable (Durand, Lecomte, Villeneuve, 2013). Thus, the number of publications dedicated to their use has considerably increased in many fields of research, such as metal recovery, gas purification, catalysis, chemical fixation of CO₂ (Li, *et al.*, 2008; Su, *et al.*, 2009), extraction of phytochemicals from plant material (Dai, *et al.*, 2013; Nam, *et al.*, 2015) and green solvents for biocatalysis (Alemán, *et al.*, 2015; Durand, *et al.*, 2012; Durand, Lecomte, Baréa, 2013; Gorke, *et al.*, 2008; Lindberg, *et al.*, 2010; Maugeri *et al.*, 2013; Zhao, *et al.*, 2011, 2013).

Recently, the term Natural Deep Eutectic Solvents (NADES) was introduced in literature as a new subfamily of LTTM, to label any mixture combining molecules abundantly present in the cellular constituents, such as primary metabolites. (Choi, *et al.*, 2011). In the article, "Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology?" Choi, *et al.* (2011), postulated that although the specific role and presence of NADES in living cells are still under investigation, NADES may be an alternative medium to water and lipids, which would explain numerous biological processes such as biosynthesis or storage of various non-water soluble metabolites and macromolecules.

LIPOPHILIZATION REACTIONS

Lipophilization refers to a strategy in which the hydrophilicity/lipophilicity balance of a selected hydrophilic bioactive molecule is adjusted by a covalent linking with a lipophilic domain. These reactions are mainly aimed at lowering the polarity of the hydrophilic molecule, and many examples of lipophilization are now found in the literature. This linking can be onto a sugar, an amino acid, a protein, a water soluble

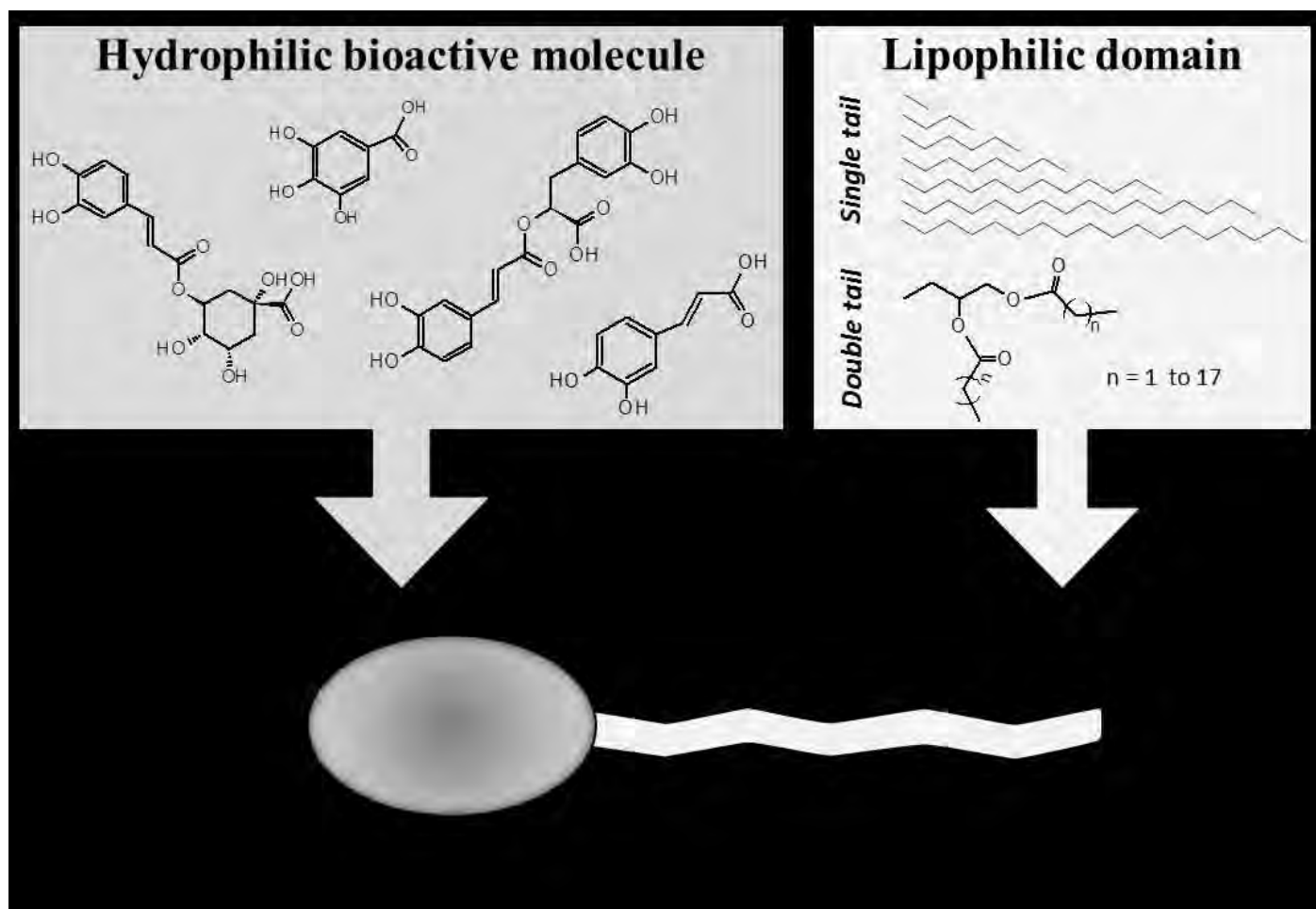


FIG. 1. General strategy for phenolipid conception

vitamin, or alternatively a (poly)phenol. Among them, phenolic acids represent a large and diverse group of secondary metabolites that are naturally widespread in the plant kingdom and of particular interest. Indeed, these products are known for their potential protective role against oxidative damage, and their action as natural antioxidants in various foods, cosmetics, or pharmaceutical systems was already proved (Huang and Cai, 2009; Soobrattee, *et al.*, 2005; Vanden Berghe, 2012).

Most of the phenolic acids express their functional properties in a hydrophilic environment, resulting in a few efficient and advanced applications in formulated-lipid dispersions. Thus, a practical approach to implement these compounds in such formulations is to increase their hydrophobicity. In that sense, lipophilization reactions are particularly advantageous and effective, and may be seen as a vectorization key unlocking the lipid barrier encountered by the bioactive molecule while maintaining its original functional properties. In the case of phenolic acids, the methods commonly used consist of attaching to the reactive carboxyl group, either a single- or double-tail lipophilic domain (usually an aliphatic with a different carbon backbone). This results in a new molecule with emulsifying properties and often greatly improved antioxidant activity (Durand, *et al.*, 2015; Laguerre, *et al.*, 2010). This reaction can be performed on simple phenolic acids derived from benzoic acid (hydroxybenzoic

acids), cinnamic (hydroxycinnamic acids), or more complex polyphenolic acids such as chlorogenic acid and rosmarinic acid with single or double tail (Fig. 1). Lipophilization of the phenolic antioxidants can be carried out chemically or enzymatically. Chemical strategies are rarely used because of the instability of these molecules at high temperatures and alkaline environments.

Concomitantly, the enzymatic alternative (using lipase as biocatalyst) has many advantages: milder reaction conditions, selectivity, reduction of by-products, and fewer purification steps. It also allows more environmentally friendly processes to be implemented. One of the main difficulties in realizing such lipase-catalyzed lipophilizations is optimizing the synthesis (in terms of yield and kinetics) with two substrates of different polarities. Therefore, it is essential to select a medium in which the two substrates will be soluble—at least partially—and where the activity/stability of the enzyme can be maintained at a satisfactory level. In nonpolar solvents such as hexane (where lipases generally maintain good activity), hydrophilic phenolics have very low solubility. Inversely, in polar organic media, the phenolic compounds have good solubility but the lipases often have limited activity. Thus, there is a technical dilemma in choosing an effective system in which a polar substrate (such as a. phenolic) and a nonpolar one (a long chain alcohol, for example) will have both high solubility and where the enzymes main-

tain a good activity (Figuerola-Espinoza and Villeneuve, 2005). Nevertheless, there are some reports dealing with esterification of phenolic acids with fatty alcohols in organic solvents, solvent-free conditions (the role of which was ensured by the excess of alcohol), or in IL (Pang, *et al.*, 2013; Weitkamp, *et al.*, 2006; Yang, *et al.*, 2012).

These studies indicate that the lipase-catalyzed reactions in organic solvents are preferable and that a binary mixture of solvents is the best solution to achieve this kind of reaction, as this allows both the solubility of the substrates and the lipase's activity/stability to be fine-tuned. On the other hand, these enzymatic reactions are often limited in performance and have extremely long reaction times. In addition, it was often observed that the use of a significant amount of biocatalyst and very high alcohol to phenolics molar ratios may cause poor mass transfer and difficulties in the separation and purification of the final products.

LIPASE-CATALYZED LIPOPHILIZATION IN DES

Few studies have looked at the use of DES for biocatalysis reactions relative to other applications, likely because use of the strong hydrogen-bond donors forming such mixtures (such as urea) is well known to denature proteins.

Some studies have shown that DES could be used. DES' potential as promising co-solvent in biocatalysis reactions was observed in the ring-opening reactions of 1R, 2R-trans-2-methylstyrene oxide into its corresponding vicinal diol, using potato epoxide hydrolase (StEH1) (Lindberg, *et al.*, 2010), where the DES as co-solvent significantly increased the K_m (up to 20 times) of the enzyme. In addition, the DES made it possible to solubilize 1.5 times more substrate than the reference solution (sodium phosphate buffer 0.1 M). Among the DES tested, cholinium chloride:glycerol (ChCl:Gly) appeared to be the most effective to increase regio-selectivity while preserving enzyme activity.

Similar results were observed with the conversion of the epoxy-styrene using EHAD1 epoxide hydrolase (Gorke, *et al.*, 2008) where the conversion, only 4.6% in the buffer solution, was increased to 92% with 25% (v/v) addition of ChCl:Gly. Interestingly, a similar addition of organic solvents (DMSO or acetonitrile) did not provoke significant improvement, suggesting that the effect was not simply due to the increased solubility of substrates, but related to the inherent properties of the DES. Moreover, it has been observed that the efficiency of proteases-catalyzed reactions (subtilisin and α -chymotrypsin) in ChCl:Gly have an activity and selectivity that depends on the water content of the mixture (Zhao *et al.*, 2011). Thus, a small amount of water (about 5% v/v) may increase the enzymatic activity while decreasing the selectivity. The positive effect of low water content in DES was also detected for peptide synthesis using protease as biocatalyst (Maugeri, *et al.*, 2013). Finally, 10% to 25% (v/v) addition of ChCl:Gly in acetate buffer allowed to significantly improve (up

to 3 times) the esterase activity for the hydrolysis of p-nitro-phenyl acetate (Gorke and Kazlauskas, 2009).

Regarding the lipase-catalyzed reactions in such solvents, the first works were carried out in 2008 by the team of R.J. Kazlauskas (Gorke, *et al.*, 2008; Gorke and Kazlauskas, 2009). These preliminary studies investigated the potential of several lipases to catalyze the transesterification of ethyl valerate with butanol in some DES. Among them, lipase B from *Candida antarctica* showed the highest activity, and the best bioconversions were obtained in ChCl:Gly and ChCl:urea. In addition, the best results observed in DES based on glycerol or urea, were five times higher than those observed in IL (BMIM[BF₄] or BMIM[Tf₂N]), but similar to those observed in toluene.

Interestingly, unexpected good lipase stability in DES was observed, despite the presence of denaturing substance, with a superior stability to those observed in the aqueous solutions of the individual component. Indeed, a 75% loss of activity was detected after only 90 min in an aqueous solution of urea, while it was almost negligible (1%) in the DES based on the same urea as component.

This surprising stability is actually explained by the strong hydrogen-bond network within the DES, which lowers the diffusion of the constituents to the protein core. The DES forms hydrogen bonds with the surface residues of the enzyme which, instead of denaturation, may stabilize the tertiary structure of the enzyme (Monhemi, *et al.*, 2014; Wu, *et al.*, 2014). This is also the reason why a very low reactivity of DES' counterparts is often observed.

Later, Zhao *et al.* (Zhao, *et al.*, 2013) confirmed the potential of DES as an alternative medium to organic solvents or IL for biotransformation catalyzed by lipases. They showed that DES made with cholinium chloride and glycerol (ChCl:Gly) could be used as green solvent for biodiesel preparation by enzymatic transesterification. A screening of different lipases has shown that the best activity (assessed by soybean oil methanolysis) was, once again, obtained with the immobilized lipase B from *Candida antarctica* (iCALB). They also confirmed the remarkable stability of iCALB in a DES based on cholinium acetate and glycerol (ChOAc:Gly), with a residual activity maintained at 92% and 50% after 48 h and 168 h.

Finally, Borse, *et al.* were able to accomplish with success a multi-component synthesis of a series of novel pyrimidin-edione- and pyrimidinetriones-based compounds using the *Rhizopus Oryzae* lipase, with reaction yields between 73% and 95% in only 6 h (Borse, *et al.*, 2013). Also, the influence of the DES has proven to be beneficial and critical to the reaction since lower yields were obtained using other reaction media such as water, methanol, dioxane, or DMF. Concomitantly, our group has been interested in conceiving the first lipase-catalyzed lipophilization in DES.

We firstly conducted preliminary studies to evaluate the best experimental conditions before initiating any investigation for such complex and sensitive biocatalysis reaction. In a first study (Durand, *et al.*, 2012) we showed that the nature of the constituents, namely the salt and the hydrogen-bond

donor (HBD), could strongly influence the physicochemical properties of the DES and the resulting biocatalytic activities. For example, by changing the nature of the salt in combination with glycerol as HBD, the performance in the alcoholysis reactions of vinyl laurate with alcohols of different alkyl chain lengths were deeply affected. The same observation may be drawn by changing the nature of the HBD in association with the cholinium chloride (ChCl) as salt.

Moreover, we observed and confirmed that some DES could react and compete with the substrates in the lipase-catalyzed reactions leading to the formation of undesirable by-products, which may be a serious weakness to their development. Among the different DES tested, ChCl:U and ChCl:Gly have clearly shown the best results since they allowed excellent bioconversions with minor influence of the polarity of the nucleophilic substrate, and with no apparent reactivity of their constituents. While providing a hopeful step forward, all the results collected from the literature so far, were performed with substrates that had little affinity with the DES. Thus, one of the evident difficulty would be the realization of lipase-catalyzed reactions with substrate(s) highly disposed to create strong interactions (mostly hydrogen bonding) with the DES' matrix.

It was previously noticed that the very low reactivity of constituents was due to the strong and well-organized non-covalent intermolecular bonds established in such mixture. Thus, as far as the lipase-catalyzed lipophilizations, the challenge faced by this study is two-fold: The reactivity of hydrophilic substrate (such as phenolics) locks up in DES and lipase-catalyzed reactions with substrates of two different polarities.

In a recent work (Durand, Lecomte, Baréa, 2013), our group highlighted the necessity to add significant quantities of water to promote lipase-catalyzed lipophilization (with 1-octanol) of phenolic compounds (coumaric and ferulic acids) in DES (ChCl:U and ChCl:Gly). For example, very high conversion rates were achieved in ChCl:U with water contents of 8% and 10% (w/w), respectively 93% and 98%. As observed in previous studies, a clear catalytic superiority of iCALB in ChCl:U compared to ChCl:Gly was obtained.

In addition, these studies have revealed that the very low lipase activity/stability in the neat or weakly hydrated DES for such complex experiments could be explained by both the strong association of the substrate into the DES' matrix and the very low thermodynamic water activity ($a_w < 0.02$). Significant enhancement in lipase initial activity (67 times faster in ChCl:U) was observed when a_w was increased up to 0.15. Also, water in DES significantly preserved the enzyme catalytic activity over the time. Regarding the pH values in the DES-water binary mixture, the gradual addition of water did not cause a significant variation but the acidic or basic state of the DES depends on the nature of the HBD. The secondary role played by the pH in lipase's catalytic activity was confirmed by the drastic differences obtained between DES based on HBD of similar chemical nature displaying similar pH values.

Finally, in a recent study our team went to investigate the structure and supramolecular organization of these solvents in order to understand how the different components (quaternary ammonium salt, HBD, water and substrates) involved in these mixtures could contribute to their functional properties and affect the lipase activity/stability (Durand, *et al.*, 2014).

This work, carried out with the greatest DES to promote lipase-catalyzed reactions (ChCl:U), provided interesting information on the availability of water to contribute to the functional properties in the environment (hydrolysis activity, hydration of the enzyme). The existence of two thermodynamically different areas that determine the influence and effect of the water was demonstrated. Thus, for a water to ChCl molar ratio below 1.75, water will interact mainly with the salt (ChCl) through very strong intermolecular bonds. Its availability will be such that it can marginally participate in the competitive hydrolysis reactions or properly intervene in the hydration state of the enzyme. However, for a water to ChCl molar ratio above 1.75, the probability of water to participate in its various activities will be greatly increased. Similarly, we have demonstrated that urea and the nucleophilic substrate could have a positive effect on reducing hydrolysis yields. The first reduced a_w , the second acted as a co-solvent to protect the product against the reactivity of water. These experiments provided substantive clarifications to finely adjust the conditions to favor lipase-catalyzed lipophilizations in DES. Thus, given the difficulties encountered when performing such biotransformations, it was possible to synthesize with high yields, a full range of lipophilic derivatives of ferulic and coumaric acids from C4 to C16 (aliphatic chain).

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FT-NIR analysis of lecithin

Lloyd Cooper and Tony Ainscough

Lecithin is a natural substance found in fatty animal tissue and plant tissues. It is composed of phosphoric acid, choline, fatty acids, glycerol, glycolipids, triglycerides, and phospholipids such as phosphatidylcholine (PC), phosphatidylethanolamine (PE), and phosphatidylinositol (PI), with minor amounts of phosphatidic acid (PA), phosphatidylserine (PS), and corresponding lysophosphatidyl derivatives (LPC, LPE, LPI, and LPS).

This article describes a fully automated near-infrared (NIR) method of analysis that:

- requires no sample preparation;
- provides accurate quantification for a number of target components within a sample;
- is inexpensive, non-destructive, and gives instant results.

Lecithin is commonly used as an additive in foods, cosmetics, and pharmaceutical products. Its composition is largely dependent on the lecithin source and its degree of purification. Due to the difficulty and expense of obtaining lecithin PC and PE and other fractions of adequate purity, it is important to develop rapid and effective analytical methods for the purpose of quality control.

CURRENT METHODS OF ANALYSIS

There are currently two AOCS approved methods for the determination of lecithin phospholipids by high-performance liquid chromatography (HPLC)—one for HPLC (Ja 7b-91), and one for HPLC coupled to a light-scattering mass detector (Ja 7c-07). These HPLC methods make it possible to separate different classes of lipids and individual compounds within a certain class. They are applicable to oil-containing lecithins, deoiled lecithins, and lecithin fractions, but not to LPC and LPE. A more accurate approach to separating these derivatives is phosphorus-31 nuclear magnetic resonance (NMR) spectroscopy which has become a recognized reference method for many lecithin manufacturers. Unfortunately, high set-up and running costs preclude its day to day use in most QA and QC laboratories.

FT-NIR BACKGROUND AND THEORY

Fourier Transform-Near Infrared (FT-NIR) makes use of molecular vibrations typically in the 800–2,000nm range. In the case of a Fourier Transform instrument, these vibrations are expressed as $12,800\text{--}3,800\text{cm}^{-1}$. Characteristic absorption bands appear in this region as a result of molecules containing the following bonds: N-H, O-H, and C-H. These absorptions are in fact overtones and combination bands of the fundamental mid-infrared absorptions.

NIR absorptions tend to generate broad overlapping peaks which make it difficult to determine specific regions for individual molecules. Attempting to apply basic Beer-Lambert Law to calculate the concentration of an individual component for anything other than a basic two- or three-component matrix is not usually possible. This problem is addressed by the use of multivariate analysis (typically Partial Least Squares, or PLS) and the building of calibration models.

NIR spectroscopy is inexpensive, quick, and non-destructive for quality control and screening and has largely replaced a number of wet-chemical-analysis methods. The technique can also be adapted using fiber optics for online applications where real-time process control data is required. FT-NIR spectroscopy does not require any sample preparation and therefore decreases costs by reducing time and reagent use. Furthermore, the FT-NIR is capable of identifying all major phospholipids and lysophosphatidyl derivatives. The instrument is portable and much more affordable than HPLC and NMR machines. It also has the benefit of being able to measure further useful parameters such as moisture content and acid value of the sample.

Attention must be paid when developing the calibration model. NIR precision and accuracy are highly dependent on the representability of the calibration samples, the quality of the reference methods, and the statistical tools used to develop the prediction model.

For the NIR calibrations used in our collection of data, an independent NMR laboratory was used to provide the reference data from multiple process samples.

A Tango FT-NIR (manufactured by Bruker Optics) was used to collect the NIR spectral data. The spectrometer configuration consisted of an extended indium gallium arsenide (InGaAs) detector in combination with a tungsten halogen lamp and quartz beam splitter.

For the feasibility study, a calibration set consisting of 74 samples was used. The samples were run in a temperature-controlled sample compartment at 40 °C (± 1 °C) for approximately 30 seconds at 8cm⁻¹ resolution in transmission.

For convenience, 8mm disposable glass vials were chosen for presenting the samples to the instrument. All components were measured simultaneously, giving a phospholipid profile in approximately 30 seconds.

MODEL DEVELOPMENT

PLS regression was used to develop calibration models from the NIR data. The first step of the process was to associate the reference values for the analyte of interest with their respective NIR data. From reference analysis, we had access to 9 parameters: four phospholipids, four lysophospholipids, and a final parameter that measured the sum of the combined phospholipids in each sample. A cross-validation-type modelling approach was adopted. The modelling software made it possible to try several iterations of pre-processing and wavelength selection to find the best models for each parameter.

Figures 1 and 2 are two examples of the cross-validation graphs that are produced from the software. Outlier points are shown in red on the graphs.

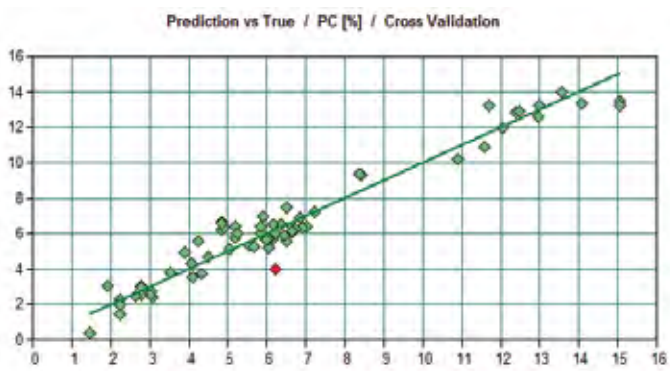


FIG. 1. Cross-validation graph for PC

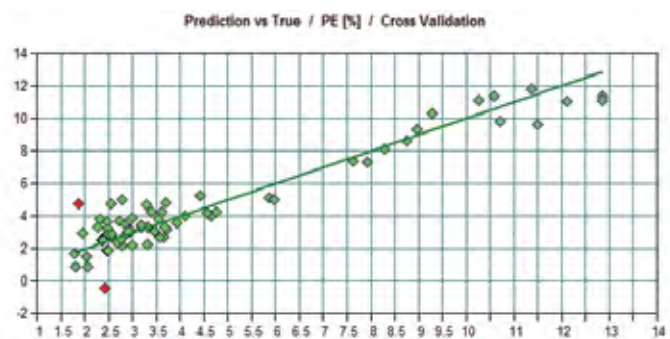


FIG. 2. Cross-validation graph for PE

A study of the available calibration statistics such as the R² and RMSECV (root mean square error of cross validation) can give a strong indication as to the usefulness of the calibration (Table 1). Here, the consequence of iterative sample removal is estimated by the calibration curve. This study reveals that FT-NIR is a valid analytical approach for phospholipids in fluid lecithins.

Component	R ² Value	RMSECV Value
LPA	0.895	0.171
LPC	0.918	0.549
LPE	0.900	0.342
LPI	0.790	0.287
PA	0.943	0.471
PC	0.943	0.814
PE	0.903	0.955
PI	0.769	0.606
SUM	0.962	1.24

TABLE 1. R² values and RMSECV values for all components. The closer the R² value is to 1, the greater the linear relationship.

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Organogels of vegetable oil with plant wax

Hong-Sik Hwang

Solid fats are widely used to provide a desired texture in structured food products such as margarine and spreads. The hydrogenation process can produce solid fats from vegetable oils that are liquid at room temperature, and partially hydrogenated vegetable oil has been a common ingredient in food products. However, trans fats generated during partial hydrogenation are known to increase the risk of coronary heart disease by raising the level of bad cholesterol (low-density lipoprotein, LDL) and lowering the level of good cholesterol (high-density lipoprotein, HDL). Consequently, the US Food and Drug Administration (FDA) has declared that partially hydrogenated oils will no longer be considered “Generally Recognized as Safe” (GRAS) and that food companies must phase out their use by 2018.

- A very small amount (0.3%, wt.) of sunflower wax in soybean oil can form an organogel.
- An organogel prepared with 2% sunflower in soybean oil can produce margarine with a similar firmness to that of a commercial spread.
- Relatively firm margarines can also be produced from sunflower wax organogels prepared with 12 other healthful vegetable oils.

PLANT WAX AS ORGANOGELATOR

Palm oil, coconut oil, fully hydrogenated vegetable oils, and their modified oils have become the most popular alternatives to trans fats in the food industry. However, these alternatives contain high contents of saturated fats.

Structuring edible oil with an organogelator has become an important research strategy for replacing trans fats without increasing the amount of saturated fats (Marangoni, 2012). An organogel, also called oleogel, is a class of gel made of a liquid organic phase immobilized by a three-dimensional network formed by an organogelator.

Although many types of organogelators have been developed, plant waxes such as candelilla wax (CW), rice bran wax (BRW), sunflower wax (SW), and carnauba wax are of great interest due to their availability, low cost, and great gelling ability. Some plant waxes have demonstrated potential health benefits. For example, when rats were fed with diets containing up to 1% SW, their serum cholesterol levels were lowered. It was also found that gelation of oil with an organogelator can control the release of lipids into the blood which, in turn, attenuates the post-prandial increases in triglycerides, free fatty acids, and insulin levels induced by the acute ingestion of fat. Therefore, one can expect multiple health benefits from food products that have been structured using organogels.

In addition, most plant waxes are by-products. For example, SW is produced during the refining of sunflower oil. Therefore, developing food products containing wax-based organogels facilitates the use of these agricultural by-products.

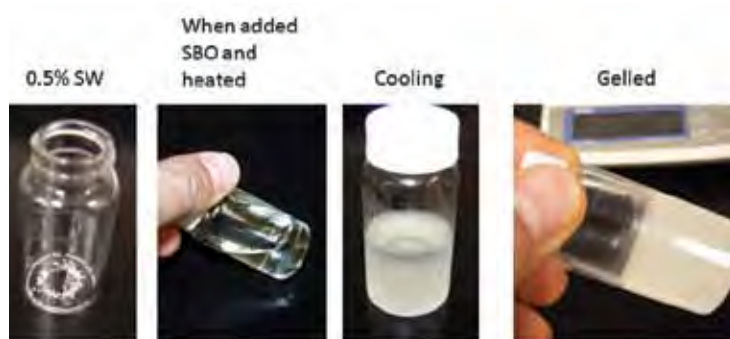


FIG. 1. Organogel formation from 0.5% sunflower wax (SW) in soybean oil (SBO) by dissolving SW with heat and cooling

GELATION ABILITY OF PLANT WAXES

Sunflower wax (SW) can make a gel with concentrations as low as 0.3 wt%. Candelilla wax and rice bran wax can also form gels at concentrations of 0.5–1 wt%. In comparison, partially hydrogenated soybean oil containing trans fats needed a minimum concentration of 18 wt% to form a gel. This indicates that only a small amount of wax may be used in place of a large amount of hydrogenated vegetable oil to achieve a similar texture. Fig. 1 shows the preparation of the organogel of 0.5% SW in SBO.

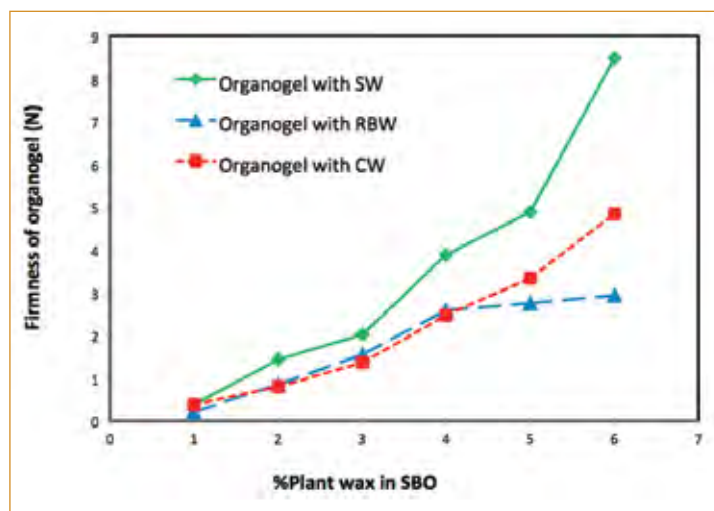


FIG. 2. Firmness (Newton, N) of organogels prepared with plant waxes

Fig. 2 shows how the firmness of organogel depends on the amount of wax. Three waxes, SW, RBW, and CW were compared. As expected, organogel firmness increased with an increasing amount of wax. SW showed the greatest firmness, followed by CW and then RBW. The organogel containing 3% SW showed greater firmness than the gel containing about 20% hydrogenated soybean oil. The excellent gelling property of SW and the high firmness of the organogel were explained by the effective way in which the oil was immobilized with networks of numerous thin plate-like crystals (Hwang *et al.*, 2015).

PREPARATION OF MARGARINE FROM ORGANOGE

A wax-SBO organogel was incorporated in a margarine formulation comprised of 80% organogel, about 20% water phase, and several minor ingredients such as emulsifiers and salt. Unfortunately, margarines containing CW showed phase separation. RBW-containing margarines showed very low firmnesses as shown in Fig. 3. Margarines prepared with SW-organogel showed the most promising results. It was found that while the firmness of commercial spread products ranged from 0.14–0.57 N, the hard margarine products showed much higher firmness ranging from 16.7–20.2 N. These results indicate that about 2% SW may be used in margarine to achieve the firmness of a commercial spread product. Firmness of the hard margarine could be achieved with 10% SW.

Fig. 4. shows the comparison between margarines prepared with SW and those with hydrogenated soybean oil. Margarines with 18–30% hydrogenated soybean oil showed slightly higher firmness than margarines with 2–6% SW. This result indicates that in terms of hardness characteristics, about 2–6 % SW may replace 18–30 % hydrogenated soybean oil in a margarine formulation.

OTHER VEGETABLE OILS

Since SW-SBO organogels worked well in the margarine formulation, a variety of healthy vegetable oils were evaluated to see whether they also could provide margarines with reasonable firmness and other properties. Fig. 5 shows the firmnesses of margarines prepared with 3% SW and 12 other vegetable oils. Their firmnesses were found to be comparable to that of SBO margarine, indicating that a number of healthful margarine and spread products can be made from vegetable oils rich in polyunsaturated fatty acids using SW as an organogelator.

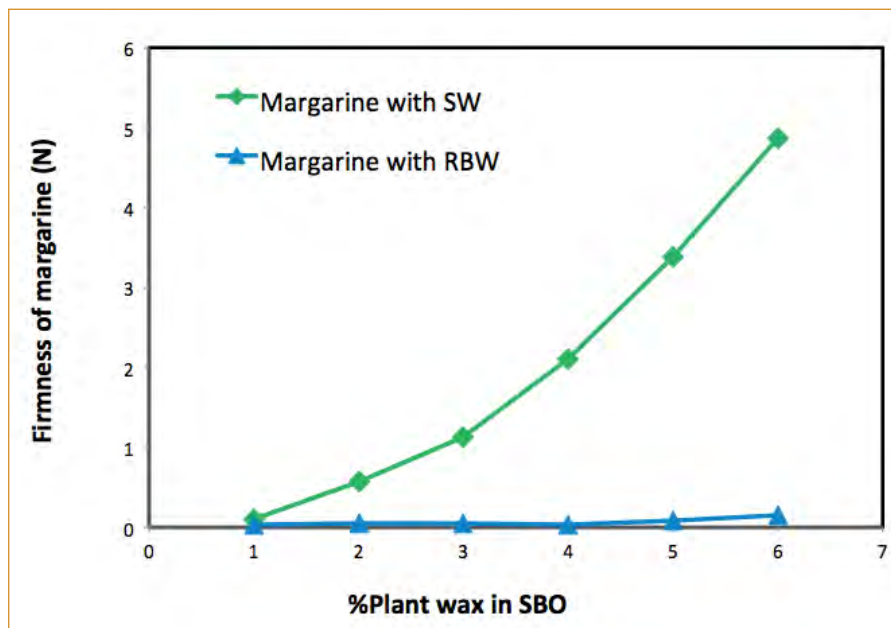


FIG. 3. Firmness (Newton, N) of margarine prepared with plant waxes

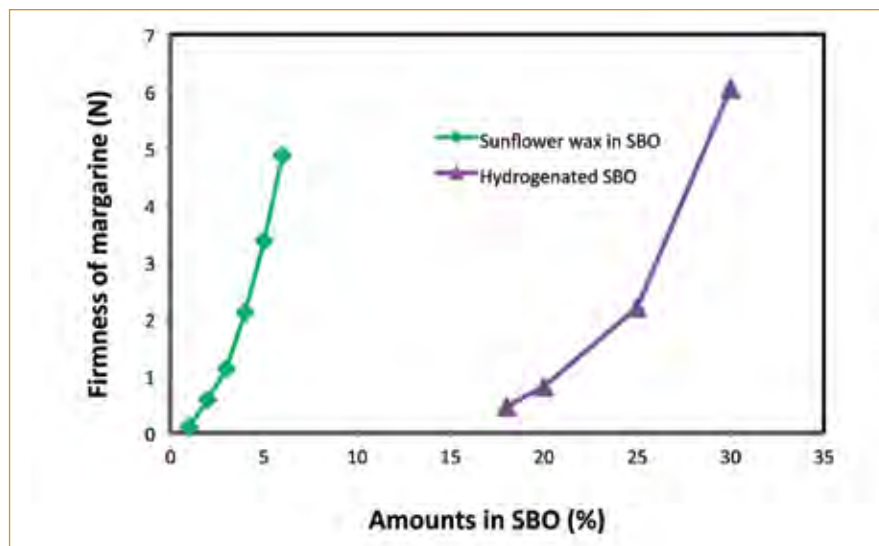


FIG. 4. Comparison of firmnesses (Newton, N) of margarines prepared with sunflower wax and hydrogenated soybean oil

SENSORY ATTRIBUTES

Yilmaz, *et al.* (2015) studied sensory attributes of organogels of 5% beeswax in virgin olive oil and 5% SW in virgin olive oil as spreadable products compared to commercial breakfast margarine. Oleogels of hazelnut oil containing 5% wax were also evaluated as butter alternatives compared with commercial butter. This study provided data on 13 sensory definition terms (hardness, spreadability, liquefaction, grassy, milky, rancid, fatty, sweet, salty, waxy, grittiness, cooling, and mouth coating) for these organogels. Consumers gave these organogels good scores with respect to hedonic attributes (appearance, odor, flavor, and spreadability). Although some scores were somewhat lower than commercial products, overall these organogels demonstrated high potential as spreads or butter alternatives and could likely be commercialized after making minor improvements in their color, aroma and taste.

Other food products with high commercial potential that have been prepared from organogels of vegetable oils include ice cream, cookies, meat, bread, and chocolate.

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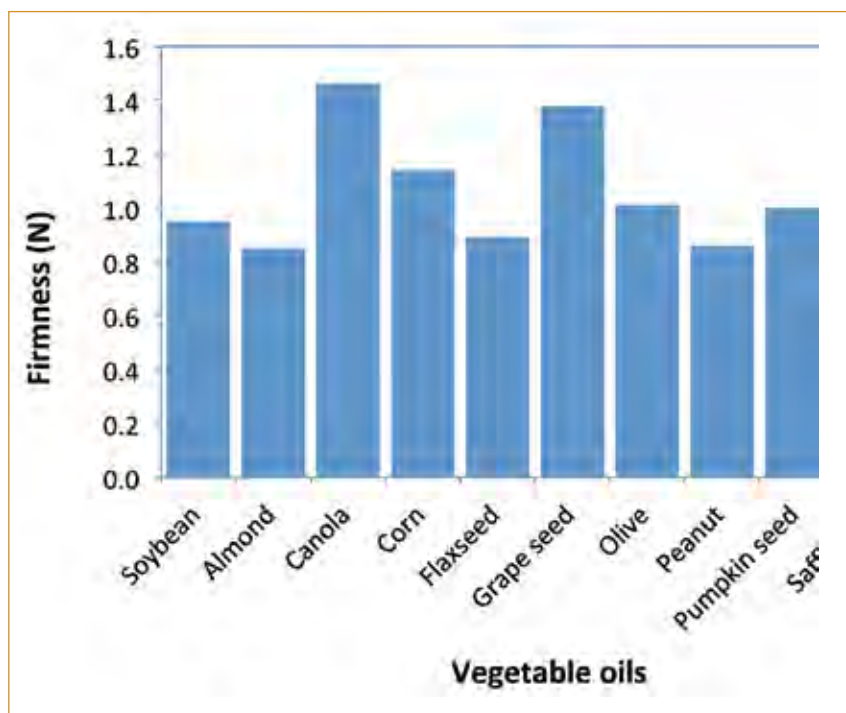


FIG. 5. Firmnesses (Newton, N) of margarines prepared with 3% sunflower wax (SW) in a variety of vegetable oils

Recommended reading

Micha, R. and D. Mozaffarian, Saturated fat and cardiometabolic risk factors, coronary heart disease, stroke, and diabetes: A fresh look at the evidence, *Lipids* 45: 893–905 (2010).

Marangoni, A. G., Organogels: An alternative edible oil-structuring method, *J. Am. Oil Chem. Soc.* 89: 749–80 (2012).

Hwang, H.-S., S. Kim, K.O. Evans, C. Koga, and Y. Lee, Morphology and networks of sunflower wax crystals in soybean oil organogel, *Food Struct.* 5: 10–20 (2015).

Yilmaz, E. and M. Ogutcu, Oleogels as spreadable fat and butter alternatives: Sensory description and consumer perception, *RSC Adv.* 5: 50259–50267 (2015).

Solazyme's first edible algal oils

Laura Cassiday

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

Solazyme, a renewable oils and bioproducts company based in South San Francisco, California, USA, has started selling its first edible oils to food companies and consumers. Founded in 2003, Solazyme's initial focus was using microalgae to produce biofuels. Then, in 2011 the company launched its Algenist line of luxury skin care products. In the second half of 2015, Solazyme's foray into the edible oil and food ingredients market has demonstrated the versatility of the company's microalgae-based platform for producing oil profiles tailored to customer needs.

Solazyme's proprietary technology uses microalgae to transform low-cost plant-based sugars into high-value oils. For their edible oils, Solazyme researchers genetically modified microalgae with plant traits to make the algae produce oils higher in monounsaturated fats and lower in saturated fats. The microalgae are grown in large indoor fermentation tanks, using sugarcane-based sucrose as a feedstock. After just a few days, the algae are pressed to release the oil, with the same method used for seed oils. The oil is then refined and bottled. For food companies, Solazyme offers two different algae oils in their AlgaWise™

Platform, both Generally Recognized as Safe (GRAS) by the US Food & Drug Administration. The AlgaWise High Stability Algae Oil contains at least 87% omega-9 monounsaturated fatty acids (oleic acid), less than 9% saturated fatty acids, and 2% polyunsaturated fatty acids (omega-3 and -6)—the lowest level of polyunsaturated fat on the market. In a frying test, AlgaWise High Stability Algae Oil had a longer frying life, produced fewer secondary oxidation products, and had reduced foaming compared with high-oleic canola oil, which Solazyme's attributes to the very low levels of polyunsaturated fatty acids in the algal oil. The taste of potatoes fried in the algal oil was indistinguishable from those fried in vegetable oil.

The high stability of the oil enables increased shelf life and eliminates or reduces the need for preservatives. "The High Stability Algae Oil offers a new solution for

products that currently use partially hydrogenated oils or preservatives such as EDTA," says Mark Brooks, senior vice president of Solazyme Food & Ingredients. Solazyme recently began selling its AlgaWise High Stability oil to Rosa Labs (Los Angeles, California, USA) for use as an ingredient in the food company's new meal replacement drink, Soylent 2.0. The bottled drink has a 1-year shelf life and does not require refrigeration. On September 9, 2015, Rosa Labs began shipping its first presales of Soylent 2.0.

Solazyme's other AlgaWise oil, Ultra Omega-9 Algae Oil, contains at least 90% monounsaturated fat, less than 4% saturated fatty acids, and 3% polyunsaturated fatty acids. "The extremely low level of saturated fatty acids can help enable a zero saturated fat label claim in applications such as dressings and mayonnaise," says Brooks. Ultra Omega-9 Algae Oil has a high smoke point (485 °F/253 °C) and a clean, neutral taste.

Solazyme's first consumer food brand, Thrive™ Culinary Algae Oil, began appearing in Gelson's Markets in the Los Angeles area the first week in October 2015. Thrive, which is also available online, contains greater than 90% monounsaturated fat, less than 4% saturated fat, and less than 4% polyunsaturated fat. Thrive has a clean taste and a high smoke point. The algal oil is suitable for sautéing, frying, baking, dressings, and other applications. "Thrive Algae Oil contains the highest level of monounsaturated fats along with the lowest percentage of saturated fats of any cooking oil on the market



today,” says Brooks. “The light, delicate taste lets the fresh, natural flavors of your food shine through.” The initial manufacturer suggested retail price of Thrive is \$11.99 for a 500-ml bottle.

The algal oils can be harvested after only a few days of fermentation, compared to months for seed oils. “When produced at our new facility in Brazil, Thrive Algae Oil will be one of the most sustainably produced cooking oils on the market, with more Thrive Algae Oil produced per acre of land, and a lower carbon and water footprint, than nearly all cooking oils,” says Brooks. He also notes that the algae left over after pressing is used as an energy source.

On October 29, 2015, Solazyme announced that the company is terminating its collaboration with Archer Daniels Midland (Chicago, Illinois, USA) to produce tailored triglyceride oils at ADM’s Clinton, Iowa, facility. From now on, algal oils will be produced at Solazyme’s new manufacturing facility in Moema, Brazil. On October 30, 2015, Solazyme announced

that the company has expanded a joint venture with Bunge Limited (White Plains, New York, USA) to include a focus on oils for food. As part of the agreement, Bunge will market the AlgaWise oils, as well as a new product, AlgaWise Algae Butter. A structuring fat, AlgaWise Algae Butter contains about 70% stearic-oleic-stearic triglycerides and is expected to find applications in bakery and confectionery. The algal butter will be available in the US market in 2016.

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

Galactosyldiacylglycerols

Lipid Snippets is a regular Inform column that features select content from The AOCS Lipid Library (<http://lipidlibrary.aocs.org/>).

This is from <http://lipidlibrary.aocs.org/content.cfm?ItemNumber=39345>.

Monogalactosyldiacylglycerols, digalactosyldiacylglycerols, and the plant sulfolipid sulfoquinovosyldiacylglycerol are the main lipid components of the various membranes of chloroplasts and related organelles, and indeed they are the most abundant lipids in all photosynthetic tissues, including those of higher plants, algae and certain bacteria. For example, mono- and di-galactosyldiacylglycerol amount to 50% and 25% of chloroplast glycerolipids, respectively. In photosynthetic tissues, monogalactosyldiacylglycerols are located exclusively in plastid membranes, but digalactosyldiacylglycerols can also be found in extra-plastidic membranes under some conditions. In non-photosynthetic tissues of plants, the proportion of these glycosyldiacylglycerols is much lower under normal growth conditions, although flowers contain appreciable amounts. The predominant structures are 1,2-di-*O*-acyl-3-*O*- β -D-galactopyranosyl-*sn*-glycerol and 1,2-di-*O*-acyl-3-*O*-(α -D-galactopyranosyl-(1 \rightarrow 6)-*O*- β -D-galactopyranosyl)-*sn*-glycerol.

In higher plants, the galactolipids of photosynthetic tissues contain a high proportion of polyunsaturated fatty acids, up to 95% of which can be linolenic acid (18:3(*n*-3)). In this instance, the most abundant molecular species of mono- and digalactosyldiacylglycerols must have 18:3 at both *sn*-1 and *sn*-2 positions of the glycerol backbone. Plants such as the pea, which have 18:3 as almost the only fatty acid in the monogalactosyldiacylglycerols, have been termed "18:3 plants". Other species, and the 'model' plant *Arabidopsis thaliana* is an example, contain appreciable amounts of hexadecatrenoic acid (16:3(*n*-3)) in the monogalactosyldiacylglycerols, and they are termed "16:3 plants". A further distinctive feature is that this acid is located entirely at the *sn*-2 position of the glycerol backbone (Table 1). Palmitic acid tends to be found only in digalactosyldiacylglycerols, usually in small amounts, when the positional distribution appears to depend on species. In non-photosynthetic tissues, such as tubers, roots or seeds, the C_{18} fatty acids are usually more saturated (c.f. the data for wheat flour lipids).

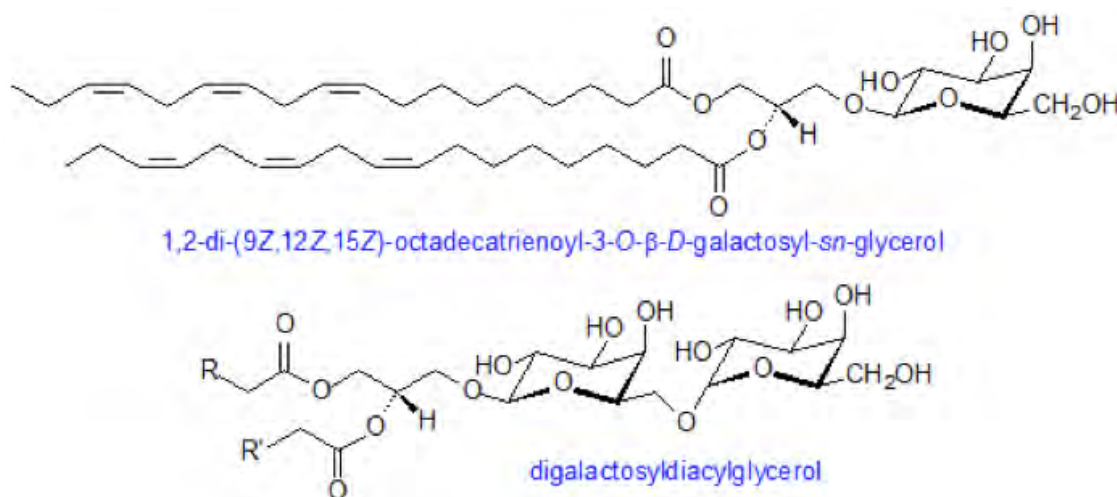


Table 1. Composition (mol %) of fatty acids in positions *sn*-1 and *sn*-2 of mono- and digalactosyldiacylglycerols from leaves of *Arabidopsis thaliana* and from wheat flour.

Position		Fatty acids				
	16:0	116:3(n-3)	18:0	118:1	118:2	18:3(n-3)
<i>Arabidopsis thaliana</i> [1]						
MGDG						
<i>sn</i> -1	2	1	trace	trace	4	93
<i>sn</i> -2	trace	70	trace	trace	1	28
DGDG						
<i>sn</i> -1	15	2	trace	2	3	76
<i>sn</i> -2	9	3	trace	trace	4	83
Wheat flour [2]						
MGDG						
<i>sn</i> -1	11	-	1	5	81	1
<i>sn</i> -2	trace	-	trace	9	83	7
DGDG						
<i>sn</i> -1	26	-	2	4	63	4
<i>sn</i> -2	2	-	trace	7	83	7

[1] Browse, J., Warwick, N., Somerville, C.R. and Slack, C.R. *Biochem. J.* 235: 25–31, 1986.

[2] Arunga, R.O. and Morrison, W.R. *Lipids* 6: 768–776, 1971.

On the basis of these structures, galactolipids are classified into two groups. The first has mainly C₁₈ fatty acids at the *sn*-1 position of the glycerol backbone, and only C₁₆ fatty acids at the *sn*-2 position, and it is termed a "prokaryotic" structure (as it is characteristic of cyanobacteria). The second class has C₁₆ or C₁₈ fatty acids at the *sn*-1 position but only C₁₈ fatty acids in the *sn*-2 position, and this is termed a "eukaryotic" structure, as it is present in most glycerolipids, such as the phospholipids, of all eukaryotic cells. The exception is phosphatidylglycerol, which is synthesised in chloroplasts via the prokaryotic pathway only. Some plants contain both eukaryotic and prokaryotic structures in the monogalactosyldiacylglycerols.

The structural differences in the diacylglycerol moiety of galactolipids from algae and higher plants are believed to originate in compartmentalization of the biosynthetic pathways or precursors in eukaryotic cells, each compartment having its own distinctive enzymes.

The main galactosyldiacylglycerols consist of 1,2-di-O-acyl-3-O-β-D-galactopyranosyl-*sn*-glycerol and its digalactosyl homologue formed biosynthetically by addition of an α-D-galactopyranosyl residue to C6 of the first galactose unit. However, other homologues occur that are formed by a continuation of this process, *i.e.* tri- and tetragalactosyldiacylglycerols. For example, trigalactosyldiacylglycerols have been found in pumpkins and potatoes, and tri- and tetragalactosyldiacylglycerols in oats and rice bran. Formation of such compounds in membranes is now known to be a normal process that contributes to freezing tolerance.

In addition, a second series has been identified consisting of all-*beta*-linked homologues, *i.e.* linear (1→6)-linked all-β-galactolipids with two to four galactose units. These have been found in a variety of plant families, algae and some bacteria. A third series has been described from one plant species that is derived from the normal (α→β)-linked digalactosyldiacylglycerol by sequential addition of 6-O-β-D-galactopyranosyl residues, resulting in alternative types of tri- and tetragalactosyldiacylglycerols. An interesting polyglycosyl glycerolipid has been found in mung beans with a terminal rhamnose unit and unusually an alkyl group in position *sn*-2 (in animal glycerolipids, the ether moiety is invariably in position *sn*-1).

Oat seeds contain an interesting form of digalactosyldiacylglycerol with an estolide linkage, *i.e.* 15-hydroxylinoleic acid is esterified to position *sn*-2 of the glycerol moiety, and the hydroxyl group of the fatty acid is esterified with linoleic acid. Further tri- and tetragalactosyldiacylglycerols with up to three estolide-linked fatty acids have now been identified.

1,2-Di-O-acyl-3-O-β-D-glucopyranosyl-*sn*-glycerol has been found in rice bran, where it occurs with the corresponding galactolipids in an approximate ratio of 1:2. Interestingly, the two forms differ appreciably in their fatty acid compositions. Triglycosyldiacylglycerols containing a high proportion of glucose have also been found in rice, but the structures have not been confirmed definitively. Although glucosyldiacylglycerols have been found in some other plants, they are always rather minor components.

The phytoplackton *Chrysochromulina polylepis* contains monogalactosyldiacylglycerol linked via the sugar moiety and an ester bond to a chlorophyll pigment. A marine algal species contains *sn*-1,2-di-palmityl-3-(*N*-palmityl-6'-desoxy-6'-amino-α-D-glucosyl)-glycerol and a homologue of this.

Under stress by mechanical wounding, bacterial infection and freezing/thawing, plants synthesise monogalactosyldiacylglycerols in which the galactose unit is acylated, often but not always by an oxylipin, depending on species.



Evidence for **EDCs** “more definitive than ever”

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

Charlotte Niemiec

Evidence that some chemicals disrupt hormones in a way that causes a range of serious health problems has become more compelling, says international scientific organization the Endocrine Society.

In late September—the same day that a key UN conference on global chemicals management opened in Geneva—the organization published a review of the evidence from the last five years. This concludes that exposure to chemicals, such as bisphenol A (BPA), phthalates, flame-retardants, and pesticides such as atrazine and DDT, is associated with an increased risk of diabetes and obesity, infertility, hormone-related cancers, prostate conditions, thyroid disorders, and neurodevelopmental issues.

“The evidence is more definitive than ever before—endocrine-disrupting chemicals disrupt hormones in a manner that harms human health,” said Andrea Gore, professor and Vacek chair of pharmacology at the University of Texas, and chair of the task force that produced the statement.

“Hundreds of studies are pointing to the same conclusion, whether they are long-term epidemiological studies in humans, basic research in animals and cells, or research into groups of people with known occupational exposure to specific chemicals.

“It is clear we need to take action to minimize further exposure,” said Gore. “With more chemicals being introduced into the marketplace all the time, better safety testing is needed to identify new EDCs and ensure they are kept out of household goods.”

In the statement, the society calls for:

- regulation to ensure that chemicals are tested for endocrine activity, including at low doses, prior to being permitted for use;
- additional research to infer more directly cause-and-effect relationships between EDC exposure and health conditions;
- advice for the public and policymakers on “how to keep EDCs out of food, water, and the air, as well as ways to protect unborn children from exposure”; and,
- chemists to create products that test for and eliminate potential EDCs.

“The science is clear and it’s time for policymakers to take this wealth of evidence into account as they develop legislation,” said society member Jean-Pierre Bourguignon, professor of pediatrics at the University of Liège.

A GLOBAL ISSUE

The executive summary says that although some countries and US states have banned some EDCs, “the fact that EDCs are ubiquitous makes it a global issue that requires international partnerships among developed and developing nations.”

It also backs the “evidence integration” philosophy of the US National Toxicology Program in deciding whether a chemical may have a health impact.

“When high-quality endocrinological studies demonstrate that a chemical interferes with hormone action in vivo and in vitro at environmentally (human) relevant concentrations, and when we have a high degree of evidence that these hormone systems are essential for normal development, it is reasonable to infer that these chemicals will produce adverse effects in humans,” says the summary.

To back up its call for the provision of “substantial information” before a chemical can be used in household products, it says BPS, which has been used to replace BPA, “is now shown to have endocrine-disrupting activity on a par with BPA.” Nongovernmental organizations welcomed the statement. The Health and Environment Alliance (HEAL) urged countries at the UN conference to back a proposed Resolution on EDCs put forward by developing countries. Healthcare Without Harm (HCWH) urged EU policy makers to identify EDCs in medical devices and to replace them with safer alternatives.

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Further reading

- Endocrine Society news release—<http://tinyurl.com/ES-release>
- Statement executive summary—<http://tinyurl.com/ES-summary>
- HEAL news release—<http://tinyurl.com/HEAL-release>
- HCWH statement—<http://tinyurl.com/HCWH-statement>

Tips from **inform|connect**

Tips from inform|connect is a regular Inform column that features tips and other discussion highlights from the community forum board at <http://www.informconnect.org/home>.

A doctoral student in food science wanted to know if bio-diesel producers would be willing to pay a premium for distillers corn oil with a lower free fatty acid (FFA) content

A research and development director at a company that produces corn oil with less than 1% FFA from a typical distillers corn oil (10–15% FFA) at a commercial-scale plant replied that such low FFA oil would have a value that is equal to or slightly higher than crude soybean oil and will find applications in biodiesel, specialty animal feed, and oleochemicals.

The cooling tower water distributor at a vegetable oil refinery was becoming partially blocked as a result of the fats carrying over. The manager of the facility asked what the best cleaning method is to prevent the problem.

Community members provided the following advice:

- The best strategy is to prevent the carryover because once carryover goes into the cooling tower, problems with the distributor and also water evaporation due to higher surface tension are bound to result. Carryover can be controlled by maintaining a proper circulation rate and temperature in the scrubber, installing a de-mister pad, and proper design of the

- hot well trap. It would also help to install a double bed in the scrubber.
- Skimming has been the traditional method of removing fat from the circulating water, but it is not 100% effective. Another approach is to dose caustic soda into the system to maintain a pH close to neutral (too high may lead to foaming) and to allow a controlled amount of wastewater to leave the system, carrying away any or other fatty material. Operating in this way would eliminate the large settling pond on the site.
- Systems that isolate the cooling circuit from the barometric water using heat exchangers eliminate dirt and smell from the towers completely and reduce the risk from infections such as legionella. There is a continual small flow of contaminated water to drain that can be easily managed. Again, the settling pond can be eliminated. Chilled water systems where the water enters the condensers at 5 to 10°C reduce the overall steam consumption of the vacuum system by more than 50%. Electricity is required to create the cooling, but usually the extra cost of electricity is quickly paid for by the saving in steam. This would have to be studied in the context of the overall energy consumption of the factory.

PATENTS

Fluid loss additives and methods of making and using same

Harris, J., *et al.*, Chevron Phillips Chemical Co. LP, US9034800, May 19, 2015

A non-aqueous wellbore servicing fluid comprising a fluid loss additive wherein the fluid loss additive comprises the reaction product of (i) a functional polymer and (ii) an oligomerized fatty acid. A method of conducting an oil-field operation comprising placing a non-aqueous wellbore servicing fluid downhole wherein the non-aqueous wellbore servicing fluid comprises a fluid loss additive comprising the reaction product of (i) a functional polymer and (ii) an oligomerized fatty acid.

Method for cleaving unsaturated fatty chains

Brandhorst, M., *et al.*, Arkema France, US9035079, May 19, 2015

The invention relates to a method for cleaving unsaturated fatty chains comprising a step of oxidative cleavage in which at least one fatty acid derivative having at least one unsaturation is reacted in the liquid phase with hydrogen peroxide in the presence of a catalyst for activating the reaction of oxidative cleavage and of molecular oxygen and in the absence of organic solvent.

Vegetable oil having high dielectric purity

Pulido Sanchez, A.J., *et al.*, Ragasa Industrias, S.A. de C.V.; Prolec-GE Internacional, S.de R.L. de C.V., US9039945, May 26, 2015

A dielectric high purity vegetable oil-free from antioxidants and/or external additives to be used in electric equipment such as transformers, as isolating element and as cooling means and a method for obtaining the same in which the dielectric high purity vegetable oil-is obtained by means of the optimization of the bleaching steps-and deodorizing-from the Refining process-known as Modified Caustic Refining Long-Mix (RBD).

Jasmonic acid compounds in cocoa products

Hurst, W.J., *et al.*, The Hershey Company, US9040096, May 26, 2015

The invention provides methods for isolating and enhancing the levels of jasmonates from cacao plant sources. In a preferred embodiment, jasmonic acid and 12-hydroxy jasmonate sulfate are detected in various cocoa products, and the levels of these compounds can be manipulated to increase the beneficial health effects of a food product made with the cocoa products. The invention includes methods to prepare edible products containing cocoa jasmonates.

Balanced fat composition and use thereof in a liquid nutritional composition suitable for enteral feeding

Van Anholt, R.D., *et al.*, N.V. Nutricia, US9044043, June 2, 2015

This invention relates to a balanced fat composition and use thereof in a liquid nutritional composition, in particular suitable for tube feeding. This invention further relates to said liquid nutritional composition for providing enteral nutrition to patients in need thereof, in particular for providing a complete enteral nutrition, in particular for providing a long-term enteral nutrition. More specifically, the balanced fat composition and the liquid nutritional composition comprising said balanced fat composition comprises specific amounts of linoleic acid (LA), alpha-linolenic acid (ALA), docosahexaenoic acid (DHA), eicosapentaenoic acid (EPA), at least one medium chain fatty acid (MCFA), and at least one mono-unsaturated fatty acid (MUFA). The invention relates further to a method for providing enteral nutrition to patients in need thereof comprising administering an effective amount of said liquid nutritional composition comprising the balanced fat composition according to the invention.

Nickel hydrogenation catalyst

Bouwman, H.J., *et al.*, BASF Corp., US9045410, June 2, 2015

The invention relates to a catalyst comprising nickel and a solid silica support, to a process for preparing such a catalyst and to a process for the hydrogenation of an unsaturated fatty material. According to the invention there is provided a catalyst comprising nickel on a solid silica support, wherein said catalyst has a specific pore volume of at least 0.4 ml/g and a TPR peak maximum within the range of 360–420 °C.

Reagent and method for detection of carboxylic acids by mass spectrometry

Gelb, M.H., *et al.*, University of Washington, US9045421, June 2, 2015

Method and reagent for converting a carboxylic acid to a positively charged amide are described. The method and reagent facilitate positive ion mass spectral analysis of carboxylic acids. The method includes reacting a carboxylic acid with a compound having formula I: wherein A and B are aromatic rings, ring A includes a quaternized nitrogen and has n additional ring atoms, each additional ring atom optionally substituted with an RA group, and n is an integer from 4 to 10, and ring B includes a carbon atom and has m additional ring atoms, each additional ring atom optionally substituted with an RB group, and m is an integer from 4 to 10. The compound includes at least one RA or RB group, and the at least one RA and RB group is -L-N(Z)H; and X- is a counterion.

Oil degumming methods

Dayton, C.L.G., *et al.*, Bunge Global Innovation, LLC, US9045712, June 2, 2015

In alternative embodiments, the invention provides phosphatidylinositol-specific phospholipase C (PI-PLC) enzymes, nucleic acids encoding them, antibodies that bind specifically to them, and methods for making and using them. Industrial methods and products comprising use of these phospholipases are also provided. In certain embodiments, provided herein are methods for hydration of nonhydratable phospholipids (NHPs) within a lipid matrix. The methods enable migration of NHPs to an oil-water interface thereby allowing the NHPs to be reacted and/or removed from the lipids. In certain embodiments, provided is a method for removing NHPs, hydratable phospholipids, and lecithins from vegetable oils to produce a degummed oil or fat product that can be used for food production and/or non-food applications. In certain embodiments, provided herein are methods for hydration of NHPs followed by enzymatic treatment and removal of various phospholipids and lecithins. The methods provided herein can be practiced on either crude or water-degummed oils.

Method for forming a vegetable oil having high dielectric purity

Pulido Sanchez, A.J., *et al.*, Ragasa Industrias, S.A. de C.V.; Prolec-GE Internacional, S.de R.L. de C.V., US9048008, June 2, 2015

A dielectric high purity vegetable oil-free from antioxidants and/or external additives to be used in electric equipment such as transformers, as isolating element and as cooling means and a method for obtaining the same in which the dielectric high purity vegetable oil-is obtained by means of the optimization of the bleaching steps-and deodorizing-from the Refining process-known as Modified Caustic Refining Long-Mix (RBD).

Crispy French fries

Bilet, M.J.J., *et al.*, Elwha LLC, US9049877, June 9, 2015

Crispy French fry-style food products are prepared by modification of the water content and the texture of the products' surface layers prior to deep frying. The surface modifications include surface firming, enzyme treatments, starch infusion and/or ultrasound treatment.

Elimination of organohalo and oxirane species in carboxylic acid ester streams

Rongione, J.C., *et al.*, Stepan Speciality Products, LLC, US9051260, June 9, 2015

The present technology provides a process of reducing, removing or eliminating organohalo, glycidol, and oxirane species from carboxylic acid esters streams and crude and refined triglyceride oils to provide a carboxylic acid ester stream or triglyceride oil with reduced levels or essentially free of organohalo, glycidyl or other oxirane species. The process includes adding to the carboxylic acid ester stream or triglyceride oil an amount of a carboxylate anion and a cation counterion sufficient to react with the organohalo, glycidyl and oxirane species present.

Cottonseed oil and uses

Liu, Q., *et al.*, Commonwealth Scientific and INDUSTRIAL Research Organisation, US9057075, June 16, 2015

The present specification relates to the production of cotton plants and seeds and oil prepared therefrom having elevated levels of oleic and reduced levels of palmitic and linoleic acids. Furthermore, cottonseeds having low levels of cyclopropane and/or cyclopropene fatty acids and/or reduced levels of gossypol are described herein. The specification also describes FatB and CPA-FAS nucleotide and amino acid sequences derived from cotton facilitating, inter alia the direct modification of plant oil content and/or composition.



EXTRACTS & DISTILLATES

Production of long-chain α,ω -dicarboxylic acids by engineered *Escherichia coli* from renewable fatty acids and plant oils

Sathesh-Prabu, C. and S.K. Lee, *J. Agric. Food Chem.* 63: 8199–8208, 2015, <http://dx.doi.org/10.1021/acs.jafc.5b03833>.

Long-chain α,ω -dicarboxylic acids (LDCAs, $\geq C_{12}$) are widely used as a raw material for preparing various commodities and polymers. In this study, a CYP450-monooxygenase-mediated ω -oxidation pathway system with high ω -regioselectivity was heterologously expressed in *Escherichia coli* to produce DCAs from fatty acids. The resulting engineered *E. coli* produced a maximum of 41 mg/L of C_{12} DCA and 163 mg/L of C_{14} DCA from fatty acids (1 g/L), following 20 h of whole cell biotransformation. Addition of a heme precursor and the hydroxyl radical scavenger, thiourea, increased product concentration (159 mg/L of C_{12} DCA and 410 mg/L of C_{14} DCA) in a shorter culture duration than that of the corresponding controls. DCAs of various chain lengths were synthesized from coconut oil hydrolysate using the engineered *E. coli*. This novel synthetic biocatalytic system could be applied to produce high value DCAs in a cost-effective manner from renewable plant oils

High production of squalene using a newly isolated yeast-like strain *Pseudozyma* sp. SD301

Song, X., et al., *J. Agric. Food Chem.* 63: 8445–8451, 2015, <http://dx.doi.org/10.1021/acs.jafc.5b03539>.

A yeast-like fungus, termed strain SD301, with the ability to produce a high concentration of squalene, was isolated from Shuidong Bay, China. The nucleotide sequence analysis of the internal transcribed spacer (ITS) region of SD301 indicated the strain belonged to *Pseudozyma* species. The highest biomass and squalene production of SD301 were obtained when glucose and yeast extracts were used as the carbon and nitrogen sources, respectively, with a C/N ratio of 3. The optimal pH and temperature were 6 and 25 °C, with 15 g L⁻¹ of supplemented sea salt. The maximum squalene productivity reached 0.039 g L⁻¹ h⁻¹ in batch fermentation, while the maximum squalene yield of 2.445 g L⁻¹ was obtained in fed-batch fermentation. According to our knowledge, this is the highest squalene yield produced thus far

using fermentation technology, and the newly isolated strain *Pseudozyma* sp. SD301 is a promising candidate for commercial squalene production.

Maternal exposure to diets containing flaxseed flour or flaxseed oil during pregnancy and lactation protects the aortic remodeling in adult male offspring of diabetic rat dams

Vicente, G.C., et al., *J. Sci. Food Agric.* 95: 2973–2980, 2015, <http://dx.doi.org/10.1002/jsfa.7041>.

Diabetes during pregnancy is associated with cardiovascular complications in the fetus and extends into adulthood. Therapeutic applications of flaxseed have been studied in cardiovascular disorders, because its oilseed is the best plant source of omega-3 fatty acid, which is currently considered by researchers to be an essential protective against cardiovascular disease. The aim of this study was to evaluate the influence of flaxseed flour and oil on cardiovascular biochemical parameters and the histoarchitecture of the aorta in adult rats which were offspring of diabetic mothers. At 100 days of age in offspring it was observed that maternal consumption of a high-fat diet containing flaxseed oil (FOG) and flaxseed flour (FFG) did not affect the serum concentration of monocyte chemoattractant protein-1, vascular endothelial growth factor, cholesterol, triglycerides, high-density-, low-density- or very-low-density-lipoprotein cholesterol. However, the thickness of the intima media layer of the aorta was significantly smaller in FOG and FFG groups; the lumen area was similar among the groups; and a higher percentage of elastic fiber was found in FOG and FFG groups. These data suggest that the use of both flaxseed flour and its oil reduces the remodeling of the aorta; however, it has not been possible to modify the cardiovascular biochemical parameters.

Specific roles of saturated fatty acids: beyond epidemiological data

Legrand, P. and V. Rioux, *Eur. J. Lipid Sci. Technol.* 117: 1489–1499, 2015, <http://dx.doi.org/10.1002/ejlt.201400514>.

In the past 50 years, saturated fatty acids (SFAs) have played a key role in hypotheses relating diet to the risk of coronary heart disease. More recently, the international debate questioning the role of reducing intakes of saturated fat in the prevention of cardiovascular diseases has been re-opened. According to the past negative assumption, SFAs are indeed still considered as a single group even if it is now well-known that they do not have similar levels in common foods, nor similar metabolic fates and cellular functions. In addition, recent findings on the metabolism and biological functions of individual SFAs show that they have important and specific roles in the cells. Elucidated biochemi-

cal mechanisms such as SFA protein acylation (N-myristoylation, S-palmitoylation and ghrelin octanoylation) and regulation of gene transcription are presented. In terms of physiology, SFAs are involved for instance in lipogenesis, fat deposition, polyunsaturated fatty acid bioavailability and apoptosis. The variety of their functions demonstrates that SFAs should no longer be considered as a single group. Consequences on the current nutritional dietary recommendations are finally discussed. The international debate questioning the role of reducing intakes of saturated fat in the prevention of cardiovascular diseases has recently been re-opened. Saturated fatty acids are indeed still considered as a single group even if it is now well-known that they do not have similar levels in common foods, nor similar metabolic fates and cellular functions. The variety of their functions demonstrates that saturated fatty acids should no longer be considered as a single group. Consequences on the current nutritional dietary recommendations are finally discussed.

Emulsifying triglycerides with dairy phospholipids instead of soy lecithin modulates gut lipase activity

Mathiassen, J.H., *et al.*, *Eur. J. Lipid Sci. Technol.* 117: 1522–1539, 2015, <http://dx.doi.org/10.1002/ejlt.201400505>.

A high energy supply and appropriate amount of polyunsaturated fatty acids is crucial for proper growth and development in neonates. The capacity for fatty acid absorption in newborns is however hampered due to an undeveloped pancreatic function combined with a low bile output. This seems in particular to limit fatty acid absorption in babies given infant formulas. Since interaction between the lipid droplet and the gastric and duodenal lipases occur through the hydrophobic/hydrophilic interface, the composition of the emulsifier may be crucial for efficient hydrolysis. We therefore determined hydrolytic rate of gastric lipase and pancreatic lipase, on their own or pancreatic lipase after gastric lipase on TAG droplets of similar size emulsified in either soy lecithin (SL) or in bovine milk phospholipids (MPL), more similar to human milk globule membrane lipids than soy lecithin. Gastric lipase activity was substantially higher on MPL-emulsified particles, while SL emulsification caused a higher rate of pancreatic lipase hydrolysis, on particles that had not been pre-treated with gastric lipase. MPL emulsification did however cause higher pancreatic lipase activity, when the particles had been pre-treated with gastric lipase. The attenuating effect of MPL-emulsification on pancreas lipase activity was validated in vivo in mice. Our results show that the activity of gastric lipase, a key enzyme in lipid absorption in neonates, is highly dependent on the phospholipid composition of the surface layer on the emulsion droplets. We furthermore show that increasing gastric lipase activity by modifying the phospholipid composition on the droplet surface, also enhance the subsequent activity of the pancreatic lipase acting in the duodenum. This implies that it is possible to strategically design the surface layer of lipid droplets in infant formulas to maximize gastric lipase activity, and that this could improve total fatty acid absorption in formula-fed neonates. This is of particular importance in the development of formula aimed at pre-mature babies, but is also highly relevant for formulas for term-born infants. Emulsifying corn

oil in milk phospholipids rather than soy lecithin causes a substantial increase in gastric lipase activity (upper). The increased gastric lipase activity on the emulsion particles also causes a threefold increase in pancreatic lipase activity, when done in sequence of gastric lipase hydrolysis (lower). MPL = milk phospholipids, SL = soy lecithin, w/o GL = without gastric lipase pre-treatment, w GL = with gastric lipase pre-treatment.

A fluorescence polarization assay to detect steroid hormone traces in milk

Varriale, A., *et al.*, *J. Agric. Food Chem.* 63: 9159–9164, 2015, <http://dx.doi.org/10.1021/acs.jafc.5b03689>.

Steroids are a class of hormones improperly used in livestock as growth-promoting agents. Due to their high risk for human health, the European Union (EU) has strictly forbidden the administration of all natural and synthetic steroid hormones to food-producing animals, and the development of new rapid detection methods are greatly encouraged. This work reports a novel fluorescence polarization assay, ready to use, capable of detecting 17 β -estradiol directly in milk samples with a low limit of detection of <10 pmol. It is based on the coupling of monospecific antibodies against 17 β -estradiol and fluorophores, capable of modulating the fluorescence polarization emission on the basis of the specific binding of antibodies to fluorescence-labeled 17 β -estradiol derivative. The successful detection of 17 β -estradiol has disclosed the development of an efficient method, easily extensible to any food matrix and having the potential to become a milestone in food quality and safety.

Visible light-induced lipid peroxidation of unsaturated fatty acids in the retina and the inhibitory effects of blueberry polyphenols

Liu, Y., *et al.*, *J. Agric. Food Chem.* 63: 9295–9305, 2015, <http://dx.doi.org/10.1021/acs.jafc.5b04341>.

The lipid peroxidation of unsaturated fatty acids (UFAs) in the retina not only threatens visual cells but also affects the physiological health of the retina. In this work, the potential damages caused by daily visible light exposure on retinal UFAs were evaluated via a simulated in vitro model. At the same time, the benefits of dietary supplementation of blueberries to the eyes were also assessed. After prolonged light exposure, lipid peroxidation occurred for both docosahexaenoic and arachidonic acids (DHA and AA, respectively). The oxidized UFAs presented obvious cytotoxicity and significantly inhibited cell growth in retinal pigment epithelium cells. Among the different blueberry polyphenol fractions, the flavonoid-rich fraction, in which quercetin was discovered as the main component, was considerably better in preventing visible light-induced DHA lipid peroxidation than the anthocyanin- and phenolic acid-rich fractions. Then the retinal protective activity of blueberry polyphenols against light-induced retinal injury was confirmed in vivo. On the basis of the above results, inhibiting lipid peroxidation of UFAs in the retina

is proposed to be another important function mechanism for antioxidants to nourish eyes.

Physical stability, autooxidation, and photosensitized oxidation of ω -3 oils in nanoemulsions prepared with natural and synthetic surfactants

Uluata, S. et al., *J. Agric. Food Chem.* 63: 9333–9340, 2015, <http://dx.doi.org/10.1021/acs.jafc.5b03572>.

The food industry is interested in the utilization of nanoemulsions stabilized by natural emulsifiers, but little research has been conducted to determine the oxidative stability of such emulsions. In this study, two natural (lecithin and quillaja saponin) and two synthetic (Tween 80 and sodium dodecyl sulfate) surfactants were used to fabricate omega-3 nanoemulsion using high pressure homogenization (microfluidization). Initially, all the nanoemulsions contained small (d from 45 to 89 nm) and anionic (ζ -potential from -8 to -65 mV) lipid droplets (pH 7). The effect of pH, ionic strength, and temperature on the physical stability of the nanoemulsion system was examined. Nanoemulsion stabilized with Tween 80, quillaja saponin, or sodium dodecyl sulfate (SDS) exhibited no major changes in particle size or visible creaming in the pH range of 3 to 8. All nanoemulsions were relatively stable to salt addition (0 to 500 mM NaCl, pH 7.0). Nanoemulsions stabilized with SDS and quillaja saponin were stable to heating (30 to 90 °C). The impact of surfactant type on lipid oxidation was determined in the presence and absence of the singlet oxygen photosensitizers, riboflavin, and rose bengal. Riboflavin and rose bengal accelerated lipid oxidation when compare to samples without photosensitizers. Lipid hydroperoxide formation followed the order Tween 80 > SDS > lecithin > quillaja saponin, and propanal formation followed the order lecithin > Tween 80 > SDS > quillaja saponin at 37 °C for autooxidation. The same order of oxidative stability was observed in the presence of photosensitized oxidation promoted by riboflavin. Quillaja saponin consistently produced the most oxidatively stable emulsions, which could be due to its high free radical scavenging capacity.

Metabolic engineering of *Pichia pastoris* to produce ricinoleic acid, a hydroxy fatty acid of industrial importance

Meesapyodsuk, D., et al., *J. Lipid Res.* 56: 2102–2109, 2015, <http://dx.doi.org/10.1194/jlr.M060954>.

Ricinoleic acid (12-hydroxyoctadec-cis-9-enoic acid) has many specialized uses in bioproduct industries, while castor bean is currently the only commercial source for the fatty acid. This report describes metabolic engineering of a microbial system (*Pichia pastoris*) to produce ricinoleic acid using a “push” (synthesis) and “pull” (assembly) strategy. CpFAH, a fatty acid hydroxylase from *Claviceps purpurea*, was used for synthesis of ricinoleic acid, and CpDGAT1, a diacylglycerol acyl transferase for the triacylglycerol synthesis from

the same species, was used for assembly of the fatty acid. Coexpression of CpFAH and CpDGAT1 produced higher lipid contents and ricinoleic acid levels than expression of CpFAH alone. Coexpression in a mutant haploid strain defective in the $\Delta 12$ desaturase activity resulted in a higher level of ricinoleic acid than that in the diploid strain. Intriguingly, the ricinoleic acid produced was mainly distributed in the neutral lipid fractions, particularly the free fatty acid form, but with little in the polar lipids. This work demonstrates the effectiveness of the metabolic engineering strategy and excellent capacity of the microbial system for production of ricinoleic acid as an alternative to plant sources for industrial uses.

Recent evidence on omega 6 fatty acids and cardiovascular risk

Poli, P. and F. Visioli, *Eur. J. Lipid Sci. Technol.* 117: 1847–1852, 2015, <http://dx.doi.org/10.1002/ejlt.201500049>.

As evidence accumulates, our knowledge of the role of individual fatty acids in cardiovascular disease improves. This re-evaluation is being applied to poly- (PUFAs) and mono- (MUFAs) unsaturated fatty acids. Among the former, omega 6 (or n-6) fatty acids from vegetables and seed oils have always been labeled as cardioprotective. However, this notion was challenged in the 80s, when in vitro data on the high oxidizability of omega 6 fatty acids, their potential pro-inflammatory effects purportedly due to the formation of prostaglandins, and their hypothesized competition for the same enzymes that elongate and desaturate omega 3 fatty acids cast doubts on their healthful roles and even led to the suggestion to limit their dietary intake. As outlined in this review and based on the most recent studies, this is most probably not the case: indeed, adequate intakes of omega 6 fatty acids appear to be extremely helpful in CHD risk reduction and a hypothetical reduction of omega 6 intake by the population at large would actually increase CHD risk.

Lipid Oxidation

Assessing interactions between lipophilic and hydrophilic antioxidants in food emulsions

Durand, E., et al., *J. Ag. Food Chem.*, online, 2015, <http://dx.doi.org/10.1021/acs.jafc.5b04152>.

Dietary lipids containing high concentrations of polyunsaturated fatty acids are considered to be beneficial to human health, yet their incorporation within formulated foods is complicated by their susceptibility to oxidation. Lipid oxidation in foods is inhibited through the incorporation of antioxidants, yet the list of antioxidants approved for food use is small, and consumers frequently demand foods without synthetic additives. As a consequence, food processors are now tasked with improving the efficacy of approved, “natural” (i.e., non-synthetic) antioxidants; a rational strategy for doing so involves localizing the antioxidants at the interface where oxidation usually occurs and regenerating the consumed antioxidants after the oxidation event has occurred. The present

study describes a procedure to evaluate antioxidant interactions in oil-in-water food emulsions, which is based on controlled oxidation reactions induced in the dispersed oil phase by the lipophilic radical generator, 2,2'-azobis(2,4-dimethylvaleronitrile). The extent of lipid oxidation is measured spectroscopically by following the loss of an oxidatively labile, lipophilic probe (methyl eleostearate), the synthesis of which is described here. Using this procedure, the ability of various aqueous phase solvated antioxidants (ascorbic acid, gallic acid, (-)-epicatechin, (-)-epigallocatechin-3-gallate) to regenerate lipid phase solvated α -tocopherol was evaluated. In all cases, the test compounds were able to inhibit oxidation reactions; however, these effects were not profoundly synergistic, and the maximum synergistic interaction observed was only ~3% using ascorbic acid.

Trans fatty acids in two classes of reformulated “zero trans” Spanish margarines by use of second derivative ATR-FTIR spectroscopy

Galvina, S., *et al.*, *LWT-Food Sci. Technol.* 65: 1066–1071, 2016, <http://dx.doi.org/10.1016/j.lwt.2015.09.047>.

This work arouses a criticism about if “no trans fat” really means no trans fat. This issue seems to be interesting because of the direct relationship between trans-fat intake and a pronounced risk of coronary heart disease. Very low amounts of trans-fat (less than 0.5 per cent, as percentage of total fat) have been found in commercial soft and hard reformulated margarine labelled as “zero trans”, by the use of the innovative recently validated second derivative procedure of attenuated total reflection-Fourier transform infrared spectroscopy. In this way the possibility to inform consumers on trans-fat content in 0.1%-trans-fat increments, from 0% to 2%, as percentage of total fat, in the Nutrition Fact label could be feasible.

Compound release from nanostructured lipid carriers (NLCs)

Dan, N., *J. Food Eng.*, In Press, 2015, <http://dx.doi.org/10.1016/j.jfoodeng.2015.10.005>.

Active compounds such as flavors, scents, vitamins or nutraceuticals enhance the quality and nutritional value of foods. Their encapsulation in nanoparticles preserves properties such as appearance, while increasing solubility and bioavailability. Nanostructured lipid carriers (NLC) composed of liquid and solid lipid domains are biocompatible and combine high encapsulation rates with mechanical stability. In this paper we use Monte Carlo simulations to investigate the effects of the solid domain properties on the rate of compound release from NLC. Quite surprisingly, solid impenetrable domains at the particle/solution interface hinder release only when the domain size is much smaller than the nanoparticle size, even if they cover a significant fraction of the interface. The geometry of the solid domains also affects the rate of release, and how the rate dependence on domain size and fraction.

Comparison of different classification methods for analyzing electronic nose data to characterize sesame oils and blends

Shao, X., *et al.*, *Sensors* 15: 26726–26742, 2015, <http://dx.doi.org/10.3390/s151026726>.

An electronic nose (e-nose) was used to characterize sesame oils processed by three different methods (hot-pressed, cold-pressed, and refined), as well as blends of the sesame oils and soybean oil. Seven classification and prediction methods, namely PCA, LDA, PLS, KNN, SVM, LASSO and RF, were used to analyze the e-nose data. The classification accuracy and MAUC were employed to evaluate the performance of these methods. The results indicated that sesame oils processed with different methods resulted in different sensor responses, with cold-pressed sesame oil producing the strongest sensor signals, followed by the hot-pressed sesame oil. The blends of pressed sesame oils with refined sesame oil were more difficult to be distinguished than the blends of pressed sesame oils and refined soybean oil. LDA, KNN, and SVM outperformed the other classification methods in distinguishing sesame oil blends. KNN, LASSO, PLS, and SVM (with linear kernel), and RF models could adequately predict the adulteration level (% of added soybean oil) in the sesame oil blends. Among the prediction models, KNN with $k = 1$ and 2 yielded the best prediction results.

Food application of an encapsulated phytochemically rich SC-CO₂ extract of a polyherbal mix of tulsi, bay and cardamom: shelf-life and frying stability of soybean oil

Ghosh, S., *et al.*, *J. Food Eng.*, In Press, 2015, <http://dx.doi.org/doi:10.1016/j.jfoodeng.2015.10.023>.

SC-CO₂ extract of a polyherbal mix of 1:1:2 tulsi leaves, bay leaves and cardamom seeds having appreciable antioxidant potency was encapsulated using spray drying technology. Maltodextrin and gum arabic (60:40) were used as wall materials at an inlet temperature of 140°C to obtain an encapsulated powder with appreciable encapsulation efficiency. The powder had smooth rounded morphology as observed by scanning electron microscope and had antioxidant activity, phenolic content, reducing power and anti-inflammatory potency. The encapsulated SC-CO₂ extract of the polyherbal mix was evaluated for its possible usage as a natural antioxidant in soybean oil. 30-day storage and frying stability studies of soybean oil samples, administered individually with the encapsulated and non-encapsulated extracts and commercial antioxidants TBHQ and BHT, established that the encapsulated polyherbal SC-CO₂ extract had the best antioxidant efficacy. This encapsulate allows controlled release of the antioxidant and is therefore advocated as a promising ‘green’ antioxidant for soybean oil.

Potential seaweed-based food ingredients to inhibit lipid oxidation in fish-oil-enriched mayonnaise

Honold, P.J., *et al.*, *Eur. Food Res. Technol.*, online, <http://dx.doi.org/10.1007/s00217-015-2567-y>.

Brown seaweed *Fucus vesiculosus* has a high potential as a source of natural antioxidants due to a high diversity of bioactive compounds in its composition. In this study, four extracts were characterized with respect to composition of bioactive compounds, in vitro antioxidant properties and their partitioning between water and octanol. Additionally, the antioxidant activity of the extracts was evaluated in a fish-oil-enriched mayonnaise. Acetone and ethanol were found to extract the highest amount of phenolic compounds and carotenoids. Water used as extraction solvent, extracted some phenolic compounds but also higher amount of metals and chlorophyll derivatives. It was proposed that extracts with high phenolic content and low iron content, such as the acetone and ethanol extract, would have the highest potential as antioxidants in foods. This was confirmed in the storage trial, where these extracts showed higher antioxidant activity.

Effect of intermittent oven drying on lipid oxidation, fatty acids composition, and antioxidant activities of walnut

Fu, M., *et al.*, *LWT—Food Sci. Technol.* 65: 1126–1132, <http://dx.doi.org/10.1016/j.lwt.2015.10.002>.

Compared with sun drying and direct oven drying methods, intermittent oven drying for walnut (*Juglans regia* L.) drying was employed, and the consequent changes in lipid oxidation attributes, such as acid value (AV), peroxide value (POV), saponification value (SV), fatty acid composition, antioxidant activity (reducing power, superoxide anion scavenging activity, and DPPH radical dot free radical scavenging activity), lipoxygenase activity, and total phenols content (TPC) and total flavonoids content (TFC) were investigated in this study. Sun drying resulted in the highest AV, POV and SV, at the end of drying that was 0.8 g/kg, 2.4 mq/kg, 230.9 g/kg, respectively, followed by direct oven drying and intermittent oven drying. Antioxidant activities and related compounds, TPC and TFC, were initially increased then declined during drying, and a significant correlation was found between antioxidant activity and TPC and TFC ($P < 0.05$). The LOX activities of all samples showed an increasing trend, although those of the sun-dried samples were the lowest (0.43 μ kat/mg). The walnuts dried with the intermittent oven drying method had much more linoleic acid than those dried by direct oven drying.

Enhancing nutraceutical performance using excipient foods: designing food structures and compositions to increase bioavailability

McClements, D.J., *et al.*, *Comp. Rev. Food Sci. Food Saf.* 14: 824–847, 2015, <http://dx.doi.org/10.1111/1541-4337.12170>.

The oral bioavailability of many bioactives (pharmaceuticals, dietary supplements, nutrients, and nutraceuticals) is limited because of physicochemical and physiological events that occur within the gastrointestinal tract (GIT) after their ingestion. These events include: (i) restricted liberation from drugs, supplements, or foods; (ii) extensive metabolism or chemical transformation during passage through the GIT; (iii) low solubility in intestinal fluids; (iv) low permeation through the intestinal cell monolayer; and (v) efflux from epithelium cells. Bioactive bioavailability can often be improved by designing the composition and structure of food matrices to control their liberation, transformation, solubilization, transport, absorption, and efflux in the GIT. This article reviews the potential impact of food composition and structure on the oral bioavailability of bioactives, and then shows how this knowledge can be used to design excipient foods that can improve the bioavailability profile of bioactives. The bioactive may be incorporated within an excipient food or co-ingested with an excipient food. The suitability of oil-in-water emulsions as excipient foods is highlighted. The utilization of excipient foods may provide a new strategy for improving the efficacy of nutraceuticals, supplements, and pharmaceuticals.

Industrial Applications

Transesterification of oil to biodiesel in a continuous tubular reactor with static mixers: modelling reaction kinetics, mass transfer, scale-up and optimization considering fatty acid composition

Likoar, B., *et al.*, *Fuel Process. Technol.* 142: 326–336, 2016, <http://dx.doi.org/10.1016/j.fuproc.2015.10.035>.

Simulations of the methanolysis of lipids in a mixer-packed bed heterogeneous flow process were performed based on the thermodynamics (equilibrium) as well as mechanism and chemical kinetics of glycerides and fatty acid methyl esters (FAME) containing different combinations of gadoleic (G), linoleic (L), linolenic (Ln), oleic (O), palmitic (P) and stearic (S) acids, bonded as glycerol (alcohol) substituents. Transport phenomena and fluid dynamics were established for emulsion interface films and through axial dispersion coefficients (Péclet number) in a fixed bed for both transient and stationary operation. Alcoholysis was also studied experimentally within a broad range of temperatures, hydrodynamic conditions in

terms of volumetric flow rates, phase ratios and base catalyst concentrations. Diffusion resistance proved to be negligible, temperature was proven as a prevalent factor, while steady state was reached only after a few residence times elapsed. Process economics were finally evaluated in terms of cost and price breakdown, allowing methodology extension to other waste oil resources. Sensitivity analysis revealed high LLL triglyceride content in oil having the greatest positive, and OOL negative effect on FAME yield. Process intensification with static mixers was proven feasible upon scaling-up from 5 to 10 mm internal diameter with no deterioration in overall process progression.

Development of purification concepts for nutraceuticals from algae – part ii: design of purification strategies

Fröhlich, H., *et al.*, *Chem. Eng. Technol.* 38: 2035–2044, 2015, <http://dx.doi.org/10.1002/ceat.201400618>.

Omega-3 fatty acids are well-known for health-preserving effects like blood pressure reduction. Main source of fatty acids is fish oil which has recorded a significant price increase. This has stimulated research on recovering omega-3 fatty acids from other sources, like the microalgae *Ulkenia* sp. These stems have in common that the fatty acids are built as storage lipids in the cell interior. Due to the cell wall stability of the cell systems, high disruption energies need to be applied which leads to formation of stable emulsions. Innovative downstream concepts are developed which in contrast to conventional processes are operated free from organic solvents. Several approaches are discussed and compared in terms of cost to common process concepts.

Turning pork processing waste into value-added chemicals for the food industry

Amorim, C.D., *et al.*, *Sustain. Mater. Technol.*, online 2015, <http://dx.doi.org/10.1016/j.susmat.2015.09.001>.

Winterization is a method to modify the characteristics of oils and fats to provide added value by concentrating the unsaturated fatty acids. The purpose of this study is to characterize a residue from pork processing and evaluate two different fractionation methods via winterization. Furthermore, the fatty-acid composition and the chemical characterization were determined from the grease waste and the fractions obtained after fractionation. The untreated grease waste showed an acidity index of 0.57 mg KOH/g, a peroxide value of 10.74 mEq/kg, 56.45% unsaturated fatty acids and 43.55% saturated fatty acids, with the predominance of oleic, linoleic and palmitic acids. The experiment, which was performed in two cooling stages and stirred at 600 rpm, showed a decrease of 27.89% in the saturated fatty-acid content, which predominantly consisted of oleic, palmitic and stearic fatty acids. The winterization process improved the quality of the grease waste, reduced the peroxide value and concentrated the unsaturated fatty acids.

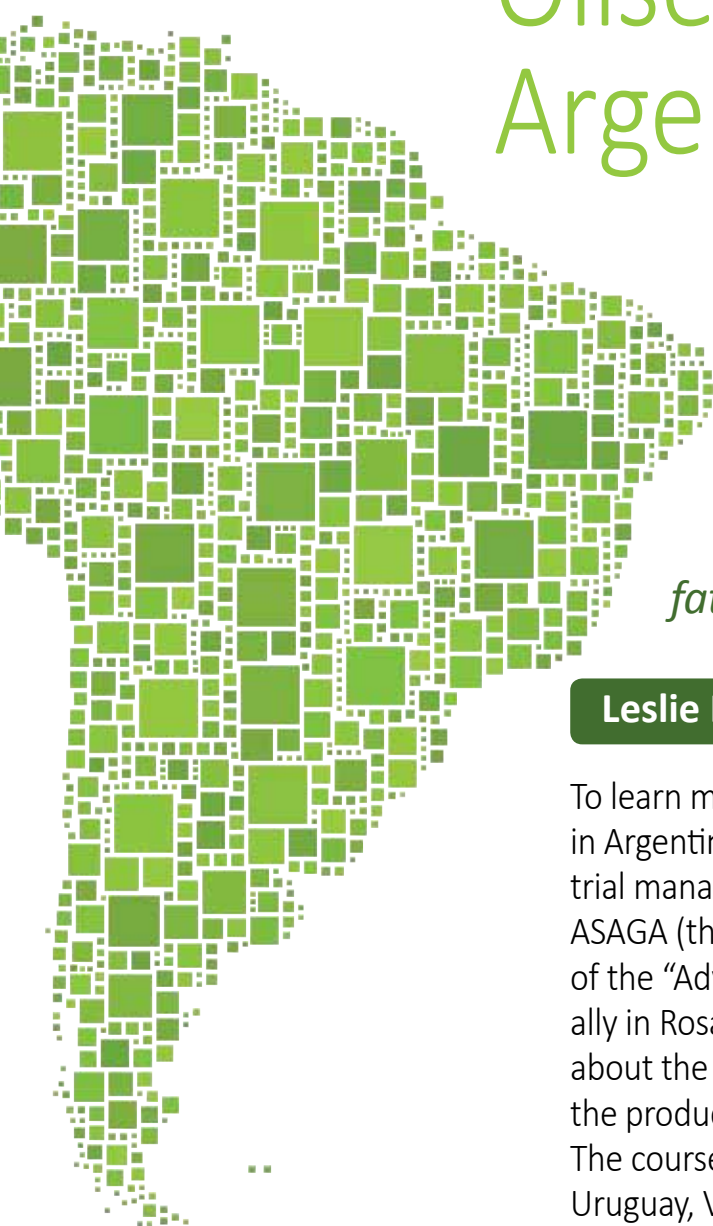
Synthetic Biology

Synthetic biology for microbial production of lipid-based biofuels

d'Espaux, L., *et al.*, *Curr. Opin. Chem. Biol.* 29: 58–65, 2015, <http://dx.doi.org/10.1016/j.cbpa.2015.09.009>.

The risks of maintaining current CO₂ emission trends have led to interest in producing biofuels using engineered microbes. Microbial biofuels reduce emissions because CO₂ produced by fuel combustion is offset by CO₂ captured by growing biomass, which is later used as feedstock for biofuel fermentation. Hydrocarbons found in petroleum fuels share striking similarity with biological lipids. Here we review synthetic metabolic pathways based on fatty acid and isoprenoid metabolism to produce alkanes and other molecules suitable as biofuels. We further discuss engineering strategies to optimize engineered biosynthetic routes, as well as the potential of synthetic biology for sustainable manufacturing.





Oilseed crushing in Argentina: soybean and sunflower

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

Leslie Kleiner

To learn more about oilseed crushing (soybean and sunflower) in Argentina, I interviewed Hector Autino, a corporate industrial manager for Bunge Argentina S.A., and founding member of ASAGA (the Argentinean Association of Fat & Oils). As an organizer of the “Advanced Course in Oilseed Crushing,” which is held annually in Rosario, Santa Fe, Argentina, Autino shared some key points about the processes that lead to oil solvent extraction as well as the production of, meal and the hull pellets used for animal feed. The course brings professionals from Brazil, Paraguay, Bolivia, Uruguay, Venezuela, Costa Rica, Mexico, and other countries to Argentina, and continues to be a success in promoting knowledge sharing in the field of oilseed crushing.

Q: HOW DOES SEED TYPE, STRUCTURE, AND MORPHOLOGY AFFECT OILSEED CRUSHING?

A: Different seeds have different fat contents, and this is an important parameter to consider during crushing. For example, soybean seed has a low fat content which facilitates the crushing process. Also, its structure and morphology can be easily modified, first by cracking to reduce its size and later by heating and passing through a flaking mill. This milling step breaks the cell walls and allows for oil extraction, which initially contains other components such as proteins and carbohydrates. If crushing is performed well, it is possible to achieve good results that can lead to excellent oil recovery after solvent extraction.

Other types of seeds (soft-seeds), such as sunflower, have a higher fat content than soybean does. These seeds require special care in terms of crushing. After de-hulling, the pulp must be heat treated before processing through the flaking mill. The main concern with these seeds is that the hulls may absorb too much fat content, which would translate to economic losses in terms of oil recovery. However, in terms of processing cost, the hulls of sunflower are commonly used as a biomass to feed steam boilers and decrease the cost of gas or fuel at the processing plant. In general, for low-protein (33%) and high-protein (38%) content sunflower pellet, the separated hulls represent 45 % to 75% of the total weight, respectively.

Q: WHAT IS THE OBJECTIVE OF OILSEED DRYING?

It is important to differentiate oilseed drying for storage, and oilseed drying for processing (crushing). In terms of storage, drying is a preventive measurement to avoid auto ignition in the silos. For soybean, if the moisture is below 13%, the seeds are usually stored and maintained under controlled aeration. Due to the higher fat content, sunflower seeds must be stored at lower moisture content than soybean seeds (~10%). In terms of processing, the moisture of the seeds needs to be controlled depending on the type of process that will be used for de-hulling. For soybean, the humidity can vary between ~ 10–13.5% depending on whether cold, warm, or hot de-hulling systems are used. For sunflower seeds, the recommended humidity for de-hulling is ~ 7%.

Q: WHAT ARE COMMON DE-HULLING PROCESSES LIKE? WHAT ARE THE MAIN DIFFERENCES BETWEEN SOYBEAN AND SUNFLOWER DE-HULLING?

A: Dehulling dramatically reduces the fiber content of the final meal and increases its protein value. For soybean seeds, cold, warm, and hot de-hulling are common processes that are performed after grinding. These can be performed in stages, first cracking the grains in half and then separating the hulls by aspiration in the second stage, until ~90% of the hulls can be separated from the rest. Cold de-hulling requires a tempering step to equalize humidity and ensure proper cracking of the grain in preparation for de-hulling. For warm de-hulling, the grain is dried and conditioned in a vertical seed conditioner until it is cracked for aspiration and separation. Hot de-hulling is similar to warm de-hulling, but it has an additional step involving a jet dryer. This drying step uses a few seconds of hot air to increase the temperature of the grain. The objective is to dilate the grain in order to facilitate the hulls removal. Both warm and hot de-hulling are more efficient in terms of hull removals and thermal energy use than the cold de-hulling process, which requires additional heating steps. However, cold de-hulling leads to increased safety at the plant. Notice that soybean and sunflower have ~ 7% and ~27% hulls by weight, respectively. For soybean, the hulls are removed after cracking the grain, while for sunflower seeds the hulls are removed by a de-hulling process that applies an impact force, and after that the hulls can be removed by particle classifications using seed screener and multi-aspirators.

Q: AFTER DE-HULLING, WHAT IS THE FATE OF THE HULLS OF SOYBEAN?

A: If the intention is to recuperate the soybean hulls, these are collected and treated to separate as many hulls as possible from the rest of the material. These hulls then undergo grinding and pelletizing in a specific press that leads to a sterilized pellet of 4-6 mm in diameter. These pellets have over 40% fiber content, ~ 10% protein, and ~ 1.5% fats, and are used for animal feed.

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



Water: the most important cleaning ingredient

Dave McCall

Formulation Science is a regular Inform column highlighting advances, trends, and challenges in cleaning product formulation

By a very wide margin, the most important ingredient in any cleaning application is water. There are many reasons this is the case and all of them are good. Most importantly, it works. Water has a well-earned reputation as the universal solvent. It dissolves many inorganic salts and polar organic compounds. Water effectively wets many insoluble inorganics, which are common soil components, and it is non-toxic, non-flammable, widely available (admittedly in a variety of qualities) and cheap. Water has so many important qualities which contribute to the cleaning process that it remains unchallenged as our most important cleaning ingredient.

However, today there is major concern worldwide that we are running out of water. Tragically, there are hundreds of millions of people worldwide have no access to clean, safe drinking water [1] That is a very real problem which we all need to be working to solve as soon as possible. Truth be told, though, we are not running out of water. Two-thirds of the surface of the planet is covered in this coveted substance. We are running out of cheap water. Rather, we are exhausting the planet's supply of cheap (fresh) water at a rate faster than it is being replenished. Everyone wants to let Mother Nature do all the hard work of evaporating water into the atmosphere and having it fall gently back to earth as rain, filling our lakes and streams with essentially distilled water, ready for us to use with very little treatment.

Water is a big issue for the cleaning industries. The majority of liquid cleaning products contain water as their primary ingredient. Manufacturers typically do not even include the price of this water in their cost of goods calculation because it is so cheap relative to the other ingredients. No one wants the cost of a product to increase because water has become expensive enough that its cost can no longer be ignored.

Additionally, most cleaning processes involve dilution of the formulated product into an enormous quantity of water to form the cleaning bath. Industries which use, or are perceived to use, large quantities of water in their processes are under constant pressure to reduce water use.

Cleaning technology has responded to this water "shortage" in a variety of ways, inventing creative ways to keep the world clean with little, or no, water. This has been achieved in varying degrees of success, not usually including excellent.



WATERLESS LAUNDRY

Perhaps the first example of waterless cleaning predates our concern about limited water supplies. Dry-cleaning of laundry uses a solvent other than water to remove oily soils from fabric. Kerosene was an early choice, accompanied not surprisingly, by an unacceptable number of laundry fires. Perchloroethylene is used today. It's nonflammable, but it's a long way from being nontoxic.

Dry-cleaning was invented primarily to protect delicate fabrics from enduring the rigors of exposure to water. Generally, you only send your finest clothes to the dry cleaner, and usually they are not very dirty. As a soil removal technique, dry-cleaning is not very effective.

During the Exxon Valdez oil spill disaster, the orange jump suits worn by the clean-up crew were being dry-cleaned. It seemed a natural application, as the soil present was entirely hydrocarbon in nature. Of course, compared to washing in water, it was also expensive. Diversey-Wyandotte (Wyandotte, Michigan, USA) was offered the opportunity to find an alternative method. We won the contract easily. Skilled application of an appropriate surfactant and builder package in a water-borne cleaning solution resulted in a cheaper process and at a much higher level of performance. We returned the jump suits cleaner than was possible with dry-cleaning.

Today, with the aid of ever-helpful government, we have struck a balance between good laundry performance and saving the planet. Most of the energy consumed in washing clothes is used to heat wash water. In order to meet new energy standards for home washers, manufacturers were forced to reduce water usage. Hence, the high efficiency washing machine (horizontal axis) has replaced the top-loader. It's not a new technology. My folks had a horizontal axis Westinghouse washer a half century ago. Now it's fashionable, and mandated, because it saves energy.

It's not waterless laundry, but it's an excellent compromise. Water usage is reduced and performance is not sacrificed. The action of the horizontal drum tumbles the clothes more effectively than a top-loader. This increased mechanical action improves cleaning performance—and also generates more foam. On the other hand, reduced water volume increases the concentration of soil in the wash water, with an increased risk of redeposition. Clever cleaning chemists have reformulated laundry detergents to reduce foam levels and provide better anti-redeposition properties. Today's high efficiency machines produce better quality laundry than the old top-loaders.

WATERLESS HAND CLEANING

Another early example of waterless cleaning is hand cleaning. These products have existed for many years—before our current worries about diminishing water supplies. Waterless hand cleaners are thickened emulsions of water and a hydrocarbon solvent. A sample formula is shown in Table. 1.

TABLE 1. Waterless hand cleaner formula

Ingredient	Wt%
Water	45
Mineral spirits	35
Anionic emulsifier	10
Nonionic emulsifier	5
Emollient	5

These products are used typically where the prevailing soil is composed of heavy greases and oils, such as might be found in a metal-working plant or in a home garage where you work to maintain your classic Chevelle, but have no ready source of running water. These products work quite well, yielding fairly clean hands and, if the product has been formulated with a reasonable emollient package, leaving the skin feeling good as well.

However, if you finish your work under the hood and then turn your attention to the upholstery, you will likely want to head to the sink and scrub your hands in the conventional way. These so-called “waterless” products generally contain about 50% water. Perhaps they might be more accurately called “no-rinse” products.

WATERLESS SHAMPOO

A truly disastrous waterless cleaning technique is hair shampoo. The product consists primarily of an absorbent, such as starch. When applied, it absorbs excess oil, the primary soil which accumulates in hair. These products are generally formulated as aerosols and have formulas similar to that shown in Table 2 [2].

TABLE 2. Waterless shampoo. Source: Spray Technology and Marketing 24: 23, November, 2014.

Ingredient	Wt%
Denatured alcohol	15
Aluminum starch complex	5
Acrylic copolymer	2
Magnesium stearate	1
Aerosol propellant	77

The product is aimed at the late sleeper who needs to “freshen” up his or her hair for the day, but has no time for a conventional shampoo. The technology is used also to further the misery of bedridden patients who are unable to navigate to the shower. Patients who have been forced by circumstances to succumb to this treatment report the results to be awful in terms of appearance and feel. The starch may absorb the oil, but it’s still in your hair. You haven’t cleaned anything, and quite possibly, have made a bad situation worse.

WATERLESS CAR WASHING

Industries which are perceived to be heavy users of water always face tough scrutiny in times of water shortages. The car wash industry is one such example. Driving through a car wash may seem like a trip under Niagara Falls, but automatic car washing does not consume all that much water. Each car requires about 12 gallons. Studies have consistently shown that driveway self-washing of a car consumes as much as 100 gallons of water, by contrast. Additionally, many car washes treat the

wash water and reuse a substantial portion of it. Car washing has been ahead of many industries in water reclamation, treatment and reuse.

Nonetheless, the perception exists that car washing is water intensive. One response is the advent of waterless car washing. The wash formula is sprayed on the vehicle and wiped off with a microfiber polyester towel. The microfiber towel has a very high surface area which traps particles of dirt and grit and isolates them from the surface of the paint—in theory.

Like waterless hand washing, water is involved. The waterless car wash formula is primarily water along with some cleaning surfactants and an array of silicones and/or waxes to leave a shine on the car. It’s not really waterless, as much as it is rinse-free. A typical waterless car wash formula is shown in Table 3.

TABLE 3. Waterless car wash

Ingredient	Wt%
Fatty ester	5
Ester quat emulsifier	5
Glycol ether solvent	10
Nonionic surfactant	10
Water	64
High MW silicone quat	1
Low MW silicone quat	5

You may fear that washing a car without water is similar to wiping it down with a sheet of sandpaper. You would be correct. All waterless car wash formulas warn you to wash the car in a conventional fashion first, if the car is heavily soiled with clay, road dirt, pebbles or mud. In other words, use the waterless system only if the car is already clean.

Waterless washing is popular with owners of show cars, who trailer their museum pieces to an indoor exhibition hall and then back home again to a climate-controlled garage. Also, there is an industry slowly forming in which a roving band of entrepreneurs washes your car at your home or place of work. They use the waterless process because all they need to carry to the site of your vehicle is a trigger-spray bottle of wash formula and a handful of microfiber towels. It’s still important that your car essentially be clean before this treatment.

WATER REMAINS THE MOST IMPORTANT CLEANING INGREDIENT

The cleaning industries have made a fair attempt to generate water-free cleaning technologies. Most of these attempts still involve at least some water, and all have been less than successful at maintaining performance.

On the other hand, we have been very successful in learning how to clean with substantially less water, how to reclaim water to be used again, and how to treat water to be discharged back to the environment possibly even cleaner than before it was used.

The current drought in California is worse than the drought of the 1970s and the state's population has nearly doubled since then. But the government has not (yet) had to impose the same draconian conservation measures on its citizens as was the case back then. That is because water conservation efforts in California, learned in the '70s, have been so successful [3].

The situation is similar throughout the United States. The US Geological Survey recently reported that water usage has reached its lowest level in 45 years. In 2010, 309 million Americans used as much water as 205 million Americans did in 1965 [4].

Of course, the cleaning industries cannot take full credit for this overall conservation effort. But, we did our part. There was a decline in water consumption in every category of water use during this time—including the cleaning industries [5].

In addition to conservation, we have learned to clean the water we have used, a job done largely by the cleaning industries. An impressive array of techniques has been developed that allow us to purify almost any source of water. Chemical manufacturers are synthesizing new surfactants which are friendly to water reclaim systems. Metal cleaning companies use ultrafiltration membranes to remove cleaners and soils from spent solutions. Car wash operators, among others use microbes to degrade detergent ingredients [6]. Water remains, and likely always will remain, the most important ingredient in the cleaning process. And we don't have to worry about that. We are not going to run out of water and we are not doomed to a dirty future.

Formulation Science is produced by Dave McCall. McCall is a chemist for Vaughan Industries, Inc., and an adjunct chemistry faculty member at Madonna University, Detroit Michigan, USA. He is a contributing editor of Inform and can be reached at DaveMcCall@aol.com.

Further reading

1. K. Parker, *Water/Waste Processing*, February, 2015, page 4,
2. *Spray Technology and Marketing* 24: 23, November 2014..
3. K. Reichardt, *Professional Carwash and Detailing* 39: 54, April, 2015.
4. *Water/Waste Processing*, December, 2014, page 18.
5. J. O'Brien, *Chemical Processing* 77: 38, March 2015.
6. *Water/Waste Processing*, February, 2015, page 12.



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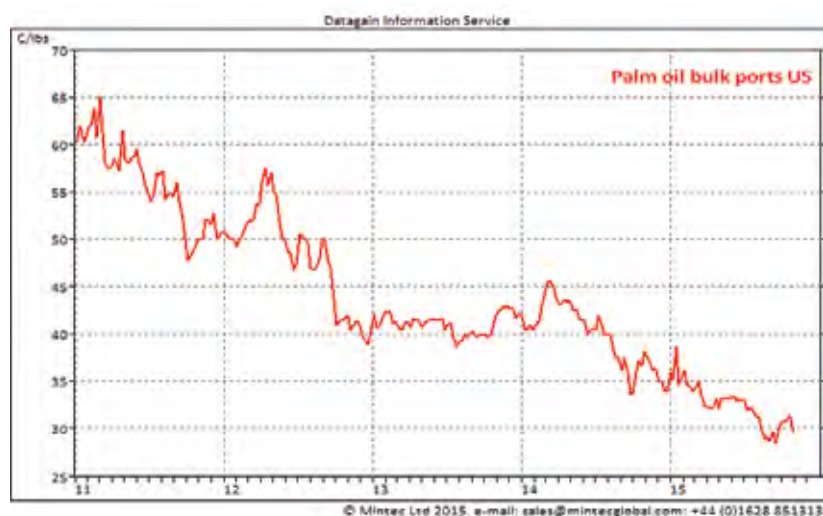
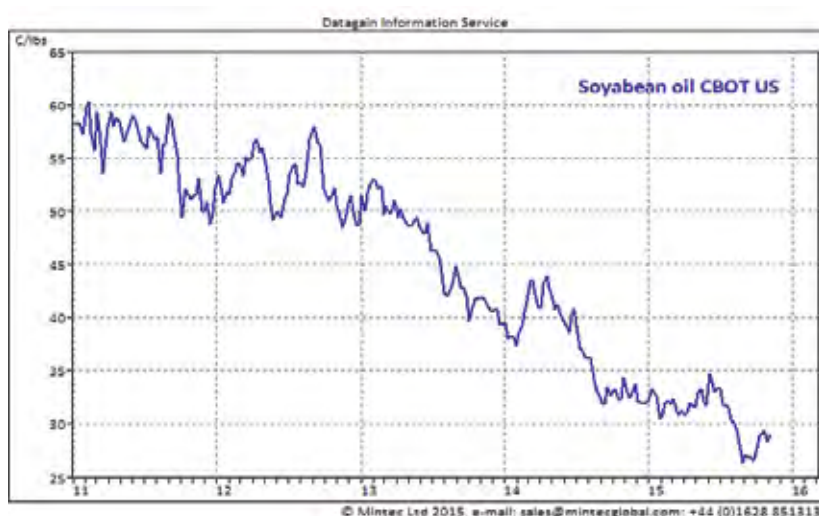

MINTEC

Palm oil prices rose at the start of the final quarter of 2015 as severe dryness and smoke from illegal forest clearing fires in Indonesia raised concerns about damage to the crops in Southeast Asia. However, prices resumed downward trends due to ample stocks in both Indonesia and Malaysia. Global production in 2015/16 is forecast at 65.2 million metric tons (MMT), up 6% year-on-year. However, the growth in palm oil production, primarily in Indonesia, is expected to slow-down in 2016 due to lower yields as a result of this year's El Niño which is forecast to be the strongest since 1997/98. The slowdown of palm oil production will also coincide with a decline in rapeseed production, which may add upward pressure to prices in the vegetable oil market.

Soybean oil prices also rose at the start of Q4 2015 due to a general upward trend in the vegetable oil market. However prices fell again due to forecasts for record production in 2015/16, up 5% year-on-year at 50.7 MMT. Demand for soybean oil is expected to increase steeply due to tight supplies of rapeseed oil and slowing production growth of palm oil. Despite this, production is expected to exceed demand. Consumption for 2015/16 is forecast at 50.2 MMT, up 5% year-on-year.

STATISTICAL ANALYSIS FROM MINTEC

Avneet K. Deol



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AOCS MEETING WATCH

May 1–4, 2016. 107th AOCS Annual Meeting & Expo, Calvin L. Rampton Salt Palace Convention Center, Salt Lake City, Utah, USA. <http://annualmeeting.aocs.org>

October 5–7, 2016. World Conference on Fabric and Home Care—Singapore 2016, Shangri-La Hotel, Singapore. <http://singapore.aocs.org>

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 Patrick Donnelly at patrick.donnelly@aocs.org.



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News from Inform SmartBrief

News from Inform SmartBrief is a regular column that features links to top news summaries from AOCS' weekly e-news, based on subscriber interest. The following are the top 10 stories of October 2015. To sign up for this free service, visit www.smartbrief.com/AOCS.

1. The money behind the fat fight

See <http://tinyurl.com/SB-Fat>

2. Experts stress the importance of fat-carb balance

See <http://tinyurl.com/fat-carb-balance>

3. Food industry could replace trans fats with high-oleic oils

See <http://tinyurl.com/high-oleic-oils>

4. ADM expands its Wilmar stake

See <http://tinyurl.com/ADM-Wilmar>

5. Study: Rapeseed oil compounds could be used in anti-aging applications

See <http://tinyurl.com/rapeseed-aging>

6. Biomimicry could help replace trans fats in food, experts say

See <http://tinyurl.com/biomimicry-trans>

7. Omega-3 suppliers launch ultra-high concentrates for dietary supplements

See <http://tinyurl.com/ultra-high-omega>

8. Lipids' "fab 5" list

See <http://tinyurl.com/lipids-journal>

9. New tech advancements could eliminate trans fat from food

See <http://tinyurl.com/eliminate-trans>

10. Recent study illustrates larger problem in nutrition research

See <http://tinyurl.com/nutrition-research-probs>

AOCS MEMBER NEWS

JAOCS selects new editor-in-chief

James A. Kenar will be the new editor-in-chief of the Journal of the American Oil Chemists' Society as of May 2016.

Kenar has been a senior associate editor for JAOCS since 2006 and an associate editor from 2000–2006. He has also served on several Annual Meeting planning committees, as well as on AOCS membership committees. He is a research chemist at the National Center for Agricultural Utilization Research in Peoria, Illinois, USA, which is a unit of the US Department of Agriculture's Agricultural Research Service.

Kenar succeeds Richard W. Hartel of the University of Wisconsin-Madison, who has been editor-in-chief of JAOCS since 2006. During Hartel's tenure, the journal experienced a significant growth in submissions, published papers, and increased international exposure.

"We congratulate Dr. Kenar, and at the same time we applaud Dr. Hartel for his vision and years of exceptional leadership," said Janet S. Brown, AOCS' director, content management. "JAOCS is—and will continue to be—a premier scientific journal thanks to their dedicated and skillful support."

Colin Ratledge Center for Microbial Lipids opens in China

On October 16, 2015, retired AOCS member Colin Ratledge opened the Colin Ratledge Center for Microbial Lipids at Shandong University of Technology in Zibo City, China. He was also named as the honorary academic director of the Centre, which will work to improve lipid production in various microorganisms.

Ratledge is an emeritus professor of biochemistry in the School of Biological, Biomedical and Environmental Sciences at

the University of Hull, UK. He is one of the foremost researchers in the field of microbial oils and is co-editor of *Single Cell*

Oils, which was published by AOCS Press in 2005. His work, principally on the biochemistry of lipid production and accumulation in oleaginous microorganisms, was developed at the University of Hull over four decades and has been internationally recognized by numerous awards, including the AOCS Stephen S. Chang Award.

King receives Fulbright award

Long-time AOCS member Jerry W. King of the University of Arkansas (USA) is spending five months in Canada as a 2015–2016 Fulbright USA-Canada Scholar. There, he is conducting research aimed at optimizing ultra-high-pressure supercritical fluid extraction employing carbon dioxide for the extraction of enhanced levels of bioactive phospholipid concentrates for use in foods and nutraceuticals. King is collaborating on the work with Feral Temelli of the University of Alberta in Edmonton; they will write a book titled *Pressurized Fluids for Food and Natural Products Processing* for Elsevier.

IN MEMORIAM

Walter A. Farr Long-time AOCS member Walter E. "Sonny" Farr, Jr., 77, died on October 30, 2015, in Olive Branch, Mississippi, USA. A native of Houston, Mr. Farr graduated from Mississippi State University in 1960 with a degree in chemistry and a minor in chemical engineering. He began his career with Wesson ConAgra in Memphis, Tennessee, and also worked for ADM, Anderson Clayton & Co., Kraft General Foods, Owenboro Grain Co., and DeSmet Ballestra. He retired in 2003 and founded The Farr Group of Companies.

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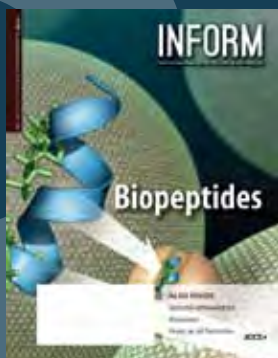
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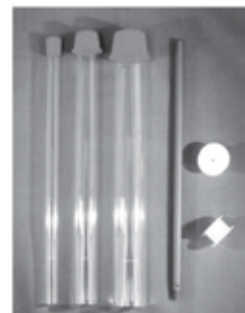
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