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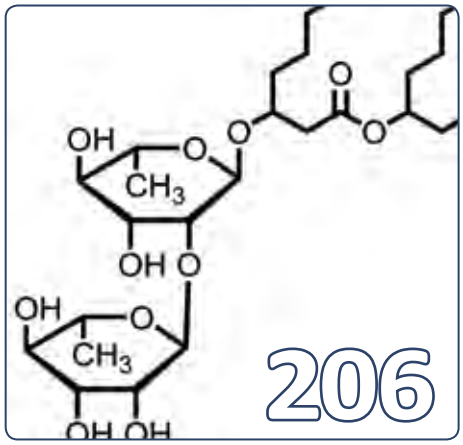






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**INFORM**

International News on Fats, Oils, and Related Materials

ISSN: 1528-9303 IFRMEC 26 (4) 193–272



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Formerly published as *Chemists' Section, Cotton Oil Press*, 1917–1924; *Journal of the Oil and Fat Industries*, 1924–1931; *Oil & Soap*, 1932–1947; news portion of *JAOCS*, 1948–1989. The American Oil Chemists' Society assumes no responsibility for statements or opinions of contributors to its columns.

*Inform* (ISSN: 1528-9303) is published 10 times per year in January, February, March, April, May, June, July/August, September, October, November/December by AOCS Press, 2710 South Boulder Drive, Urbana, IL 61802-6996 USA . Phone: +1 217-359-2344. Periodicals Postage paid at Urbana, IL, and additional mailing offices. **POSTMASTER:** Send address changes to *Inform*, P.O. Box 17190, Urbana, IL 61803-7190 USA.

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# President's profile: **Manfred Trautmann**

First, let me thank you for your trust and support in electing me to become the next president of AOCS; it is a tremendous honor. Looking back at the names of past presidents, I am humbled to be in such company. As your next president, I will follow in the footsteps of my predecessors and do all I can to uphold the image and value of our Society around the world. AOCS's long-term success is driven by a talented and diverse membership that, together with the governing board, CEO, and staff, will collectively support our progress in guiding AOCS to an even brighter future—one in which we will provide a diverse and international audience with high-quality technical content, global networking opportunities, and specialized technical services.

*Trautmann*

My very first exposure to AOCS was in 1982 at the annual meeting in New Orleans, Louisiana, USA. I was impressed from the start and am happy to see that several members I met for the first time at the 1982 convention are still active in the Society. Since then, as an active member of AOCS, I have had the good fortune to be a speaker at subsequent annual meetings.

My background is in surfactants, particularly as they relate to applications in the detergents and personal care industries. In April 1966, I started as an apprentice at the German chemical company Hoechst AG in Frankfurt, Germany. The company supported me in obtaining an engineering degree from the University of Darmstadt, Germany, in 1976. After a stint of three years in Hoechst's central engineering group, I moved toward the applications department for surfactants used in detergents, and later learned more about their use in personal care applications.

An opportunity arose in 1986 to move to the United States for a long-term assignment. Although my education was technical, I moved step by step toward the commercial side of the business. The move to Charlotte, North Carolina, USA, was a major change in my and my family's life. On July 1st, my wife Eva and our two children, Thomas, 6, and Iris, 8, were faced with adjusting to a new environment in a different country. It was astounding for all of us how quickly we felt at home and welcome by people in the company and even more so by people in the neighborhood and almost everywhere we went. Most of my business contacts from that time are still valid and have helped me in my career development as well. Several of the people I worked with at that time are well-known professionals today, holding or having held CEO positions across our industry.

After 10 years of enjoying work and life in the United States and specifically in Charlotte, we moved back to Germany in 1996. Shortly thereafter, our businesses, among other activities at Hoechst, were merged with those of the former Sandoz Specialty Chemicals into the recently created Clariant Co. In 2005, we moved to Clariant's headquarters in Muttenz, Switzerland. Meanwhile, I took on increasing responsibilities that led in 2009 to my appointment as the global business unit head for Clariant's detergents and intermediates business. Four years later, this business was sold to a privately held investment group, International Chemical Investors Group (ICIG), where I continued to be responsible within the WeylChem group of companies for the acquired detergents and intermediates business as well as for the Nease Co. in Cincinnati, Ohio, USA.

Throughout those years, I stayed close to AOCS and participated in the Society's annual meetings. Starting with the 1998 World Conference on Fabric and Home Care in Montreux, Switzerland, I became involved in the organization committee that plans the content and selects the speakers for that conference. Since 2006, I have served on the conference's executive committee, through which we heightened the importance of the conference by inviting more and more CEOs from our industry as keynote speakers, added another

venue in Singapore in 2012, and made this conference the prime meeting place for top-level representatives of the detergents and personal care industry as well as their suppliers and partners.

In 2009, I was asked by the then incoming president (Keith Grime) and current president (Ian Purtle) of AOCS to join the AOCS Board as a member-at-large. I became vice president in 2014, and was elected to serve as AOCS president from 2015–2016. Serving on the governing board helped me observe the inner workings of AOCS, and better understand the things that work and the things that don't work. We've made tough decisions, and helped change the organization's approach to financial stability. Under the guidance of a number of talented presidents, I have watched the AOCS governing board develop into a working board with defined subcommittees, and observed the creation and implementation of a strategic planning process that, with the strong support of AOCS' outstanding CEO, Pat Donnelly, will help lead us into the future.

During my 48-year career working with various companies in technical sales, sales, marketing, and finally general management, I have travelled the world. These travels have taken me to more than 50 different countries and counting. It is a wonderful experience to meet people from all different kinds of ethnic and cultural backgrounds. The lesson I have learned over time is that the world is full of remarkable people.

Today, we find ourselves in an era with an unprecedented rate of change in how we communicate, learn, and adapt to new technology. Globalization is challenging us in everything we do, but it also offers opportunities for the Society and its partners to grow. At AOCS, we are embracing these technological changes to increase our reach and capabilities. As president of AOCS, it is my responsibility to help lead the members, governing board, CEO, staff, and the Society forward—guided by our vision of growth that is implemented through the strategic plan—into becoming a truly global organization.

Thanks for the trust you've shown me to become your next president!

# An introduction to COSMETIC TECHNOLOGY

Perry Romanowski

Cosmetic science is not a subject typically covered in an undergraduate chemistry program, but it is the basis of an entire industry in which many chemistry graduates find themselves working. This review will introduce the basic technology and ingredients used by cosmetic formulators to create functional products.

The definitions for cosmetics differ slightly around the world, but they are basically any substance or mixture that is intended to be applied to the external parts of the human body or the teeth and mucous membranes for the purposes of improving the appearance. In the United States, cosmetics are regulated by the Food and Drug Administration, which defines cosmetics as "articles intended to be rubbed, poured, sprinkled, or sprayed on, introduced into, or otherwise applied to the human body . . . for cleansing, beautifying, promoting attractiveness, or altering the appearance" [Food, Drug and Cosmetic Act, Sec. 201(i)].

## INGREDIENTS IN COSMETICS

There are a number of ways to discuss the ingredients used to make cosmetics, but focusing on their primary purpose for being in the formula makes the most sense. This isn't perfect, since some ingredients have multiple functions, but it provides a good framework for the discussion. Basically, there are three reasons to use an ingredient in a formula: functionality, aesthetics, and marketing.

Functional ingredients provide the primary benefit to consumers who use the product. These are the ingredients that clean the skin, condition hair, and provide moisturization or even color. They are also the so-called active ingredients that make over-the-counter (OTC) drugs work.

The problem with many functional ingredients is that they do not feel nice or apply well on their own. They may even smell bad. Aesthetic ingredients are technologies that make formulas look and feel better; they improve the overall experience of using cosmetics.

Marketing ingredients are ingredients that are not expected to do anything in the formulation but are added specifically to help support the marketing story. Such ingredients are important, since they often provide the entire reason for purchasing a product, but they are not actually expected to have a significant impact on the formula's performance. For example, consumers prefer to buy moisturizing products with aloe vera rather than petrolatum—even though the latter is the ingredient that actually provides the benefit. Marketing ingredients are not the focus of this review, but it is important to know how they are used.

The cosmetic ingredients that have the most impact on the way cosmetics work are the functional ingredients. These include:

- surfactants,
- conditioners/moisturizers,
- colorants,
- polymers, and
- active ingredients.

This review will focus on the first two categories, which include surfactants as well as lipids and oils.

# SURFACTANTS AND THEIR APPLICATIONS IN COSMETICS

**Surfactants and lipids are important ingredients in cosmetics. This article describes:**

- **their key properties and functions in cosmetics,**
- **the four types of surfactants used in cosmetics, and**
- **some common applications for surfactants and lipids in cosmetics.**

Surfactants are perhaps the most important of all cosmetic ingredients. Surfactants have so many useful applications that the cosmetic industry probably wouldn't exist without them. In cosmetics, surfactants are used for cleansing, foaming, thickening, emulsifying, solubilizing, penetration enhancement, antimicrobial effects, and other special effects.

The key property of surfactant molecules that makes them useful cosmetic ingredients is that they are compatible with both water and oil. When put in a water solution, they naturally create structures with lipophilic portions aligning with lipids and hydrophilic portions aligning with water. The exact structure that is produced depends on the concentration of the surfactant solutions but the most important structure for cosmetics is micelles.

**DETERGENCY.** One of the most common applications of surfactants in cosmetics is for cleansing formulations. When skin and hair get dirty there are really two types of dirt: solid particulates and oily deposits. The oily deposits come from natural sebum which is produced in the hair follicles. Solid particulates are just naturally picked up from the environment. They remain on hair and skin via Van der Waals forces.

Although rinsing the surface with water can remove some of the dirt, oily deposits will tend to adhere to the more lipophilic surfaces of hair and skin. Surfactants in detergent help get rid of these oily deposits. The lipophilic ends of the molecules are attracted to and align with the lipids on the surface of hair and skin. Meanwhile, the hydrophilic ends of the molecules align toward the surface of these deposits, thereby increasing the hydrophilicity. That allows the lipid deposits to lift off the surface of skin or hair where the rinse water washes them away.

**WETTING.** Surfactants are also wetting agents that reduce the contact angle between a solution put on a surface and the surface. This property allows surfactants to spread more easily on the surface and inject themselves between the oily deposit and the skin or hair surface. This lifts up the oil and allows it to be removed. Wetting also makes the product easier to spread and prevents it from balling up on the surface. This is useful in cosmetic creams and lotions.

**FOAM.** Foam is an important characteristic of cleansing cosmetics. It is formed when air is dispersed in a continuous liquid medium. The air bubbles are surrounded by thin layers of liquid, and the surfactants help stabilize the bubbles that are formed, creating foam. It's important to note that foam doesn't really contribute much to the removal of dirt but consumers like it, so it's very important for a cleansing product to foam.

**THICKENING.** In a water/surfactant solution in which water is the major ingredient, surfactants align themselves in structures called micelles. These are tiny spherical structures in which the lipophilic tails orient inwards and the polar heads orient outwards toward the water. Micelles are important for the creation of emulsions and for thickening.

The thickness of a surfactant solution depends on how closely the micelles pack together. Since cleaning products are typically made from

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charged surfactants, the outer surfaces of the micelles have a specific charge density that causes them to repel other micelles. The more distance between the micelles, the thinner the solution. When the surface charge density is lowered—by adding salt, for example— the particles pack together more closely, and the solution thickens. For this reason, salt is frequently added to adjust the viscosity of detergent systems.

**EMULSIFICATION.** Another major application of surfactants to cosmetics is in the creation of semi-stable mixtures of oil and water, or emulsions. Emulsions are the creams and lotions that deliver beneficial lipid materials to the surface of skin and hair. They can be simple oil-in-water or water-in-oil emulsions or more complex multiple emulsions. Each type has benefits that make it ideal for certain cosmetic applications. An entire article can be written about emulsions, but for our purposes, suffice it to say that nearly all creams and lotions are created using surfactants.

## TYPES OF SURFACTANTS

Surfactants can be classified according to the charge of their counterion or whether they form ions in solution or not. There are anionic surfactants, which have a negatively charged ion. There are amphoteric surfactants, which are capable of both positive and negative charges depending on the pH conditions of the solution they are in. There are cationic surfactants, which are positively charged. And, finally, there are nonionic surfactants, which have no charge at all. All four of these surfactant types are used in cosmetics for different reasons.

**ANIONIC.** Anionic surfactants, the most common of which are the alkyl sulfates, are really the primary ingredient used in cleansing products. They are positively charged surfactant ions. Examples include sodium lauryl sulfate and ammonium lauryl sulfate (ALS).

Sometimes anionic surfactants are modified to make them less irritating. For example, ALS is commonly "ethoxylated" by reacting it with ethylene oxide to produce ammonium laureth sulfate. This additional chemical processing makes the final product significantly less irritating and slightly more water soluble.

Nowadays there is a tendency for companies to get away from using ingredients with the name "sulfate" in them, so other options are used. Other anionic surfactants include sulfosuccinates, alkyl benzene sulfanate, acyl methyl taurates, acyl sarcocinates, the isethionates, propyl peptide condensates, monoglyceride sulfates and fatty glycerol, ether sulfanates. These are all anionic surfactants that have been used in shampoos or body washes.

Anionics are used primarily as the main detergent in cosmetics because they are good at removing dirt and oil, they produce pleasing amounts of foam, and they are relatively inexpensive. Their primary drawback is that they can be irritating. This is why they are often blended with amphoteric surfactants.

**AMPHOTERIC.** Amphoteric surfactants can have both a negative charge and a positive charge, depending on the pH. These materials are also referred to as zwitterionic materials, and they include ingredients such as cocamidopropyl betaine, cocoamphopropionate, and sodium lauraminopropionate. These three ingredients are probably the most commonly used amphoteric surfactants in cleansing products, particularly in shampoos.

Amphoterics are used because they have good detergency and are less irritating than the anionics. They also can help thicken a formula and have a positive effect on foam, as they make the bubbles smaller and feel creamier. The main drawback to using them is that they are significantly more expensive and, on their own, don't really foam well enough to produce a good shampoo.

**NONIONIC.** Nonionic surfactants are molecules that do not have a charge. When placed in a solution of water, the molecules do not dissociate as the previously mentioned surfactant molecules do. Salt also has no effect on whether these chargeless surfactants thicken or not. Some types include fatty alcohols and fatty alkanolamides, including lauramide diethanolamine (DEA) and cocamide DEA. Other nonionic surfactants found in cosmetics include amine oxides such as lauramine oxide or stearamine oxide.

There are a variety of reasons to use nonionics in cosmetics. They are good foam enhancers (when used with anionics) and can reduce irritation. They also can thicken systems and provide a conditioning effect. Additionally, they are very good for solubilizing fragrances and other natural oils in formulating. Finally, gentle cleansers such as baby shampoos are based on nonionics, the most common of which is PEG-80 sorbitan laurate. Nonionic surfactants are also the primary surfactants used to create emulsions.

The reason these surfactants aren't used as the primary cleansing surfactant in most formulas is that they don't foam nearly as well on their own and are significantly more expensive. Overall, nonionics do not work as well as anionics in shampoos.

**CATIONICS.** These are positively charged surfactant molecules. They are not used for cleansing formulas because they don't clean, rinse, or foam as well, and they are more irritating—so they have a lot of drawbacks. They are also not compatible with anionics, so their positive benefits can't be obtained from formulations that also contain an anionic surfactant.

That being said, cationics are great for conditioning. They are substantive during use and are the primary ingredients for rinse-off hair conditioners.

## CONDITIONING INGREDIENTS

Conditioning and moisturizing ingredients are materials that improve the feel or condition of whatever surface they are put on, including the skin or hair. They typically have an "oily" nature and , to be effective, they must also be substantive or left behind on the surface in some way. Materials that are easily washed away do not make good conditioning or moisturizing ingredients.

There are a wide range of different types of conditioning and moisturizing ingredients but the most common include: cationic surfactants, or quats; occlusive; emollients; and humectants.

Cationic surfactants used for conditioning are also known as quaternary ammonium compounds, quaternized compounds, or just simply "quats." They contain at least one nitrogen atom bonded to four other hydrocarbon groups. Some common examples include stearalkonium chloride, dicetyldimonium chloride, and behentrimonium chloride.

Although cationic surfactants don't make good cleansing products, they are excellent conditioning ingredients, particularly for hair care products. The main reason is because they are substantive to the damaged, negatively charged protein sites on hair and skin. When a quat is put on hair or skin, the positive portion of the molecule is attracted to the negatively charged damaged site creating an electrostatic bond. While water rinses most things away, the cationic surfactant remains.

Since these are hydrocarbon molecules, the longer the hydrocarbon chain is, the more conditioning they will do. So, all things being equal, a material such as behentrimonium chloride, which is a C22 carbon chain, will be more conditioning than a shorter chain molecule such as cetrimonium chloride, which is a C16 carbon chain.

**OCCLUSIVES.** Perhaps the most effective skin moisturizing ingredients are occlusive agents. These are oily materials that can create a thin coating on the skin or hair. The most common types of occlusive agents used in cosmetics include petrolatum, mineral oil, and dimethicone.

When occlusive agents are put on the skin (or hair) they form a thin, continuous film on the surface. This film is flexible but feels slightly greasy to the touch, which is why only a small amount is used in formulations. The occlusive film is also resistant to water, which helps explain its moisturizing effect.

The body naturally loses water through skin. When atmospheric humidity is low, more moisture is lost and skin feels dryer. Occlusive agents create a film on the skin which slows the water loss. As water tries to leave the body, it hits this barrier and starts to accumulate in the outer layers of the skin (the epidermis). This extra moisture improves the way the skin looks and feels and also can reduce itching and redness.

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Occlusives such as petrolatum are so effective they can actually be used as OTC drugs for skin protection.

**EMOLLIENTS.** Emollients were some of the first ingredients used as cosmetics. They are not typically compatible with water and include ingredients such as oils, butters, waxes, and esters. Emollients are similar to occlusive agents, except that they tend to be lower-molecular-weight molecules and don't have the ability to form a continuous film to block water. But, emollients are important ingredients for improving the way the surface of the hair and skin feel, and they impart shine, which is the primary reason they are used.

When creating skin creams, lotions, and even hair products, emollients are used to modify the way formulations feel, how they rub into the skin, the ease at which they spread, and the length of time they remain "workable."

Common examples of emollients include natural oils such as coconut oil, argan oil, almond oil, or olive oil. There are also a number of excellent esters that are emollients, including myristyl myristate, cetyl palmitate, and lauryl laurate. Each of these feels slightly different and has different abilities to absorb into the skin. In addition, many silicones make excellent emollients, as they provide great slickness and shine.

**HUMECTANTS.** Humectants have been used as cosmetic compounds for as long as cosmetics have existed. They include natural materials such as honey, aloe, or glycerin, and are typically mild. The property that makes humectants useful is their ability to attract and hold water like a sponge. In fact, glycerin can hold as much as three times its weight in water. Such humectants are especially useful for surfaces that tend to dry out, such as skin or hair.

The most common humectants used in cosmetics include glycerin, propylene glycol, sorbitol, sodium pca, hyaluronic acid, and various hydrolyzed proteins.

Humectants have few significant negatives: They feel sticky and are easily rinsed away. This limits their use to cosmetic products that will be left on, making them great for skin lotions and leave-on hair conditioners but not so great for shampoos, body washes, or rinse-out hair conditioners.

There are numerous other technologies used to create cosmetic formulas, including colorants, preservatives, fragrances, polymers, and other active ingredients. You can find more information about the ingredients in cosmetics at http://chemistscorner.com.

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*Perry Romanowski is publisher of Cosmetic Chemists Corner, a website written for cosmetic chemists by cosmetic chemists. Romanowski has been formulating cosmetic products and inventing solutions to solve consumer problems since the early 1990's. He has written and edited numerous articles and books, taught continuing education classes for industry scientists, and developed successful websites. More information on cosmetic ingredients can be found at http://chemistscorner.com.*

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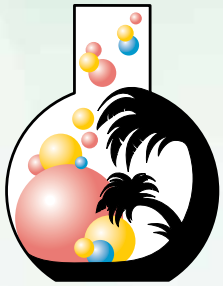

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# **Rhamnolipids and related biosurfactants** for cosmetics and cosmeceutical markets

**Chett J. Boxley, Jeanne E. Pemberton, and Raina M. Maier**

Demand for effective and environmentally compatible specialty surfactants is steadily increasing in the cosmetic industry. In the search for suitable candidates to meet this demand, scientists have turned to the microbial world for inspiration. After all, over the past 3.5 billion years, bacteria and other microorganisms have evolved structurally unique molecules, including surfactants. Microbial surfactants, also known as biosurfactants, are a diverse group of molecules produced by a wide array of bacteria, archaea, and fungi (Soberon, Chavez, and Maier, 2010). Biosurfactants exhibit a structural elegance which, in many cases, defies conventional chemical intuition that would predict little surface activity. In fact, these molecules exhibit powerful surfactant activity at both liquid and solid surfaces.

- **Biosurfactants not only exhibit powerful activity at both solid and liquid surfaces; they often confer antibiotic, antifungal, anti-aging, anti-wrinkle, insecticidal, antiviral ~~anti-aging~~, anti-microbial, and other biological properties that could be useful in cosmetic and cosmeceutical applications.**
- **Unfortunately, biosynthesizing the highly purified materials needed for such applications is very challenging, and batch-to-batch variability has led to high costs and low availability.**
- **This article describes how recent advances in synthetic production make it possible to produce low-cost, high-purity rhamnolipids whose chemical properties can be tailored for different applications.**

Since their initial discovery and introduction to the marketplace in the 1960's, biosurfactants have experienced a steady rise in interest and potential applications as "green" alternatives to traditional petroleum-based surfactants. This is due to a combination of their environmentally friendly characteristics, including low toxicity and ready biodegradability, their excellent surfactant attributes, and their unique head group structures. In certain cases, these materials confer additional attractive properties for cosmetics, including the potential for anti-aging and anti-microbial activity. Biosurfactants are expected to reach global sales of $2.8 billion in 2023. The largest impediments to their use, and the reason this number is not higher, are the high cost of production, a lack of consistent availability, and the fact that biosurfactants are produced as complex mixtures of up to more than 40 congeners where the hydrophilic head groups are fairly conserved and the hydrophobic tail groups have considerable variation. Component congeners within these complex mixtures have

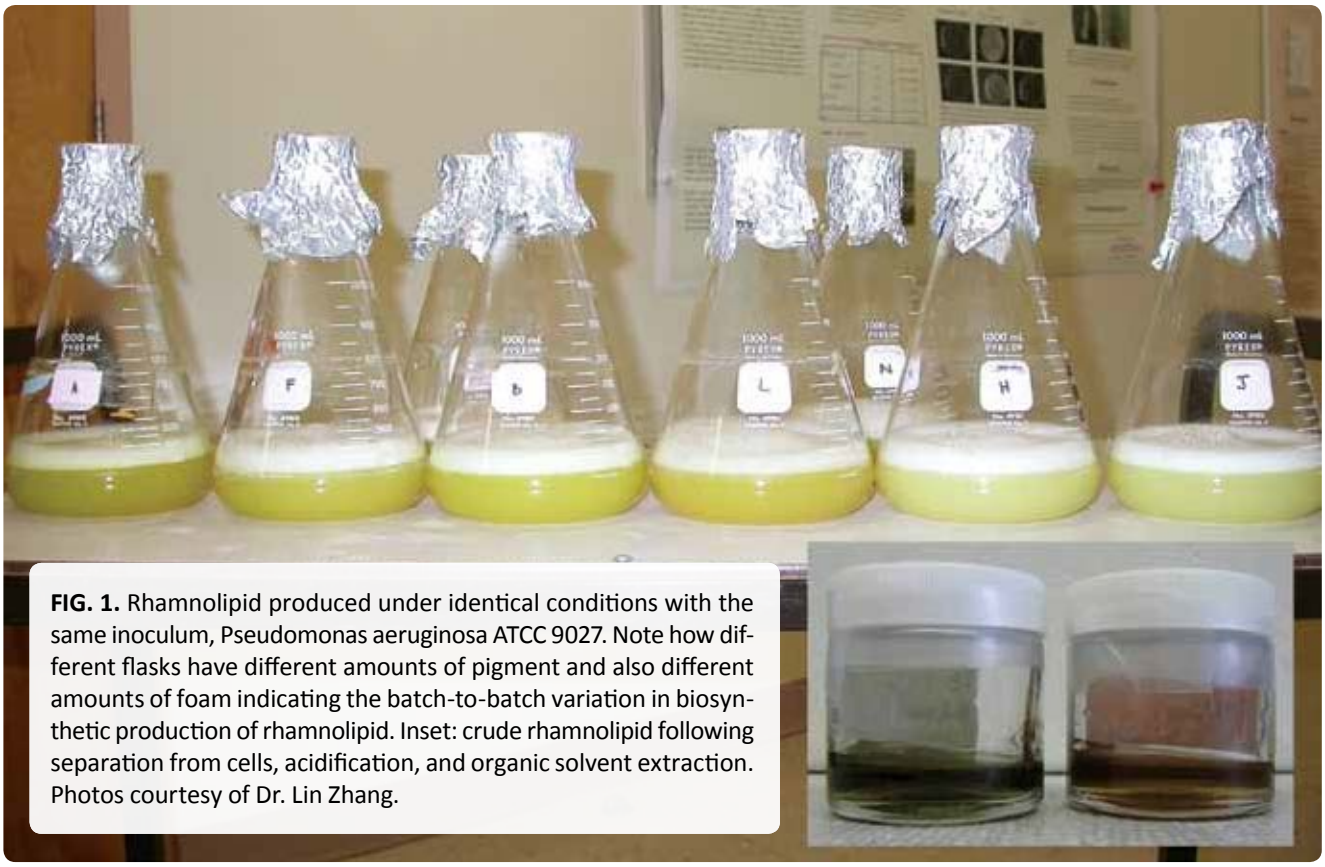

**FIG. 1.** Rhamnolipid produced under identical conditions with the same inoculum, Pseudomonas aeruginosa ATCC 9027. Note how different flasks have different amounts of pigment and also different amounts of foam indicating the batch-to-batch variation in biosynthetic production of rhamnolipid. Inset: crude rhamnolipid following separation from cells, acidification, and organic solvent extraction. Photos courtesy of Dr. Lin Zhang.

different properties due to differences in their hydrophobe structures, and the fact that the congener mixture distribution has batch-to-batch variation renders the performance attributes of these materials somewhat variable (Fig. 1).

Biosurfactants have a wide range of chemical structures and are generally classified according to molecular weight and the chemical composition of their head group. Low-molecular weight biosurfactants include lipopeptides, fatty acids, phospholipids, flavolipids, and a class of compounds known as *glycolipids* which are comprised of sugar-based headgroups connected to an alkyl chain-containing hydrophobe. The best-studied biologically produced glycolipids are the bacterially produced rhamnolipids and the sophorolipids, which are produced by yeast (Fig. 2, page 208). Sophorolipids are currently used more widely in commercial applications due to their lower manufacturing costs (~100X lower due to higher production yields and simpler purification) and the use of a non-pathogenic production organism. A recent article in *Inform* thoroughly outlines the state-of-the-art technology and applications for sophorolipids (Develter, 2013). Despite the clear current advantages of sophorolipids, the rhamnolipids are believed to possess better surfactant performance metrics as well as additional beneficial anti-aging and anti-microbial/anti-fungal properties.

Biosynthetic production and purification of rhamnolipid is a complex process that is challenging to scale. Rhamnolipids are produced and then excreted from the cell into the production medium by *Pseudomonas* spp. and other closely related gram-negative bacterial genera. Rhamnolipids have been reported to be produced at levels up to 100 g/L in comparison to sophorolipids which can be produced at levels exceeding 400 g/L. Active research is ongoing internationally to improve rhamnolipid yields (and reduce costs) by isolating new bacterial strains or by genetically modifying existing strains. One challenge of these materials is that some of the species that are good rhamnolipid producers are opportunistic pathogens, which adds to the cost of handling the organism and producing the biosurfactant. The rhamnolipids produced biosynthetically are part of a complex mixture of spent medium, extracellular pigments and other

CONTINUED ON NEXT PAGE

## Further reading


- Coss, C.S., T. Carrocci, R.M. Maier, J.E. Pemberton, and R. Polt. Minimally competent Lewis acid catalysts: indium(III) and bismuth(III) salts produce rhamnosides (=6-deoxy-mannosides) in high yield and purity, *Helv. Chim. Acta*, *95*:2652–59, 2012.
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- Soberon-Chavez, G., and R.M. Maier, Biosurfactants: general overview. *In Biosurfactants: From Genes to Applications. Microbiology Monographs*, Springer, pp. 1–11, 2010.
- Stipcevic, T., A. Piljac, and G. Piljac, Enhanced healing of full-thickness burn wounds using dirhamnolipid, *Burns 32*:24–24, 2006.


**FIG. 2.** Chemical structures of the two best-known classes of biosurfactants. Left: mono- and dirhamnolipids; right: sophorolipids (free acid form).

impurities, and cells. Following centrifugation to remove the cells, the rhamnolipids are acid precipitated and isolated with an organic solvent extraction. These steps produce a crude oily mixture of rhamnolipid, pigments, and other impurities which must undergo further purification steps for cosmetics or pharmaceutical applications (see inset, Fig. 1). Thus, purification of rhamnolipid is a major cost factor that has limited wider adoption of these green materials. Downstream purification processing costs of rhamnolipids have been estimated to be responsible for 70–80% of the total production costs. As mentioned, research in the area of rhamnolipid production to lower production costs is extremely active; however, this research has been primarily focused on increasing and optimizing rhamnolipid production rather than on separation and purification of the biosurfactant following production.

## RELATED BIO-INSPIRED GLYCOLIPID SURFACTANTS

Synthetically produced sugar-based surfactants (glycolipids) are receiving increased attention in the exciting and growing field of sustainable surfactants. Although many of these glycolipids have been well-known for decades, they have been used only for niche applications due to their high cost and relatively limited availability. Researchers at the University of Arizona in Tucson, Arizona, USA, have developed a transformative approach for production of glycolipids using chemical synthesis techniques (Coss, *et al.*, 2012). Glycolipid structures ranging from simple (e.g. O- and S-linked alkyl pyranosides) to complex (e.g. rhamnolipids) have been synthesized using this process. These "bio-inspired surfactants" have some distinct differences as well as some key advantages over their biosynthetic counterparts (Fig. 3). Advantages include production at very high purities and low cost, and the opportunity for tailoring of surfactant performance.

Using rhamnolipids as an example, this synthetic approach yields high-purity, single congener surfactants. The specific congener of interest is chosen for synthesis eliminating the production of multiple congener mixtures and associated batch-to-batch variation that results from biosynthesis. One major difference between synthetic and biosynthetic rhamnolipids is that synthetic rhamnolipids are produced as a mixture of four diastereomers (R-,R-; S-,S-; S-,R-; and R-,S-) reflecting the two chiral centers in the molecule. In contrast, the biosynthesized rhamnolipids are

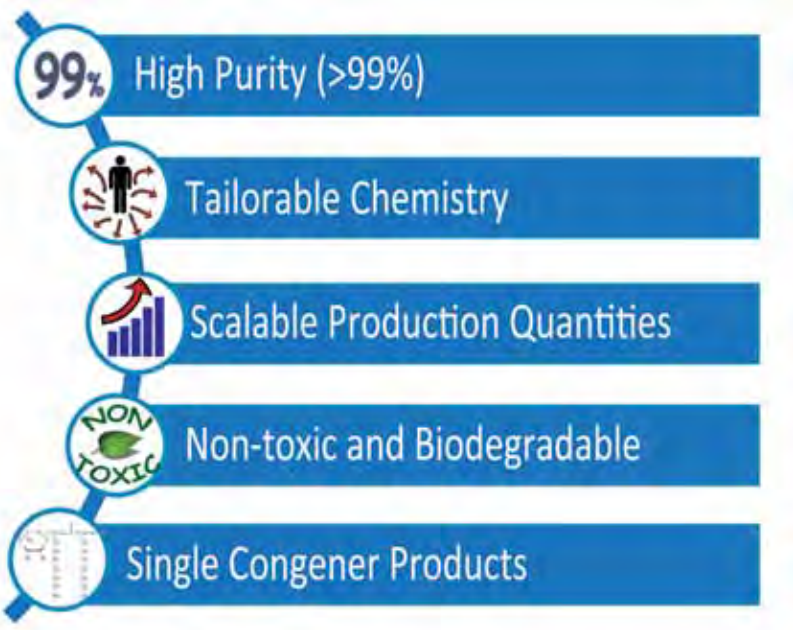


**FIG. 3.** Advantages of synthetically produced glycolipids.

produced stereospecifically as the R-,R- diastereomer. Early research is showing that although all four synthetic diastereomers appear to be biodegradable, there is variation in surfactant activity and other properties among them.

An additional major advantage to the synthetic rhamnolipids is that their production can be scaled to amounts that have been previously unavailable in the marketplace. Associated production costs are orders of magnitude lower than biosynthesized rhamnolipids of equivalent purity. The synthetic rhamnolipids produced by this patent pending technology are being offered by GlycoSurf, LLC, a company started by the University of Arizona researchers who developed this approach.

## USE OF RHAMNOLIPIDS IN COSMETICS AND COSMECEUTICALS

Cosmetics, cosmeceuticals, and other personal care products such as shampoos and skin-care formulations represent areas of intense research and development for rhamnolipids. These applications require that ingredients be compatible with skin application showing low irritancy or even anti-irritating effects. Interest in rhamnolipids stems from a recent study that demonstrates both tolerance and enhanced healing of burn wounds following topical treatment with 0.1 wt% of a biosynthesized dirhamnolipid mixture (Stipcevic, *et al.*, 2006). Both the rhamnolipids and rhamnose, the sugar component of rhamnolipids, have also been shown to have beneficial anti-aging and anti-wrinkle effects. Such anti-wrinkle and anti-aging formulations are experiencing a surge in consumer demand in developed countries because of their aging populations. Rhamnolipids have the added benefit of inhibitory activity against certain bacteria and fungi that can act as opportunistic pathogens, including *Escherichia coli, Micrococcus luteus, Alcaligenes faecalis, Serratia marcescens, Aspergillus niger, Chaetonium globosum,* and *Enicillium crysogenum*. With the possibility of further tailoring the properties of rhamnolipids through chemical synthesis approaches coupled with excellent chemical stability and shelf life, the rhamnolipids would seem to have an exciting future in cosmetics and cosmeceutical markets.

## POTENTIAL ENHANCED BY SYNTHETIC PRODUCTION

Biosurfactants comprise a diverse group of surface active compounds that have been explored for a variety of environmental and agricultural applications that do not require pure materials. These materials additionally display important biological activities, including antibiotic, antifungal, anti-aging, anti-wrinkle, insecticidal, antiviral, immunomodulator and anti-tumoral activities. However, applications in the cosmetics and cosmeceuticals industries that could take advantage of these properties require highly purified materials. Biosynthetic

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production of highly purified biosurfactants is challenging, and this, combined with batch-to-batch variability in multi-congener mixtures, has led to high costs and low availability of pure materials, even for research and development testing. Synthetic production of rhamnolipids through a scalable process is a recent breakthrough that results in low cost, high purity materials whose chemical properties can be tailored for different applications. For the first time, these glycolipid biosurfactants are available at reasonable cost and in sufficient quantities to allow testing for many new applications, including cosmetics and cosmeceutical formulations.

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# BRIEFS

The Supreme Court of India dismissed an appeal by the Food Safety and Standards Authority of India (FSSAI), according to *The Hindu Business Line* (http://tinyurl.com/canola-India), thereby permitting importers of canola oil to refer to it by its internationally traded name. Previously, FSSAI had required that canola oil be labeled as "rapeseed oil—low erucic acid."

■■■

A new quarterly journal from Springer—ChemTexts—provides peer-reviewed texts for academic education in chemistry and biochemistry. The articles may be used by students for learning, by lecturers for teaching, or by researchers and professionals as a recap of essential knowledge. The journal is primarily aimed at the bachelor's and master's level, but material at the graduate level is also being considered. For more information, visit http://tinyurl.com/Springer-ChemText.

■■■

The European Food Safety Authority (EFSA) has ruled that European adults require on average 0.83 g of protein/kg body weight. EFSA used nitrogen balance data to establish a Population Reference Intake that equals 58.1 g of protein daily for a 70 kg adult. See http://tinyurl.com/EFSA-protein (PDF) for the complete opinion.

■■■

Ag Processing Inc. (AGP; Omaha, Nebraska, USA) announced that the company's board of directors has approved plans for the construction of a soybean oil refinery at AGP's Sergeant Bluff, Iowa, facility. Current plans anticipate completion of the new refinery in the spring of 2017.

■■■

Archer Daniels Midland Co. (ADM; Chicago, Illinois, USA) is selling its global cocoa business to Olam International Ltd. (Singapore) for $1.3 billion. The proposed sale, which is contingent on customary regulatory approvals, is expected to close during the second quarter of 2015. "This transaction does not impact the sale of ADM's chocolate business to Car-

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# NEWS & NOTEWORTHY

## Patent applicants prefer disclosure

Common wisdom and prior economic research suggest that an inventor filing a patent would want to keep the technical knowledge secret as long as possible. However, a new study of nearly two million patents in the United States shows that inventors are not as concerned with secrecy as was previously believed. Researchers found that since 2000, most inventors when given the choice opted to disclose information about their patents before patent approval.

"Do inventors really value the secrecy that economists assumed they did based on the prior literature? Our findings are that overwhelmingly, and in every category that we can test, inventors don't," said Stuart Graham, study co-author and assistant professor at the Georgia Institute of Technology's Scheller College of Business (Atlanta, USA).

The study, co-authored with Deepak Hegde of New York University (NYU; New York, USA), was published in the journal *Science* (http://dx.doi.org/10.1126/science.1262080, 2015).

In 2000, the length of time that inventors could keep patents secret after filing was cut in half. The American Inventors Protection Act (AIPA) was signed into law that year, requiring publication of patent applications 18 months after first filing. Prior to 2000, the applications filed only in the United States were kept secret and made public after approval, typically 36 months after filing.

During the congressional debate over AIPA, prominent inventors raised concerns that reduced secrecy would harm not only small inventors, but undermine the inventive spirit in the United States. Therefore, a loophole was included in the bill, allowing inventors to maintain secrecy of their patent applications if they were not also filing for parallel foreign patent protection on the same invention. In the United States, that accounts for about half the granted patents.

The change in the law created an opportunity for Graham and his colleague Deepak Hegde, an assistant professor of management

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and organizations at NYU's Stern School of Business, to examine which inventors were choosing to opt into the secrecy loophole, and whether their patents differed in important ways. Graham and Hegde examined 1.8 million granted patents filed at the United States Patent and Trademark Office (USPTO) from 1995 to 2005 and analyzed the disclosure preferences of the inventors.

The researchers found that, among those not seeking foreign protection, about 85% of inventors filing a patent since 2000 chose to disclose information about their patents prior to their approval.

"Overwhelmingly, those inventors patenting only in the United States are choosing 18-month disclosure," co-author Hegde said.

The patents examined in the study are called utility patents, which are available on new and useful processes, machines, manufactured articles, or compositions, and protect technologies like software, laptops, medical devices, and drugs. Utility patents are the most common type of patent, with more than 570,000 filed at the USPTO in 2013 alone.

When the AIPA was passed, one of the biggest complaints was that the publication requirement would hurt independent US inventors, but the scientists found that individuals and small companies still opted for disclosure during the study period.

"Small US inventors are not choosing the secrecy route," Graham said. "When they patent only in the United States, they are choosing secrecy in only about 15% of the cases, not statistically different than the rate among all other types of inventors."

"This study is a first window into what inventors are really doing. The next question is why are they doing it?" Graham said. "It remains for us to figure out why inventors seeking to maximize the value of their inventions are not particularly interested in pre-patent secrecy."

## ADM, Unilever expand partnership in fats, oils

Archer Daniels Midland Co. (ADM; Chicago, Illinois, USA) has signed a Joint Business Development Plan (JBDP) to continue to expand its relationship as an oils and fat supplier for Unilever in Europe, North America, and Africa. The JBDP defines the long-term strategy and goals for the relationship and provides a clear framework for how ADM and Unilever will work together to achieve those objectives. It also sets measurable goals around volume, new product development, growth, innovation, and sustainability.

Existing joint programs will continue, the companies said in a news release. These include the ADM/Unilever Soybean Sustainability Program in the United States, through which ADM sources and processes sustainable soybeans and supplies Unilever with oil for Hellmann's Mayonnaise. The companies also maintain a partnership with LEAF (Linking Environment and Farming) in Europe, which promotes sustainable agricultural practices at the farm level to produce sustainable rapeseed oil for Unilever's Flora spreads, as well as for Hellmann's UK. The JDBP will also strengthen ADM's existing European sustainability initiatives, particularly in Central and Eastern Europe, enhancing the company's supply chain to

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provide Unilever with more sustainably produced oils and fats products, according to the news release.

## Mars, IBM partner on food safety

Scientists from IBM Research and Mars, Inc. have established the Consortium for Sequencing the Food Supply Chain (http://www.mars.com/ibmconsortium), a collaborative food safety platform that will leverage advances in genomics to understand what makes food safe.

The companies said in a news release that they will conduct the largest-ever metagenomics study to categorize and understand microorganisms and the factors that influence their activity in a normal factory environment. This work could be extended into the larger context of the food supply chain—from farm to fork—and lead to new insights into how microorganisms interact within a factory.

As a first step, the consortium's scientists will investigate the genetic fingerprints of living organisms such as bacteria, fungi, and viruses and how they grow in different environments. These data will be used to further investigate how bacteria interact, which could result in completely new ways to view supply chain food safety management.

"Genome sequencing serves as a new kind of microscope—one that uses data to peer deeply into our natural environment to uncover insights that were previously unknowable," said Jeff Welser, vice president and lab director, IBM Research–Almaden. "By mining insights from genomic data, we're seeking to understand how to identify, interpret, and ultimately create healthy and protective microbial management systems within the food supply chain."

For more information about the consortium, visit www.ibm.com/wildducks.

## ASA: support neonicotinoid seed treatment

The American Soybean Association (ASA; St. Louis, Missouri, USA) reiterated support for pollinator health and the benefits of neonicotinoid seed treatments to soybean farmers in comments to the US Environmental Protection Agency (EPA).

EPA released an analysis in October 2014, which contended that neonicotinoid seed treatments do not contribute to improving soybean yield; however, ASA says it has anecdotal evidence, especially in the northern and mid-south growing regions of the United States, that growers are seeing insect control benefits from the use of neonicotinoid seed treatments.

ASA pointed to reports of falling oilseed production in Europe, attributed to the EU's restriction on the use of three neonicotinoids: clothianidin, imidacloprid, and thiametoxam, citing reports of many farmers having to plow up their autumn-sown crops after flea beetle attacks. ■

gill, which is progressing as planned," the company noted in a news release.

## NEWSMAKERS

Floyd E. Friedli, a long-time AOCS member, retired from Akzo Nobel Surface Chemistry at the end of 2014 after 36 years in the surfactants industry. He spent 12 years as an account manager for Akzo and prior to that was in R&D for 24 years—ending as technology manager–Synthesis & Fabric Care—with Sherex, which became Witco, then Goldschmidt, then Degussa, and, finally, Evonik. Friedli is a former associate editor of the *Journal of the American Oil Chemists' Society* and the *Journal of Surfactants and Detergents (JSD)* as well as a member of the Rosen Award and *JSD* Best Paper Committees. He has formed Friedli Chemical Consulting, LLC, and can be reached at floydefriedli@yahoo.com.

■■■

AOCS member David C. Ailor, formerly executive vice president of regulatory affairs for the National Oilseed Processors Association, has opened Ailor Consulting in San Diego, California, USA. He will continue to advise NOPA on regulatory issues and will also serve as president of the American Coke and Coal Chemicals Institute. He can be reached at dailor@nopa.org.

## IN MEMORIAM

Emeritus member, Award of Merit winner, and former Smalley Committee Chair Jim M. Ridlehuber died on January 15, 2015. According to his daughter Sue, he was "always proud of his chosen profession and his association with AOCS. His 94 years were filled with love, joy and learning, and AOCS played an important role in his long and wonderful life."

■■■

*Inform* has received word that AOCS Fellow Kenkichi Oba, 78, died on January 24, 2015. Dr. Oba, who rose to the position of executive director and general manager of Lion Corp.'s R&D Headquarters, was also president of the Japan Oil Chemists' Society (JOCS) from 1999–2001. His tireless work for AOCS included serving on the executive committees for a number of conferences as well as establishing the JOCS/AOCS Joint Symposium in 1999. Further, Dr. Oba was a member of the editorial advisory board of AOCS' *Journal of Surfactants and Detergents* from the journal's inception in 1998. ■

# SUSTAINABILITY WATCH

## US EPA expands Design for the Environment program

The US Environmental Protection Agency (EPA) Office of Chemical Safety and Pollution Prevention has expanded its Design for the Environment (DfE) Safer Chemical Ingredients List (SCIL) with chemicals in new and existing functional component classes.

The SCIL currently contains more than 650 chemicals that meet DfE's safer chemical criteria and are eligible for use in the DfE Safer Product Labeling program. To date, SCIL-listed chemicals have been used primarily in cleaning and detergent products, including surfactants, solvents, chelants, and colorants.

EPA has posted a "Steps to SCIL Listing" document at www.epa.gov/dfe/howtoscil to guide chemical manufacturers through the submission process. Cleaning product formulators may also list their safer chemicals at www.cleangredients.org/home. Profiles prepared for SCIL listing may also be used to qualify for CleanGredients, although some information requirements may vary.


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## Reinventing China's aquaculture

China's aquaculture sector is putting a strain on the world's wild fisheries. Nevertheless, there are ways to relieve this pressure while improving both environmental and nutritional standards, according to the authors of a Policy Forum in *Science* magazine (http://dx.doi.org/10.1126/science.1260149, 2015).

Ling Cao and colleagues examined the connections between China's aquaculture industry, which accounts for about 72% of the country's reported domestic fish production, and its wild fisheries, most of which are overexploited. The researchers suggest that fish-processing wastes, including fish oils and so-called "trash fish," could be used more efficiently for aquafeeds in order to reduce China's dependence on capture fisheries and increase net fish supplies at the same time. The authors suggest that such fish-processing wastes could meet almost half of the country's current demand for fishmeal in aquafeeds, relieving pressure on wild fish stocks, if appropriate technologies are developed, nutritional qualities can be improved, and food safety can be guaranteed. The scale and complexity of China's aquaculture industry places it in a precarious position between adding to and depleting global seafood availability, the authors say.

## Extending Brazil's Soybean Moratorium

Brazil's Soybean Moratorium (SoyM) was the first voluntary zero-deforestation agreement in the tropics, where major soybean traders agreed not to purchase soy grown on lands deforested after 2006 in the Brazilian Amazon. The agreement is set to end in May 2016, but Holly Gibbs and colleagues argue that SoyM should be extended as the best available protection against deforestation in the region.

In another Policy Forum (see previous item) from *Science* magazine, the researchers note that nearly 30% of soy expansion occurred through deforestation in the two years before the 2006 agreement. As of 2014, deforestation for soy cultivation had decreased to only about 1% of expansion into the Amazon. Although the national government can use property registration and licensing practices to protect against deforestation, its enforcement efforts have not been as successful as SoyM, and will take time to strengthen and develop, Gibbs and colleagues say. Expanding SoyM into the Cerrado biome of Brazil, which currently is not covered under the agreement, would also be useful in protecting native vegetation against encroachment by soy farming.

The Policy Forum article, from January 2015, is available at http://dx.doi.org/10.1126/science.aaa0181.

# BRIEFS

*Nanowerk News* reports that the *Fistulifera solaris* diatom "is emerging as a promising candidate for next-generation biofuel technology." Among the microalga's attractions: It grows quickly and, at the same time, produces high levels of oil. By contrast, other oil-producing microalgae produce their peak amounts of oil during periods when they grow slowly, if at all. *F. solaris* was originally isolated from samples taken at the junction of two rivers in Japan. A team of scientists in Japan and France then worked to reveal the molecular underpinnings of simultaneous growth and oil production by sequencing the diatom's genome. Their study appeared in *The Plant Cell* (http://dx.doi.org/10.1105/tpc.114.135194, 2015).

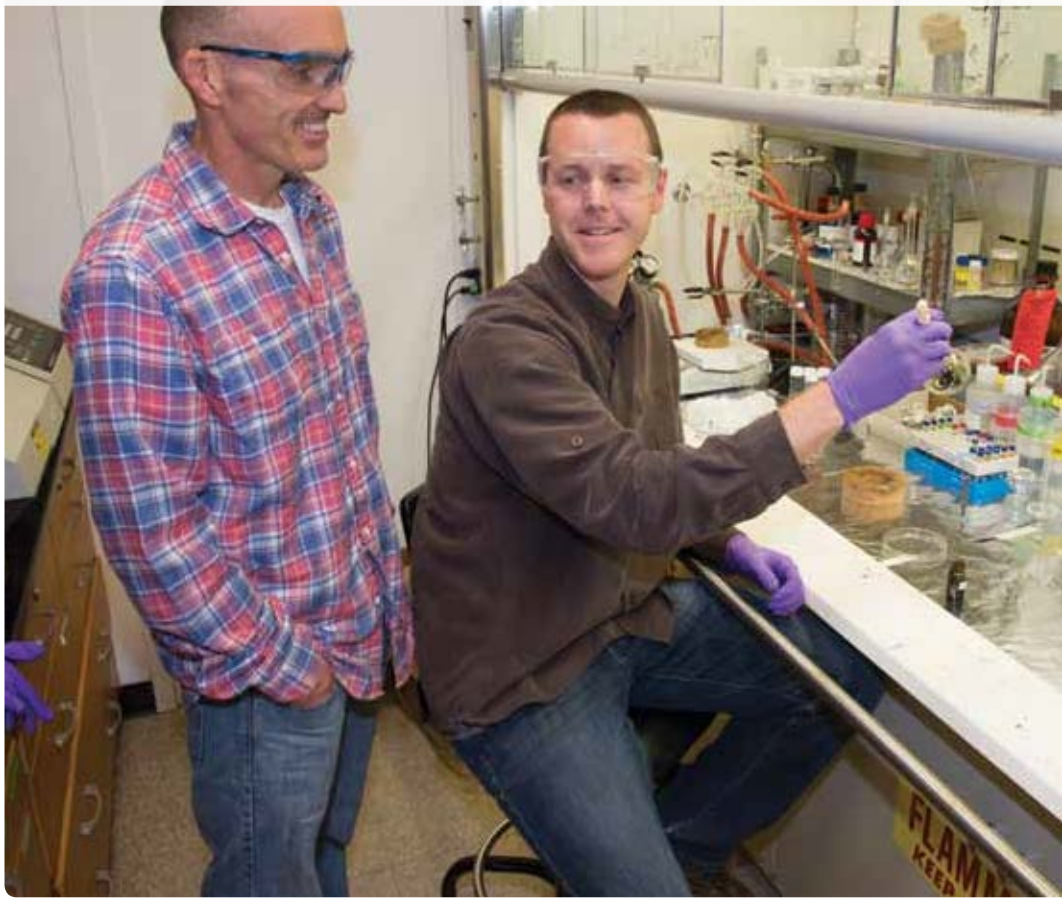
■■■

Biodiesel made from animal fat reduces greenhouse gas emissions by 85% compared to fossil fuels, according to calculations carried out in the context of the International Sustainability & Carbon Certification process. These calculations have now been verified through a study that was commissioned by the European Fat Processors and Renderers Association and was conducted by the Institute for Energy and Environmental Research (IFEU) in Heidelberg, Germany. The IFEU research specifically looked at how the greenhouse gas emissions resulting from the processing of animal by-products should be allocated. See more at http://tinyurl.com/EFPRA-animal-fat.

■■■

ASTM International, an organization that sets industry consensus standards for fuels and lubricants, has voted to approve performance specifications for blends of 6%–20% biodiesel with traditional heating oil. The mixture of biodiesel and heating oil is marketed as Bioheat® fuel, a registered trademark. The updated ASTM D396 Standard Specification for Fuel Oils will be made final and published by ASTM for public use after the usual ASTM review and editing process. ASTM has also revised ASTM D1655—a standard for jet fuel. The revised standard increases the allowable cross-contamination of fatty acid methyl esters in jet fuel from 5.0 parts per million to 50 parts per million. ■

# ENERGY



Researchers Greg O'Neil, right, of Western Washington University and Chris Reddy of Woods Hole Oceanographic Institution. (Photo by Tom Kleindinst, Woods Hole Oceanographic Institution)

## Two fuels from one alga

A common alga commercially grown to make fish food holds promise as a source for both biodiesel and jet fuel, according to a new study.

A research team led by Greg O'Neil of Western Washington University (Bellingham, USA) and Chris Reddy of Woods Hole Oceanographic Institution (WHOI; Woods Hole, Massachusetts, USA) exploited an unusual and untapped class of chemical compounds in the organism to synthesize two different fuel products, in parallel, from a single alga.

"It's novel," says O'Neil, the study's lead author. "It's far from a cost-competitive product at this stage, but it's an interesting new strategy for making renewable fuel from algae."

For their study, O'Neil, Reddy, and colleagues targeted a specific algal species called *Isochrysis* for two reasons: First, because growers have already demonstrated they can produce it in large batches to make fish food. Second, because it is among only a handful of algal species around the globe that produce fats called alkenones. These compounds are composed of long chains with 37 to 39 carbon atoms, which the researchers believed held potential as a fuel source.

Biofuel researchers may have dismissed *Isochrysis* because its oil is a dark, sludgy solid at room temperature, rather than a clear liquid

CONTINUED ON NEXT PAGE

that looks like cooking oil. The sludge is a result of the alkenones in *Isochrysis*—precisely what makes it a unique source of two distinct fuels.

Alkenones are well known to oceanographers because they have a unique ability to change their structure in response to water temperature, providing oceanographers with a biomarker to extrapolate past sea surface temperatures. Nevertheless, biofuel scientists were largely unaware of alkenones. "They didn't know that *Isochrysis* makes these unusual compounds because they're not oceanographers," says Reddy, a marine chemist at WHOI.

Reddy and O'Neil began their collaboration first by making biodiesel from FAME converted from oil produced by *Isochrysis*. Then they had to devise a method to separate the FAME and alkenones in order to achieve a free-flowing fuel. The method added steps to the overall production process, but it supplied a superior quality biodiesel, as well as "an alkenone-rich . . . fraction as a potential secondary product stream," the authors write.

"The alkenones themselves, with long chains of 37 to 39 carbons, are much too big to be used for jet fuel," says O'Neil. However, the researchers used olefin metathesis to cleave carbon-carbon double bonds in the alkenones, breaking the long chains into pieces with only 8 to 13 carbon atoms. "Those are small enough to use for jet fuel," O'Neil says.

The scientists believe that by producing two fuels—biodiesel and jet fuel—from a single alga, their findings hold some promise for future commercialization. They stress that this is a first step with many steps to come, but they are encouraged by the initial result.

"It's scientifically fascinating and really cool," Reddy says. "This [alga] has got much greater potential, but we are in the nascent stages."

They will next try to produce larger quantities of the fuels from *Isochrysis*, but they are also exploring additional co-products from the algae. The team believes there are many other potential products that could be made from alkenones.

"Petroleum products are everywhere—we need a lot of different raw materials if we hope to replace them," says O'Neil. "Alkenones have a lot of potential for different purposes, so it's exciting."

The study was published in *Energy & Fuels* (http://dx.doi.org/10.1021/ef502617z, 2015). It was funded by the National Science Foundation, the Massachusetts Clean Energy Center, and Woods Hole Oceanographic Institution.

## First-ever ranking of airline biofuel use

Air travel emits more than 650 million metric tons of carbon pollution annually—equivalent to the pollution from 136 million cars—making the increased use of sustainable biofuels an important aspect of reducing the industry's carbon footprint.

According to a first-of-its-kind scorecard released by the Natural Resources Defense Council (NRDC), an environmental advocacy group based in New York, New York, USA, the industry is making strides in adopting sustainable biofuels.

NRDC's Aviation Biofuel Sustainability Scorecard (http://tinyurl.com/NRDC-survey) evaluated airlines' adoption of biofuels, focusing on the use of leading sustainability certification standards, participation in industry initiatives to promote sustainability certification, public commitments to sustainability certification in sourcing, and the monitoring and disclosure of important sustainability metrics. The top-scoring carrier was Air France-KLM, followed by British Airways, United Airlines, Virgin Atlantic, Cathay Pacific, and Alaska Airlines.

The industry has made significant strides in embracing biofuels in recent years, NRDC said in a news release. "In the past five years, more than 40 commercial airlines around the world have flown as estimated 600,000 miles powered at least in part by biofuels," the release noted. Other milestones include Lufthansa's study of the long-term effect of aviation biofuels on engines, which found no adverse impacts. In addition, KLM has conducted 26 long-haul flights demonstrating it is possible to organize and coordinate a complex supply chain and fly regularly scheduled flights on aviation biofuel blends.

## NREL's CelA catalyzes plant cell walls faster

Scientists at the US Energy Department's National Renewable Energy Laboratory (NREL; Golden, Colorado, USA) say they have developed an enzyme that could change the economics of biofuel conversion by converting biomass to sugars up to 14 times faster and much more inexpensively than competing catalysts.

This enzyme, called CelA, is a cellulase from the bacterium *Caldicellulosiruptor bescii*, and the fact that it is from a bacterium and not a fungus is just one reason why NREL researchers are calling it a "potential game-changer." Here are some others:

- Unlike most catalysts, CelA can digest two major components in biomass: both cellulose and xylan.
- CelA works in two mechanical realms, not just one. It is an ablator, scraping the valuable material off the cell walls of the plants. However, it is also a borer, digging deep into the wall to grab more of the digestible biomass. It is the only enzyme known to dig pits into biomass; others only ablate.
- It can operate at much higher temperatures than other enzymes. Also, because it can operate above the boiling point of alcohol, the alcohol is separated naturally, saving a costly step in the conversion process—and the high temperatures kill many of the microorganisms that would otherwise interfere with the process.

In one scenario, the most effective commercially used enzyme converted sugars at a rate of 30% in seven days. CelA converted twice that amount. Moreover, whereas it took the alternative enzyme seven days to achieve a 30% conversion, CelA, with a small boost from an extra β-glucosidase, achieved doubled conversion in just about two days.

If the enzyme continues to perform well in larger tests, it could help drive down the price of converting cellulose and, with it, the price of everything from jet fuel to ethanol, butanol, drop-in fuels, and numerous chemicals.

NREL has filed for patent protection on the enzyme formulation and the improvements made to the enzyme. To access the NREL news release, visit http://tinyurl.com/NREL-enzyme.

## REG expands into Europe

Renewable Energy Group, Inc. and IC Green Energy Ltd. (REG; Ames, Iowa, USA) have acquired, through a wholly owned subsidiary, ICG's majority equity ownership position in German biodiesel producer Petrotec AG.

ICG, Israel Corp.'s vehicle for investing in the alternative energy market, accepted an offer from REG European Holdings B.V. to purchase ICG's 69% equity ownership in Petrotec AG for $20.9 million.

Petrotec is a fully integrated company utilizing more than 15,000 collection points to gather used cooking oil (UCO) and other waste feedstocks to produce biodiesel at its two biorefineries in Emden and Oeding, Germany. Petrotec's nameplate production capacity is 55.5 million gallons (185,000 MT) per year, produced predominantly from UCO. Petrotec's collection service, treatment processes, and biorefineries, are certified by both German and European regulators. Its biodiesel is compliant with EU standard EN 14214. ■

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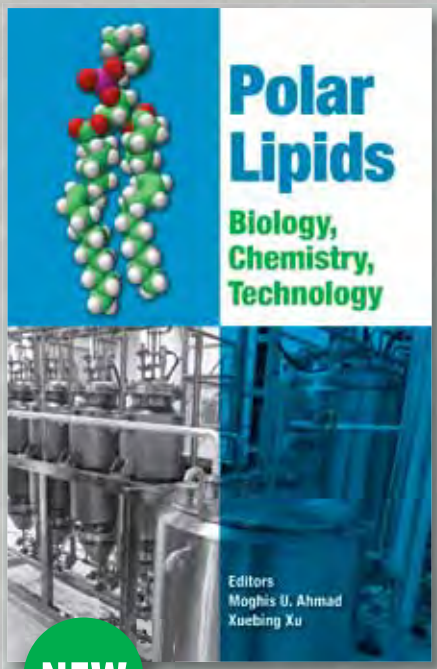


NEW

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Edited by Moghis U. Ahmad and Xuebing Xu
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ISBN 978-1-630670-44-3. Product code 275
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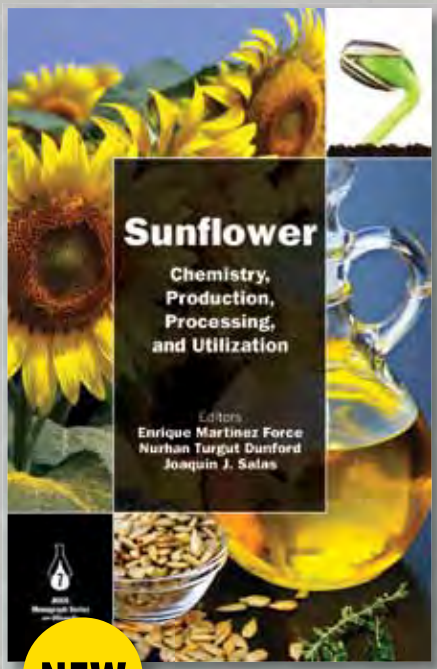
*Polar Lipids* will be a valuable reference resource providing thorough and comprehensive coverage of the application and utilization of polar lipids in food and nutrition, and health and disease. Chapters cover chemistry and chemical synthesis, biosynthesis and biological effects, functional and nutritional properties, applications, processing technologies, and future trends of a variety of polar lipids—including glycolipids, ether lipids, phenol lipids, serine phospholipids, omega-3 phospholipids, rice lecithin, palm lecithin, sunflower lecithin, sugar- and protein-based lipids, lysophospholipids, and more.




NEW

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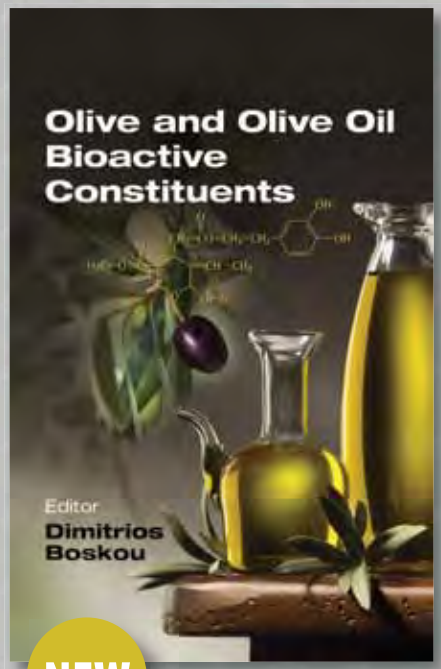


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# BRIEFS

A story published on the news site *Civil Eats* titled "Why Farmed Salmon is Losing its Omega-3 Edge" describes how farm-raised salmon today contains half the amount of omega-3 fatty acids than it did a decade ago, according to the trade group International Fishmeal and Fish Oil Organization (IFFO; London, UK). "As the producers of fish oil, we thought it would be a good idea to inform everybody. Some retailers put it on the package. Some don't," Andrew Jackson, IFFO technical director, told *Civil Eats*. "We're pushing for more informed decision making." Read the story at http://tinyurl.com/Omega3Salmon.

■■■

A team of students from the University of California, Davis (USA) took home the grand prize in the 2014 International Genetically Engineered Machines (iGEM) competition for the development of an electrochemical biosensor that detects rancidity in olive oil. The device comes complete with software necessary to read rancidity levels in a single drop of oil. "The students' goal was to generate an affordable device to detect a comprehensive profile of signature rancidity compounds that match what we smell," said Selina Wang, research director for the UC Davis Olive Center, in a news release. Read more about the device at http://tinyurl.com/OliveOilSensor.

■■■

A study published in *Cell Metabolism* reveals a high-fat diet can help postpone impaired hearing and excessive weight loss in mice with genetic defects in their DNA repair system (see http://dx.doi.org/10.1016/j.cmet.2014.10.005, 2014). The defects are similar to those in humans who have Cockayne syndrome, which causes patients to prematurely age and die at an age of 10–12 years. "A diet high in fat also seems to postpone the aging of the brain," said lead author Vilhelm Bohr of the University of Copenhagen (Denmark) and the National Institutes of Health (Washington, DC, USA). ■

# FOOD, HEALTH & NUTRITION

## Researchers identify compounds that convert white fat to brown fat

Fat cells have a bad reputation, largely attributed to the more well-known type of fat, known as white fat, which is linked to the development of obesity, diabetes, and heart disease. But there is a second type of fat, known as brown fat, which has been linked to several health benefits in mice, including lower triglyceride levels and reduced insulin resistance. Research on brown fat in humans has shown that people who experienced brown fat activation by exposure to cool temperatures burned more calories while remaining inactive than if their brown cells had not been activated. These results have compelled scientists to seek out chemical methods for activating brown fat cells and/or boosting the level of brown fat in the body, which could be the first step in the development of a clinical treatment for obesity.

Now, researchers report the discovery of two compounds that divert human fat stem cells, which normally develop into white fat cells, into brown-like fat cells. The study, led by Harvard University researchers Annie Moisan and Chad Cowan, is published in *Nature Cell Biology* (http://dx.doi.org/10.1038/ncb3075, 2014).

"We report a screening platform for the identification of small molecules capable of promoting a white-to-brown metabolic conversion in human [fat cells]," the authors write.

Although the discovery is promising, the researchers emphasize there are several

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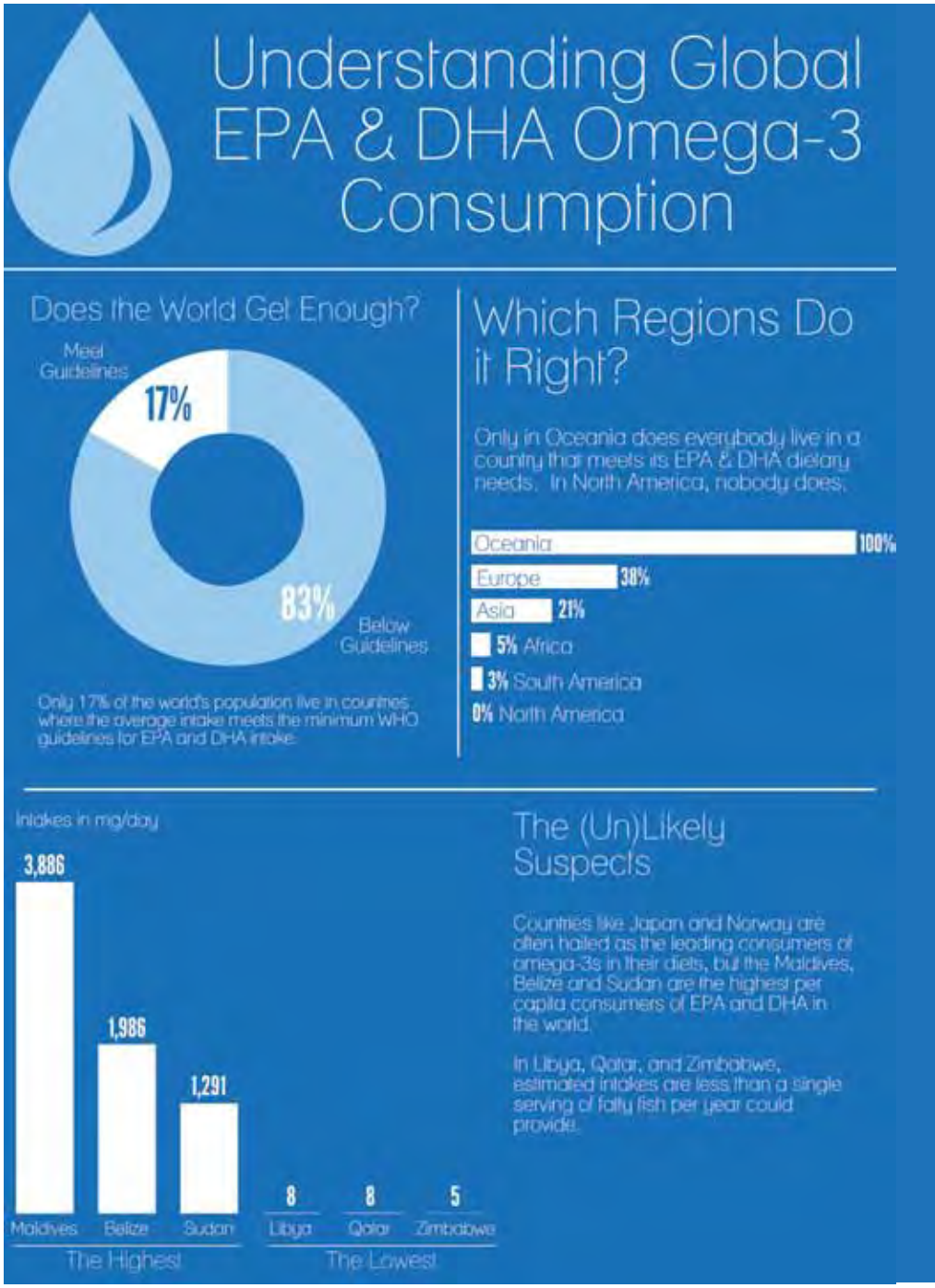
hurdles to overcome on the road to a safe and effective medication for obesity. The two compounds identified in the study target the same molecule, Janus kinase (JAK), which plays a role in the inflammatory response. One of the compounds is already on the market as a treatment for rheumatoid arthritis. Therefore, if the compounds were administered to a patient for a long time, the person could become immune-compromised, Cowan said in a news release. For this reason, in order for the compounds to be effective in the body, they "would almost certainly need to be delivered locally and prevented from spreading systemically," the authors write, or be chemically modified so that they selectively target fat cells.

Speculating about the future development of obesity treatments based on these or similar molecules, the researchers add: "One could also conceive of a cell-based therapy wherein JAK inhibition of patient-derived [fat cells] is followed by transplantation to treat obesity, but this therapeutic [approach] would need to overcome numerous and significant obstacles before becoming a reality.

"A further limitation of the current study is the lack of evidence that JAK inhibition would promote metabolic browning in [the body], in particular in humans, where evidence supporting this phenomenon is scant," the authors continue. "Thus, additional research is required before inhibition of [this signaling pathway] could be used therapeutically for the treatment of metabolic disorders."

The research was performed in collaboration with Roche Pharmaceuticals (Nutley, New Jersey, USA). However, the collaboration has since ended, and Cowan said his team is now in discussions with other pharmaceutical companies about continuing the work. Additionally, a collaborator in Germany has begun testing the two compounds in mice.

"The compounds appear to work the same way in mice," Cowan said, "but we don't know what the long-term metabolic or immune system effects are."

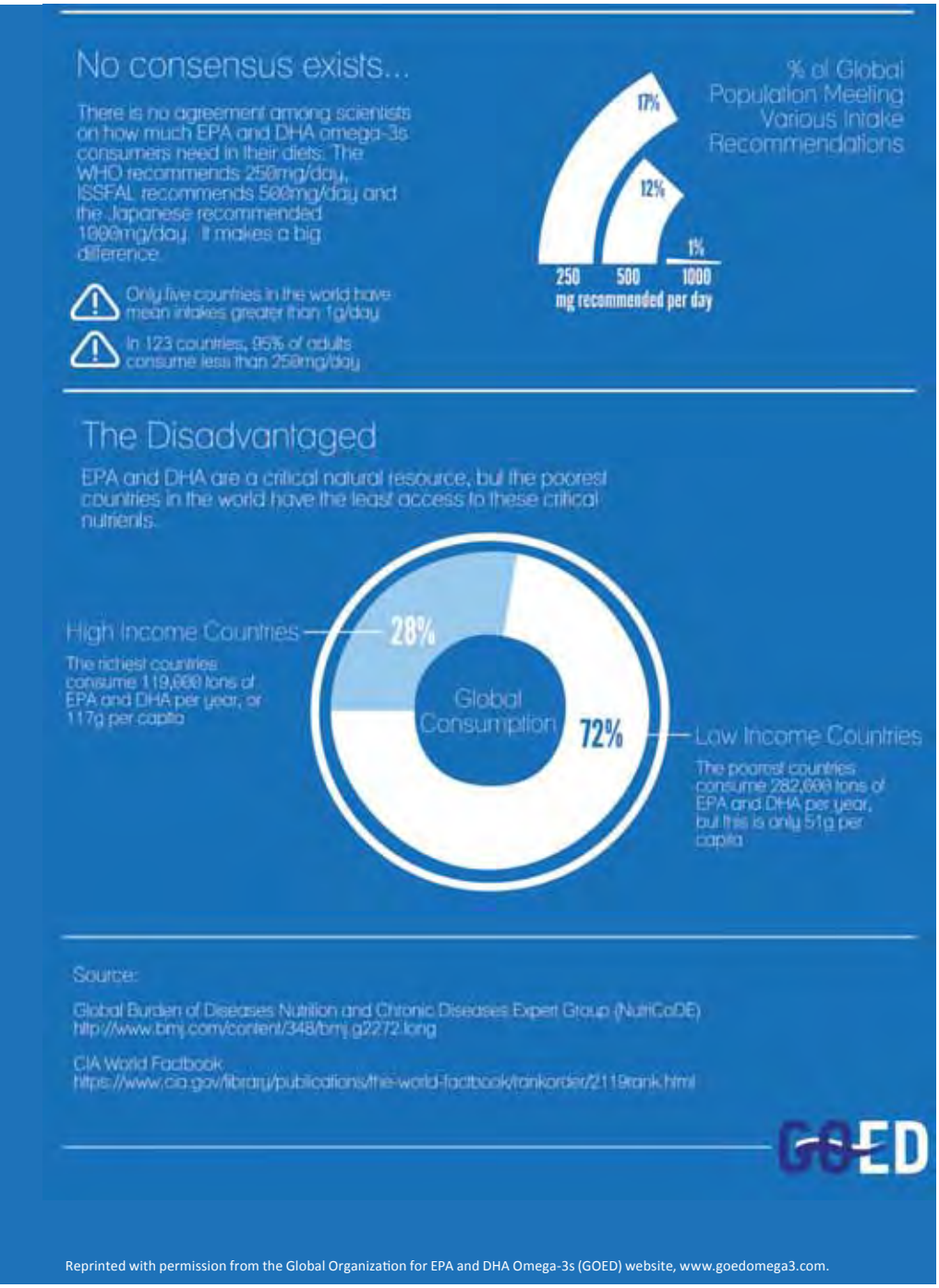



## Egg-free mayo an oxymoron? Hellmann's thinks so

In late 2014, Anglo-Dutch consumer products giant Unilever, which makes mayonnaise products, filed a lawsuit against Hampton Creek (San Francisco, California, USA) for calling its egg-free mayonnaise-like sandwich spread "Just Mayo."

The suit accuses the Hampton Creek of false advertising, since mayonnaise, according to a standard set in 1957 by the US Food & Drug Administration, must contain "egg yolk-containing ingredients."According to the lawsuit filed by Unilever's lawyers, Just Mayo's rising sales have "caused consumer deception and serious, irreparable harm to Unilever and to the product category the industry has taken great care to define in a way consistent with consumer expectations" and have hurt the market share of Unilever's mayonnaise products, known as Hellmann's or Best Foods.

"Despite its name, Just Mayo does not contain just mayonnaise," the lawsuit reads. "In fact, it is not mayonnaise at all. Rather, it is a plant-based vegan alternative to real mayonnaise. . . .

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In addition to lacking the taste of real mayonnaise, Just Mayo does not perform like real mayonnaise when it is heated, as mayonnaise often must be in common consumer uses.

"Real mayonnaise is commonly used because its blend of ingredients effectively binds together the elements of the sauce and adds flavor and texture in the process," the lawsuit continues. "Because Just Mayo is a vegan product lacking the same emulsifying ingredients as real mayonnaise, when it is heated, its oils separate and do not bind the ingredients together. Consumers and cooks have an expectation that mayonnaise should both taste and perform like mayonnaise. Just Mayo does neither."

Unilever is asking Hampton Creek to recall all confusing products, ads, and promotional materials, remove the illustration of an egg from its label, and stop claiming Just Mayo is superior to Hellmann's or Best Foods, in addition to paying three times its profits in damages plus legal fees.

Mayonnaise is the top-selling condiment in the United States, with consumers spending about $2 billion a year on the product, according to data from Euromonitor International, a privately owned London-based marketing intelligence firm.

## Nanoparticle-encapsulated vegetable oil fights gastric disease bacteria

A new therapeutic nanoparticle delivers a payload of α-linolenic acid, killing the bacteria *Helicobacter pylori* in mice. The particles are described in a study published in the *Proceedings of the National Academy of Sciences* (see http://dx.doi.org/10.1073/pnas.1418230111, 2014).

*H. pylori* infection is associated with gastric ulcers and certain forms of cancer. Typical treatment involves antibiotics, but researchers are interested in developing new therapeutic approaches to bacterial infection to overcome the major challenge of antibiotic resistance.

"Because of the rapid emergence of *H. pylori* strains resistant to existing antibiotics, current treatment regimens show a rapid decline of their eradication rates," the authors write. Liangfang Zhang, co-lead author and researcher at the University of California San Diego (USA), explained in a news release that his team's goal was to "develop a nanotherapeutic that can tolerate the harsh gastric environment, kill *H. pylori*, and avoid resistance."

The team created nano-sized liposomes, or spherical vesicles composed of a lipid bilayer of α-linolenic acid. The roughly 100-nm-sized particles, known as LipoLLA, directly deliver their lipid payload by fusing themselves with the membranes of bacterial cells. The researchers found LipoLLA was able to penetrate the mucus layer of the mouse stomach and be retained for up to 24

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hours after oral administration. LipoLLA was more effective at getting rid of bacteria than standard antibiotic therapies and was not toxic to the mice. The particles also reduced levels of certain markers of inflammation. The team is now working on making the particles more stable and effective.

The authors acknowledge funding from the National Institute of Diabetes and Digestive and Kidney Diseases, which is part of the US National Institutes of Health.

## Trans fats linked to diminished memory in adults

Men who consumed higher levels of trans fats performed worse on word memory tests, according to a study presented at the American Heart Association's Scientific Sessions in 2014. The study, led by University of California San Diego (USA) researcher Beatrice Golomb, involved roughly 1,000 healthy adult males. The strength of the association between trans fat consumption and memory remained even after researchers took into account factors such as age, education, ethnicity, and depression.

Study participants completed a dietary questionnaire, from which the researchers estimated trans fat consumption. To assess memory, researchers presented participants with a series of cards showing words and asked them to state whether each word was new or duplicated from a prior card.

A news story by the *Cable News Network* points out that while this is not the first study to reveal a link between dietary fat and memory, it is among the first to examine such a large group of working-age men. Although this study does not prove cause and effect, the researchers speculate that consuming large amounts of trans fat may lead to cellular damage caused by oxidative stress.

"From a health standpoint, trans fat consumption has been linked to higher body weight, more aggression, and heart disease," Golomb said in a news release. "As I tell patients, while trans fats increase the shelf life of foods, they reduce the shelf life of people."

## Fish oil boosts response to anti-rheumatic drugs

The results of a randomized, double-blind controlled trial suggest a daily dose of fish oil may increase the response rate of patients to anti-rheumatic drugs. The study, led Susanna Proudman, researcher at Royal Adelaide Hospital (Australia), is published in *Annals of the Rheumatic Diseases* (see http://dx.doi.org/10.1136/annrheumdis-2013-204145, 2015).

The trial involved 140 patients diagnosed with early rheumatoid arthritis. Participants were treated with a "triple therapy" composed of conventional disease-modifying anti-rheumatic drugs (DMARDs) including oral methotrexate, sulfasalazine, and hydroxychloroquine. The average age of participants was 56, and three-quarters were women. Patients in the active treatment group received 10 mL per day of fish oil, which contained 5.5 grams of eisosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), while those in the control group were given sunflower oil (Sunola brand) with a small amount of fish oil to provide a fishy odor.

After a year of treatment, roughly 1 in 10 patients receiving fish oil failed to respond to treatment, compared with 1 in 3 patients in the control group.

"It's too early to tell for sure if fish oil should be recommended for patients with rheumatoid arthritis," James R. O'Dell, chief of rheumatology at the University of Nebraska in Omaha (USA), told *MedPage Today*. "But if this can be replicated, this could have a very big impact on rheumatoic arthritis treatment." ■

# BRIEFS

A study published in *PLOS ONE* reports feral genetically modified (GM) oilseed rape (*Brassica napus* L.) was found growing in four sites in Switzerland in 2011 and 2012, despite cultivation and seed import bans (http://dx.doi.org/10.1371/journal.pone.0114477, 2014). The GM plants, which were located along railway lines and in port areas, were all identified as glyphosate-resistant GM event GT73 (Monsanto; St. Louis, Missouri, USA). Analyses revealed outcrossing of transgenes from GT73 into two non-GM oilseed rape plants, but outcrossing into related wild species was not observed. The source of the GM seeds was not determined.

■■■

Cibus Global (San Diego, California, USA) and Rotam (Chaiwan, Hong Kong) have announced the launch of their first nontransgenic commercial product, SU Canola™ (Sulfonylurea Tolerant). "SU Canola is an optimal fit for rotation with glyphosate-tolerant soybeans," said Cibus Vice President Dave Voss. "Many participants in the canola industry . . . will benefit from SU Canola as the oil and meal derived from this canola will address the growing demand for nontransgenic food ingredients." SU Canola is commercially available in the United States, and the SU trait has received approval from the Canadian Food Inspection Agency and Health Canada.

■■■

Although nearly one-fifth of US consumers say they will not accept the presence of nanotechnology or genetic modification (GM) technology in foods under any circumstances, roughly 60% say they would buy such products if they had enhanced nutrition or food safety. This is according to a nationally representative survey of 1,117 US consumers performed by researchers from North Carolina State University (Raleigh, USA) and the Uni-

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# BIOTECHNOLOGY

## Maximizing crop yields with genetic tools

Scientists have discovered a set of gene variations that can boost crop yields. The study, led by Cold Spring Harbor (Cold Spring Harbor, New York, USA) researcher Zachary Lippman and published in the journal *Nature Genetics*, found that the fruit production of a tomato plant could be increased two-fold by breeding the plants to contain several genetic mutations (see http://dx.doi.org/10.1038/ng.3131, 2014). The set of mutations may enable farmers to maximize yields in other flowering plants, including oilseed crops.

"Traditionally, plant breeders have relied on natural variation in plant genes to increase yield, but yield gains are plateauing," Lippman said in a news release. "There is an immediate need to find new ways for plant breeders to produce more food."

Prior work by Lippman and colleagues showed that a mutation in a hormone known as florigen could shift the balance between vegetative growth and flowering, leading to a modification in plant architecture that increases yields. In the new report, the researchers identify an array of genes that can be mutated and then mixed and matched to fine-tune the balance of florigen and its opposing hormone, anti-florigen. "Together, our collection of mutations forms a powerful toolkit for breeders to pinpoint a new optimum in flowering and architecture that can achieve previously unattainable yield gains," Lippman said.

Mutations that affect florigen and anti-florigen are already known to play a role in controlling plant architecture for the oilseed crops rapeseed and sunflower. The team is planning to next apply this genetic tweaking approach to soybeans, which share many growth similarities with tomato.

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## Review: challenges and opportunities in breeding of European oilseed crops

A review article by researcher Patrick Vincourt of the Laboratoire Interactions Plantes Microorganismes (Toulouse, France), published in the journal *Oilseed & fats, Crops and Lipids,* outlines the challenges and opportunities of breeding oilseed crops in Europe, with an emphasis on oilseed rape (*Brassica napus*) and sunflower (*Helianthus annuus*), Europe's two main oilseed crops (see http://dx.doi.org/10.1051/ocl/2014043, 2014). As the demand for oilseed-derived products worldwide continues to rise, thanks in part to developing countries in Asia, Europe will continue to have a major role to play, particularly in winter oilseed rape and sunflower breeding, Vincourt writes. The article presents a review of the literature that discusses the challenges of growing healthy, high-yielding crops, including overcoming disease resistance and increasing yields, nitrogen use efficiency, and crop resilience toward drought and other environmental stresses.

## Scientists create new human milk fat substitute

A new fat, composed of lard, vegetable oils, and single cell oils, holds promise for serving as a substitute for human milk fat in infant formulae. Researchers at the universities of Jiangnan and Aarhus led by Xiaoqiang Zou blended the oils and then enzymatically interesterified the blended oils using 1,3-selective lipases. The team determined the optimal vegetable oil blend was lard/sunflower oil/palm kernel oil/palm oil/algal oil/microbial oil (an arachidonic acid-rich oil obtained from *Mortierella alpine*) with weight proportions 1.00/0.10/0.50/0.13/0.12/0.02/0.02. The team optimized the reaction conditions and found the best results were achieved with an enzyme load of 11 wt%, a temperature of 60°C (140°F), water content of 3.5 wt%, and a reaction time of 3 hours.

"Under optimized enzymatic transesterification conditions, the resultant product possessed strong similarity to human milk fat," said Douglas G. Hayes, senior associate editor of the *Journal of the American Chemical Society*, where the study was published (see


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http://dx.doi.org/10.1007/s11746-014-2533-z, 2014). The milk fat substitute exhibited 92.5% similarity for the total fatty acid profile, 90.3% similarity for the 2-position fatty acid profile, 61.5% similarity for polyunsaturated fatty acid (PUFA) composition, and 71.9% similarity for composition of triacylglycerol (TAG) molecules.

# Bio-sourced propylene announced by Global Bioenergies

Propylene is a central building block in the manufacturing of plastics. With more than 80 million metric tons (valued at $100 billion) produced yearly, it is the petrochemical industry's second largest market after ethylene. Now, Global Bioenergies (Evry, France) has announced the creation of a proprietary prototype strain that is able to convert glucose into propylene at laboratory scale. The company is the first to produce propylene using an entirely biological production, without any additional chemical steps required.

Previously, propylene has only been produced through fossil resources and has been obtained primarily from naphtha cracking, a refinery process that involves heating a hydrocarbon mixture in the absence of oxygen and presence of water vapor until the hydrocarbon molecules break apart to release olefins, including propylene. "Because of the decrease in naphtha cracking capacities, there is a need for alternative routes to light olefins, and in particular to propylene," said Thomas Buhl, head of business development at Global Bioenergies, in a news release.

Global Bioenergies is one of the few companies worldwide, and the only one in Europe, that is developing a process to convert renewable resources into hydrocarbons through fermentation. In addition to propylene, the company produces isobutene and butadiene via fermentation.

# GM potato engineered to produce less acrylamide

A genetically modified (GM) potato strain, made by J. R. Simplot Co. (Declo, Idaho, USA) to produce less acrylamide, has been approved by the US Department of Agriculture.

Acrylamide ($C_3H_5NO$) is a chemical compound that is created during frying and is suspected to be a human carcinogen. In 2002, Swedish researchers led by Margareta Törnqvist discovered the chemical was present in starchy foods, including potato chips, French fries (crisps), and breads that had been exposed to temperatures greater than 120˚C (248˚F), but was absent in foods that were boiled or not heated at all (see http://dx.doi.org/10.1021/jf020302f). Although the exact mechanism of acrylamide production remains unclear, some studies have suggested it is a byproduct of the Maillard reaction between the amino acid asparagine and sugars, such as fructose and glucose, or other compounds with reactive carbonyls.

The new GM potatoes, known as Innate potatoes, have lower levels of asparagine, making them less prone to creating acrylamide during frying. They contain genes from wild and cultivated potatoes, are 40% less prone to bruising caused by impact than conventional strains, and, according to a company statement, introduce no new allergens.

"With full market penetration . . . in the [United States], Innate will reduce annual potato waste by an estimated 400 million pounds in the foodservice and retail industries," the company said. But McDonald's USA, a long-time buyer of Simplot potato products, has issued a statement saying it will not source the GM potatoes. According to a news report in the *Idaho Statesman*, Simplot spokesman Doug Cole said he believes consumers will be receptive to the GM potatoes for their health benefits.

If the potatoes receive a positive review from the FDA, they could be introduced in limited test markets in early 2015. The FDA review had not been completed at the time *Inform* went to press. ■

versity of Minnesota (Minneapolis, USA) and published in the *Journal of Agricultural Economics* (http://dx.doi.org/10.1111/1477-9552.12090, 2014). Another 23% say they base their shopping decisions primarily on cost, regardless of the presence of GM or nanotech.

■■■

Verdezyne, Inc. (Carlsbad, California, USA), a privately held industrial biotechnology company that produces renewable chemicals, has announced an agreement with Bio-XCell Malaysia (Kuala Lumpur) to construct its first commercial-scale renewable chemicals manufacturing facility in Bio-XCell's biotechnology and ecosystem park in Nusajaya, Iskandar, in southern Malaysia. The plant will be capable of producing roughly 30 million pounds (14,000 metric tons) of dicarboxylic acids per year, including dodecanedioic acid, which is used in antiseptics, paint, surfactants, and plastics.

■■■

Academic scientists in southeast Asia spend an average of 10% of their time communicating about biotechnology with the public, according to a survey conducted by the International Service for the Acquisition of Agri-Biotech Applications (ISAAA). Of the 217 survey respondents from the Philippines, Malaysia, and Indonesia, 60% worked in the area of crop biotechnology. The survey results show that students and staff from other institutions are the primary recipients of the public engagement, and the greatest need for improving science communication is training. ISAAA is an international not-for-profit organization that supports the advancement of crop biotechnology.

■■■

The European Food Safety Authority has issued a scientific opinion for placing insect-resistant genetically modified cotton MON 15985 (Monsanto; St. Louis, Missouri, USA) on the market for food and feed uses. The engineered strain is resistant to major lepidopteran cotton pests thanks to the expression of two proteins, known as Cry2Ab2 and Cry1Ac. Molecular characterization did not give rise to safety issues, leading the EFSA Genetically Modified Organism (GMO) Panel to conclude the strain is as safe and nutritious as its conventional counterpart and nongenetically modified varieties. There is a very low likelihood of adverse environmental impacts, the statement says. (Read the entire report at http://tinyurl.com/EFSA-MON15985). ■

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# BRIEFS

A recent study on 187 personal care products formulated for children showed that most contained at least one known skin allergen even if the products were marketed as hypoallergenic. Some researchers are calling for the US Food and Drug Administration to regulate such products, according to an article in *Chemical & Engineering News (C&EN)*. For now, however, it is up to consumers to shop by trial and error, *C&EN* notes (see http://cenm.ag/hypo).

■■■

Ashland Specialty Ingredients, a unit of Ashland Inc. (Covington, Kentucky, USA), has introduced Strodex FT-68, a low-VOC (volatile organic compound) phosphate ester surfactant for waterborne architectural coatings. The new product, which does not include alkylphenol ethoxylates, is "designed to impart superior stability to latex paints, including freeze-thaw as well as mechanical stability."

■■■

In similar news, Clariant (Muttenz, Switzerland) has introduced a new glucose- and oil-based surfactant range known as GlucoTain®, "offering sensory benefits and new possibilities for sulfate-free and cocamidopropylbetaine-free skin and hair care formulations." The surfactants are readily biodegradable products with a 94–95% RCI (Renewable Carbon Index), a high content of nontropical biomass, and a good ecotox profile.

■■■

Researchers in the Andriy Voronov group at North Dakota State University (NDSU; Fargo, USA) are investigating soybean oil-based polymeric surfactants (SBPS) in model shampoo formulations. Johnson & Johnson and L'Oreal are working with the team. Biodegradability of the nonionic SBPS "is an important characteristic that needs to be evaluated to determine commercial viability," Voronov notes in a blog entry at https://cpmvoronov.wordpress.com. "For this purpose, we will first carry out synthesis, characterization, and evaluation of physico-chemical properties of SBPS in our labs at NDSU; confirm surface activity and cleaning ability of the synthesized material; and transfer the SBPS samples to our commercial partners for their specific testing and evaluation." ■

# HOME & PERSONAL CARE

## Oleoline forecasts global fatty alcohol capacity

Integrated oils-to-alcohols producers will account for just over one-third of global capacity for detergent alcohols by the end of 2015, according to the Hong Kong-based Oleoline market research and consultancy firm.

The firm's January 2015 survey of global detergent alcohol producers notes that new alcohols projects in 2014 and 2015 include projects from Ecogreen, KLK, Hotung, Saudi Kayan (SABIC), and the Sinar Mas–Cepsa joint venture. The synthetic alcohols capacity, for those grades used in detergent products, is estimated to be just 23% of total global capacity, whereas natural fatty alcohols will reach 77% of total global capacity, according to the report (see Table 1, page 230).

Over the last few years, several trends have emerged in detergent alcohols manufacture. First, plantation owners and producers of lauric oils (palm kernel oil and coconut oil) have invested heavily in fatty alcohols manufacture. This back-integration trend started in the 1990s with IOI and Felda in Malaysia, but has subsequently accelerated such that by the end of 2014, vegetable oil producers had installed 1.9 million metric tons (MMT) per year of alcohols plant capacity (40% of the global total), with 1.1 MMT per year (24%) of that amount produced using new process technology.

With a few exceptions, most new natural fatty alcohols plants are linked to fatty acids manufacture using the Distilled Fatty Acids (DFA) process, which permits the preselection of fatty

CONTINUED ON NEXT PAGE

**Table 1. Leading detergent alcohol producers at the end of 2014**

| Supplier | Locations | Nameplate total capacity (Ktpa) | Feedstocks | Process Technology |
|---|---|---|---|---|
| **Shell** | US and UK | 590 | Own ethylene and olefins | Shell mod Oxo only |
| **Sasol** | Germany, US, Italy, South Africa, and China | 580 | Buy lauric oils and ethylene in US and Germany | Operates most processes; synthetic and natural + Guerbet |
| **Ecogreen** | Indonesia and Germany | 405 | Own PKO | Lurgi types 1 and 2 plus Davy ME |
| **BASF(Cognis)** | Germany, France, and US | 390 | Buy PKO and olefins, own butene | Henkel ME natural + BASF Oxo and Guerbet C10 2PH |
| **Kao Chemicals** | Malaysia and Philippines | 350 | IOI JV for PKO; buy CNO in Pilkao | Own methanolysis process natural |
| **Wilmar Oleo** | Indonesia and Netherlands | 300 | Own PKO | Davy DFA/Me ester |
| **Musim Mas** | Indonesia | 280 | Own PKO | Davy DFA/Me ester |
| **KLK Oleomas** | Malaysia | 280 | Own PKO | Davy DFA/Me ester |
| **Oxiteno** | Brazil | 200 | Buy PKO | Davy DFA/Me ester |
| **P&G/FPG** | US and Malaysia | 195 | Felda PKO and buy PKO | Own ME natural |
| **Jiahua** | China | 135 | Buy PKO | Davy DFA/Me ester |
| **PTT Chem** | Thailand and Malaysia (Emery) | 210 | Buy PKO | Henkel Methanolysis |
| **VVF** | India | 120 | Buy PKO | Lurgi wax ester x2 |
| **Teck Guan** | China | 100 | Own and buy PKO | Lurgi wax ester |
| **Hotung JV** | China | 100 | Buy PKO | Own/Henkel ME |
| **Saudi Kayan** | Saudi Arabia | 100 | Buy PKO | Lurgi wax ester |
| **Emery Oleo** | Malaysia | 80 | Own PKO | Henkel methanolysis |
| **Huaxin Group** | China | 40/(220) | Buy PKO | Own/Henkel ME |
| **PT Bakrie** | Indonesia | 40/(160) | Own PKO | Lurgi wax ester x2 |
| | Total | 4415 Ktpa = 94% of global capacity | | |

Abbreviations: 2PH, 2-propylheptanol; DFA, distilled fatty acid; JV, joint venture; Ktpa, kilotons per annum; ME, methyl ester; Me ester, methyl ester; PKO, palm kernel oil. Source: Adapted with permission from material supplied by Oleoline.

acids before conversion to esters, followed by hydrogenation into fatty alcohols. "This technology allows the manufacture of alcohols to match the higher market needs for mid-cuts better," the report says.

Of the twelve operators using new process technology, eight are operating Davy Process Technology using low-pressure hydrogenation of methyl esters and four operate the Lurgi Wax Ester process, using low-pressure hydrogenation of waxy esters of fatty alcohols and fatty acids. The increase in plants using new process technology has reduced excess stocks of long-chain alcohols, leading in the last two years to more stable long-chain prices and to a shortage and higher prices for short-chain alcohols.

The Oleoline report forecast over the next five years suggests that:

- Long-established alcohols producers such as Sasol, Shell, and BASF will have much stronger competition from the

plantation owners' group. "Presently, Sasol is investing in US shale gas ethylene for conversion to Ziegler synthetic alcohols, but this new capacity will not be onstream before 2018," the report notes. "BASF appears to have no mid-cut alcohols projects, but Shell was expected to [have de-bottlenecked its] Geismar Neodol units by the end of 2014."

- Most new alcohols capacity is located in Southeast Asia and China, mainly using new process technology, with Davy preferred over Lurgi. Indonesia is set to become the largest alcohols-producing country with an up-to-1-MMT-per-year capacity by the end of 2015.
- Downstream moves from alcohols into surfactants production are accelerating, with the following recent investments:
    - Ecogreen bought Ifrachemie (France) in 2012, with its ethoxylation and sulfonation capacity.
    - Wilmar bought Huntsman's European surfactants operations in April 2014.
    - KLK bought TensaChem's sulfonation operations in August 2014 to link up with its Kolb ethoxylates unit.
    - Musim Mas is building ethoxylation capacity in Belgium and is expected to add sulfonation capability.
- Older plant closures are expected to continue. At the time of the report, Pan Century, ShangQiu, Wuhan, and Jiangsu DongTai had closed older facilities that were not expected to come back on line.
- Low-cost ethylene produced from natural/shale gas is already feeding into projects that manufacture α-olefins and synthetic (Ziegler) alcohols in the United States. With the advent of more gas-based ethylene, plus coal-to-liquids- and methanol-to-olefins-based ethylene in the Middle East and China, new synthetic alcohol capacity is forecast to become competitive.

More information about subscribing to this Oleoline report, which was written by Brian Rossall, is available at www.oleoline.com or at oleo@oleoline.com. An updated edition of the report is expected to be published by August 2015.

# New twist on hygiene hypothesis

Research out of Sweden has provided a new twist on the hygiene hypothesis, or the idea that the overuse of alcohol-based hand sanitizers and cleaning products by germophobic consumers in developing countries has actually compromised children's immune systems.

Scientists led by Bill Hesselmar of the University of Gotheburg collected questionnaire data from the parents of 1,029 children, aged 7 or 8. The team found that children of parents who said they mainly washed dishes by hand were to some degree less likely to develop allergic asthma and hay fever. These children were also significantly less likely to have eczema, compared to children from families who used automatic dishwashers.

Hesselmar was quick to tell National Public Radio, which covered the story in the United States, that there are other possible explanations. For example, "certain other lifestyle characteristics—eating fermented foods regularly, and tending to buy some foods straight from the farm—seemed to strengthen the 'protective' effect in families without dishwashers."

The study was published online first in *Pediatrics* in February 2015 (see http://tinyurl.com/Pediatrics-allergy).

# W.R. Grace splits into two companies

Specialty chemical manufacturer W.R. Grace & Co. (Columbia, Maryland, USA) said in February 2015 it would split into two companies to "improve its strategic focus, simplify operations, and allow for better use of capital."

The Reuters news service said one new company, which would have sales of about $1.8 billion, would consist of the W.R. Grace businesses that make compounds used in the refining, petrochemical, personal care, and tire and rubber industries. The other company will comprise Grace's specialty construction chemicals and specialty building materials unit and have sales of about $1.5 billion, according to Reuters.

# Annual report: ACI Charter for Sustainable Cleaning

Twenty-five member companies of the American Cleaning Institute (ACI) completed the requirements for the first year of ACI's Charter for Sustainable Cleaning, a voluntary initiative of the cleaning products industry to promote and demonstrate continual improvement in the industry's sustainability profile. ACI is a trade association based in Washington, DC, USA.

The announcement was made at the end of January during ACI's 2015 Annual Meeting & Industry Convention in Orlando, Florida, USA. The 2014 ACI Charter members include AkzoNobel; Amway; Arylessence, Inc.; BASF Corp.; Chemia Corp.; Church & Dwight Co., Inc.; The Clorox Co.; Colgate-Palmolive Co.; Croda, Inc.; The Dow Chemical Co.; DuPont Industrial Biosciences; Ecolab Inc.; Evonik Corp.; Firmenich Inc.; GOJO Industries, Inc.; Henkel Consumer Goods Inc.; Huntsman Corp.; International Flavors & Fragrances, Inc.; Novozymes; Procter & Gamble; Sasol; SC Johnson; Seventh Generation; Shell Chemical LP; and Stepan Co.

For more information, see www.cleaninginstitute.org/charter. ■

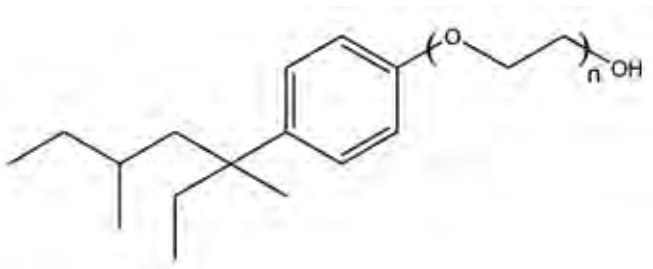
# Requiem for the nonylphenol ethoxylates

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

**Dave McCall**

The second most important component in any cleaning formulation, after water, is the surfactant package. If surfactants appeared only in cleaners, they would still be enormously important, but surfactants are a vital part of formulation science in virtually every industry. The array of surfactants available to the formulator is huge, and any attempt to embark upon a complete inventory would fill many library shelves. In fact, the near 100 volumes in the *Surfactant Science Series* prove just that.

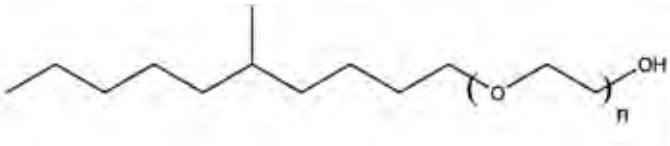
Despite the numerous choices available, for more than a half century , one family of surfactants has stubbornly remained the workhorse group across a wide range of industries. Since their introduction in the first half of the 20th century, the nonylphenol ethoxylates (NPEOs) have remained the formulator's choice because of their low cost, high quality, and excellent performance. They have retained their popularity even under unrelenting attack from the regulatory community. They have been the hardest-working, and least appreciated, group of all the nonionic surfactants. Now that their days appear to be numbered, it might be instructive to review why they have endured so long.




One advantage of the NPEOs is ease of manufacture. Almost any alcohol can be reacted with ethylene oxide (EO) to produce a surface-active material, and sometimes it seems that almost every alcohol has

been used in this way. The NPEOs are based on nonylphenol—an aromatic alcohol with a pKa of about 6. The addition of the first EO to nonylphenol is clean and rapid, as the pKa of the growing EO chain is much higher than the nonylphenol starting material. There remain only traces of unreacted nonylphenol in any NPEO.

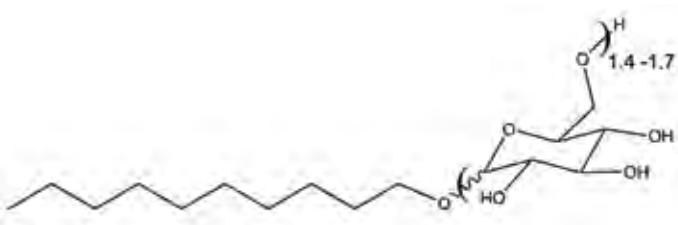
Alcohol ethoxylates (AEO), long positioned to take the place of NPEOs, are based on aliphatic alcohols with pKa values of about 18, a value similar to the pKa of the growing EO chain. The addition of the second EO to a growing surfactant molecule competes effectively with the addition of the first EO. As a result, AEOs contain substantial concentrations of unreacted alcohol—sometimes as high as 30 wt %. The presence of unreacted alcohol results in a product with an undesirable odor, a much higher volatile organic compound (VOC) level (Sharp, K. and M. Sharp, *Paint and coatings industry magazine 28*: 48–53, 2013) and a negative impact on hydrophile-lipophile balance (HLB). Shown is a typical example of an ethoxylated oxo alcohol.




Much effort has gone into reducing this problem, including exotic (expensive) catalysts or steam stripping (high energy cost) to produce narrower range ethoxylates. Thus, the NPEOs always have an inherent manufacturing advantage.

A second advantage of the NPEOs is their extreme versatility. Commercial materials are readily available from 1.5 EO to 100 EO. Each EO added to nonylphenol adds a single oxygen atom, most of them as medium polarity ether bonds. The result is a family of surfactants with HLB values ranging from 4.6 to 19.0 (*McCutcheon's*, 2014). This range allows the formulator to fine-tune any desired property. Examples include from low foam to high foam, oil soluble to water soluble, and tiny incremental adjustments within the classic detergent range.

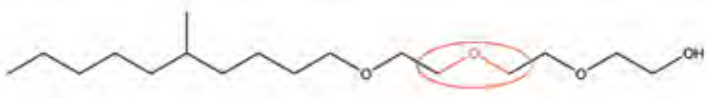
The alkylpolyglucosides (APGs) have made a big splash in the last few decades as potential successors to the NPEOs. They rightfully brag about being made from all "natural" components, but they cannot brag about their structural versatility. The hydrophile is composed of glucose units. The addition of just one glucose adds five oxygen atoms to the surfactant molecule, most of which are very highly polar hydroxyl groups, as shown here.




The range of average glucose units added to each molecule is 1.4 to 1.7. Coupled with slight variations in the length of the alcohol hydrophobe, the range of HLB values available is only from 11.6 to 13.6 (US5527892, June 18, 1996; http://tinyurl.com/mml8uwv). There are no APGs that are oil soluble or low foam.

At least one attempt has been made to expand the versatility of the APGs (US6958314, October 25, 2005). Capping some of the glucose hydroxyls as methyl ethers yields hydrophiles composed of carbon-oxygen-carbon fragments, circled in the illustration.


*This is fundamentally the same molecular fragment that composes an EO chain, circled in this typical AEO.*



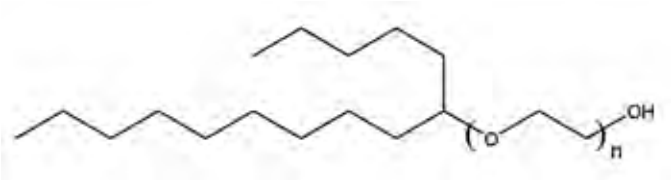

*Methyl capping has substantially broadened the possible HLB range of the APGs, producing molecules with excellent surface activity and a low foam profile. These materials have not been commercialized.*

A third advantageous feature of the NPEOs is the size and shape of nonylphenol, the hydrophobe. The nonyl group is highly branched and consists of numerous isomers. The example shown early in this article is the most common, yet accounts for only 7% of the total mass. The benzene ring also contributes to the general bulkiness of the molecule. While the benzene contains six carbon atoms, the ring adds less length to the chain than six carbons in a linear arrangement.

Whatever effect this short, bulky structure of 15 carbon atoms contributes to performance of the NPEOs, AEO manufacturers have attempted to mimic it. Secondary alcohols have been reacted with EO to produce surface-active agents which are reported to more closely match the characteristics of NPEOs than linear, or near linear, AEOs. The argument is that the branched structure of the secondary alcohol occupies approximately the same volume of space as the nonylphenol group. The example shown is but one isomer of a

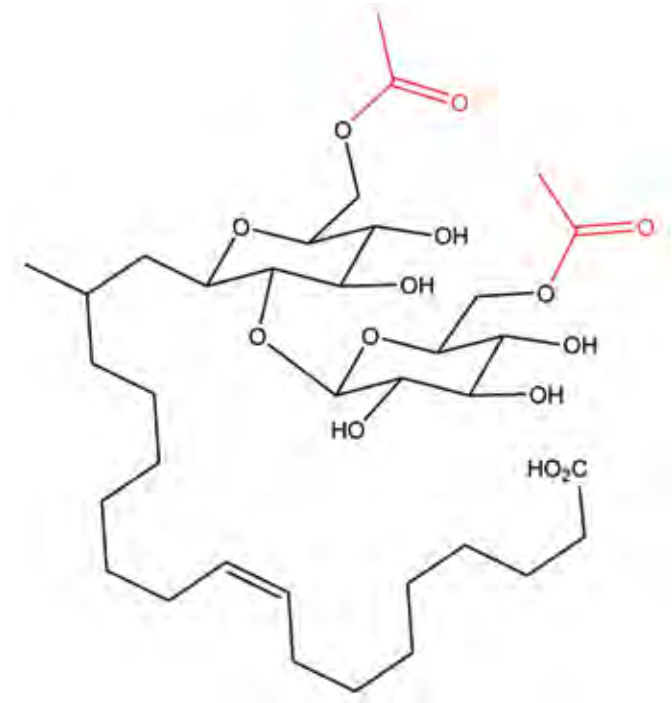
CONTINUED ON NEXT PAGE

mixture, with the alcohol appearing in various places along the carbon chain.




These materials suffer the same disadvantages during the EO addition process as all the other AEOs. They are successful articles of commerce. But, they do not so closely match the properties of the NPEOs that they have threatened to crowd them out of the market.

The latest and greatest materials now attracting attention are biosurfactants. They are all "natural" because they are made by some hard-working microbe rather than in a chemical plant. In addition to being expensive, biosurfactants suffer a severe lack of structure variability. Of the various biosurfactants under consideration, the sophorolipids have attracted the bulk of the attention. Shown here, the structure is a little odd for a surfactant.




There is a hydrophile on both ends. That is uncommon, but known. When nature needs a hydrophile, there is a strong tendency to use glucose. We see that in the sophorolipids. One end of the molecule is elaborated with two glucose units, leading to all the trouble identified for the APGs. This hydrophile is too polar to allow for applications demanding a low HLB surfactant. The situation is addressed in a limited way by acetylating some of the hydroxyl groups, shown in the diagram in red. That is not a great solution for the formulator, however. The acetyl group is attached via an ester bond, which is intolerant of pH extremes. Neutral pH products are all the rage these days, but a formulator cannot afford to be handcuffed to pH 7.

Research is underway to modify the biochemical pathways to the sophorolipids in the hopes that structure variability can be improved (Bogaert, I. E. and W. Soetaert, *Inform*, September 2014, 528–531). Even if ultimately successful, there is no guarantee of commercial success. If variability is achieved by altering the diet of the microbes, the animal rights activists might claim cruelty to microbes. If the organism is modified to produce different surfactant structures, the non-GMO folks will reject them. Any plan to improve the performance of these surfactants is fraught with high risk. Perhaps one day these fairly exotic materials will be produced in sufficient yield to find a place in the market. If so, we will learn how to use them. That will not, however, make make them a superior performance option to the NPEOs.

From a chemical point of view, it's difficult to identify a class of surfactants that can beat the NPEOs on cost, performance and versatility. However, they have been on the regulatory hot seat for decades.

The first wave of attack focused on their biodegradability. It was fueled, in part, by the introduction of the AEOs. There is no doubt that the AEOs degrade faster than the NPEOs. Somehow, that fact was perverted into the conclusion that the NPEOs do not degrade, or perhaps do not degrade fast enough to avoid being an environmental problem. Considering the tonnage of NPEOs produced each year, we would see meter deep foam on the coasts of all our waterways if these materials were not degrading.

Several studies have measured the concentrations of NPEOs and their metabolites in the environment. Included are studies of river waters and their sediments (Naylor, C., *et al*., *Journal of the American Oil Chemist' Society 69*: 60–70, 1992), a group of 130 US streams (Kaplan, D. W., *et al*., *Environ. Sci. Technol. 36*: 1202–1211, 2002), septic systems (Naylor, C., *et al*., presentation at 2000 AOCS Annual Meeting & Expo) and biosolids applied to land as fertilizer (http://tinyurl.com/o4vt2wc). All have found concentrations of troublesome compounds to be present below the no-observed-effect level. Even those studies which insisted on concluding that the NPEOs are environmentally harmful, reported concentrations below the level of concern.

The second attack coincided with a fad of worry about the estrogenic potential of compounds in the environment. NPEOs were declared weak estrogen mimics and it was feared the reproductive cycle of numerous organisms would be adversely affected. Importantly, at concentrations of NPEOs found in the environment, no estrogenic activity was detected (Nichols, K. M., *et al*., *Environ. Toxicol. Chem. 20*: 51–22, 2001). Further study revealed that many materials are estrogen mimics—including many naturally occurring materials. Also, birth control drugs are far more estrogenic than NPEOs—by a factor of several tens of millions, and they are very slow to degrade in the environment (Britton, L. N., *Journal of Surfactants and Detergents (JSD) 1*:

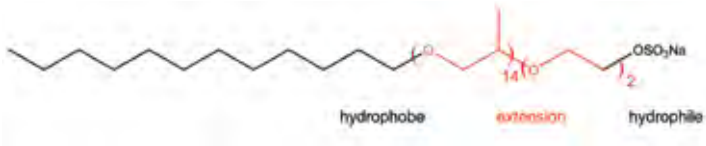
109–117, 1998). Few were willing to give up artificial contraceptives. We have stopped talking so much about the estrogenic potential of the NPEOs.

Current thinking is that we must ban the NPEOs because their metabolites are fish toxic. It's true; NPEO metabolites are more toxic to aquatic organisms than the metabolites of many AEOs. If these materials were persistent in the environment, it would be necessary to eliminate them. But, the studies cited above all conclude NPEOs are effectively degraded quickly enough from properly functioning waste treatment plants and septic systems to pose no problem of persistence in the environment.

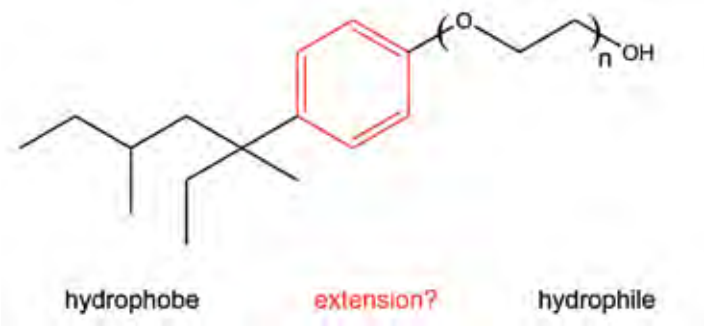
None of that matters. It appears that in the long run, the NPEOs will disappear from the formulator's tool box, probably for considerations more political than scientific in nature. They had a great run. We will miss them. We will learn to use the new materials introduced to take their place. Maybe someday there will be a surfactant group that will surpass the performance characteristics we have come to enjoy from the NPEOs.

It's entirely possible that the NPEOs have already provided the inspiration for the next surfactant generation. Research at the University of Oklahoma in Norman, Oklahoma, (Witthayapanyanon, A., *et al.*, *JSD 9*: 331–339, 2006; Do, L. , *et al.*, *JSD 12*: 91–99, 2009; Sabatini, D. A. , *JSD 13*: 313–319, 2010) has introduced extended surfactants to the world. Typical surfactants are thought to be composed of two distinct parts. One end of the molecule is water soluble (the hydrophile) and the other end is water insoluble (the hydrophobe).

Extended surfactants include a middle portion between these two extremes. This middle portion, the extension, is of intermediate polarity and makes the transition between hydrophile and hydrophobe less severe. An example is shown, with an extension formed of polypropylene oxide and poly EO, shown in red.




Is it possible that the NPEOs were the first extended surfactants?




Sandwiched between the nonyl group (highly hydrophobic) and the EO chain (highly hydrophilic) is a benzene ring, highlighted in red. Benzene is appreciably polar. It is 36 times more soluble in water than cyclohexane—its nonaromatic analog (*The Merck Index*, 11th Ed., Budaran, S. Editor, Merck and Co: Rahway, New Jersey, USA, 1989). Perhaps this is reason the NPEOs have provided such spectacular performance over the years.

***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.***

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# Cholesterol and cholesterol esters: structure, occurrence, physical properties, and function

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

In animal tissues, cholesterol (cholest-5-en-3β-ol, Fig. 1), is by far the most abundant member of a family of polycyclic compounds known as sterols. It can also be described as a polyisoprenoid or a triterpene because of its biosynthetic origin. It was first recognized as a component of gallstones as long ago as 1770, while the great French lipid chemist Chevreul isolated it from animal fats in 1815. However, it was well into the 20th century before the structure was fully defined by the German Chemist Heinrich Wieland, who received the Nobel Prize in Chemistry for his work in 1927, the first of many so honored for research on cholesterol and its metabolism.

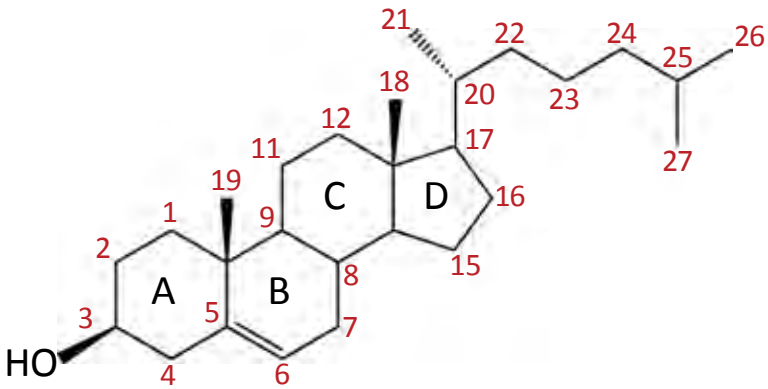


Fig. 1. The sterol cholest-5-en-3β-ol

In essence, cholesterol consists of a tetracyclic cyclopenta[a] phenanthrene structure with an iso-octyl side-chain at carbon 17. The four rings (A, B, C, D) have trans ring junctions, and the side chain and two methyl groups (C-18 and C-9) are at an angle to the rings above the plane with β stereochemistry (as for the hydroxyl group on C-3 also). There is a double bond between carbons 5 and 6. Thus, the molecule has a rigid planar four-ring nucleus with a flexible tail. There are two recognized numbering systems in use - one originally described by Fieser and Fieser in 1959 and a second by IUPAC-IUB in 1989; the first appears to be preferred by many current authors.

Cholesterol has vital structural roles in membranes and in lipid metabolism in general. It is a biosynthetic precursor of bile acids, vitamin D and steroid hormones (glucocorticoids, oestrogens, progesterones, androgens and aldosterone). In addition, it contributes to the development and working of the central nervous system, and it has major functions in signal transduction and sperm development. It is found in covalent linkage to specific membrane proteins or proteolipids ("hedgehog" proteins), which have vital functions in embryonic development. However, because plasma cholesterol levels can be a major contributory factor to atherogenesis, media coverage has created what has been termed a 'cholesterophobia' in the population at large.

Cholesterol is a ubiquitous component of all animal tissues (and of some fungi), where much of it is located in the membranes, although it is not evenly distributed. The highest proportion of unesterified cholesterol is in the plasma membrane (roughly 30–50% of the lipid in the membrane or 60–80% of the cholesterol in the cell), while mitochondria and the endoplasmic reticulum have very low cholesterol contents, and the Golgi contains an intermediate amount. Cholesterol is also enriched in early and recycling endosomes, but not in late endosomes. It may surprise some to learn that the brain contains more cholesterol than any other organ, where it comprises roughly a quarter of the total free cholesterol in the human body. Of all the organic constituents of blood, only glucose is present in a higher molar concentration than cholesterol. It occurs in the free form, esterified to long-chain fatty acids (cholesterol esters), and in other covalent

and non-covalent linkages in animal tissues, including the plasma lipoproteins. In plants, it tends to be a minor component only of a complex mixture of structurally related "phytosterols," although there are exceptions, but it is nevertheless importance as a precursor of some plant hormones.

Animals in general synthesize a high proportion of their cholesterol requirement, but they can also ingest and absorb appreciable amounts in their diets. On the other hand, many invertebrates, including insects, crustaceans and some molluscs cannot synthesise cholesterol and must receive it from the diet, although some species are able to convert plant sterols such as β-sitosterol to cholesterol. Spiny lobsters must obtain exogenous cholesterol to produce essential sex hormones. Similarly, it must be supplied from exogenous sources to the primitive nematode Caenorhabditis elegans, where it does not appear to have a major role in membrane structure, but rather some ill-defined signalling functions controlling development. Prokaryotes lack cholesterol entirely, apart from a few species that acquire it from eukaryotic hosts.

It is generally believed that the main function of cholesterol is to modulate the fluidity of membranes by interacting with their complex lipid components, specifically the phospholipids such as phosphatidylcholine and sphingomyelin. As an amphiphilic molecule, cholesterol is able to intercalate between phospholipids in lipid bilayers, spanning about half a bilayer. In its three-dimensional structure, it is in essence a planar molecule that can interact on both sides. The tetracyclic ring structure is compact and very rigid. In addition, the location of the hydroxyl group facilitates the orientation of the molecule in a membrane bilayer, while the positions of the methyl groups appear to maximize interactions with other lipid constituents (Fig. 2).

The α-face of the cholesterol nucleus (facing down) is "smooth" and can make good contact with the saturated fatty-acyl chains of phospholipids down to about their tenth methylene group; the β-face (facing up) is made "rough" by the projection of methyl groups from carbons 10 and 13. The interaction is mainly via van der Waals and hydrophobic forces with a contribution from hydrogen bonding of the cholesterol hydroxyl group to the polar head group and interfacial regions of the phospholipids, especially sphingomyelin. Intercalated cholesterol may also disrupt electrostatic interactions between the ionic phosphocholine head groups of nearby membrane phospholipids, leading to increased mobility of the head groups. Indeed, there is evidence that cholesterol forms stoichiometric complexes with the saturated fatty acyl groups of sphingomyelin and to a lesser extent of phosphatidylcholine.

Experiments with mutant cell lines and specific inhibitors of cholesterol biosynthesis suggest that an equatorial hydroxyl group at C-3 of sterols is essential for the growth of mammalian cells. The Δ5 double bond ensures that the molecule adopts a planar conformation, and this feature also appears to be essential for cell growth, as is the flexible iso-octyl side-chain. The C-18 methyl group is crucial for the proper orientation of the sterol. While plant sterols appear to be able to substitute for cholesterol in supporting many of the bulk properties of membranes in mammalian cells, cholesterol is essential for other purposes.

In the absence of cholesterol, a membrane composed of unsaturated lipids is in a fluid state that is characterized by a substantial degree of lipid chain disorder, i.e. it constitutes a liquid-disordered phase. The function of cholesterol is to increase the degree of order (cohesion and packing) in membranes, leading to formation of a liquid-ordered phase. In contrast, it renders bilayers composed of more saturated lipids, which would otherwise be in a solid gel state, more fluid. Thus, cholesterol is able to promote and stabilize a liquid-ordered phase over a substantial range of temperatures and sterol concentrations. Further, high cholesterol concentrations in membranes reduce their passive permeability to solutes. These effects permit the fine-tuning of membrane lipid composition, organization and function.

Cholesterol also has a key role in the lateral organization of membranes and their free volume distribution, factors permitting more intimate protein-cholesterol interactions that may regulate the activities of many membrane proteins. Some membrane proteins bind strongly to cholesterol, including some that are involved in cellular cholesterol homeostasis or trafficking and contain a conserved region termed the "sterol-sensing domain." In addition, cholesterol forms a well-defined and essential association with the sphingolipids in the formation of the membrane sub-domains known as rafts, which are so important in the function of cells. It appears that the synthesis of cholesterol and of the sphingolipids, especially sphingomyelin, is regulated co-ordinately to satisfy the requirements of membrane composition and function. The interaction of cholesterol with ceramides is essential for the barrier function of the skin.

In comparison to other lipids, cholesterol can flip rapidly between the leaflets in a bilayer, and the trans-bilayer distribution of cholesterol in some biological membranes is uncertain. While some models propose that cholesterol is on the outer leaflet, other studies suggest that most of the sterol is in the inner leaflet of human erythrocytes, for example. This fact is important in that cholesterol promotes negative curvature of membranes and may be a significant factor in bringing about membrane fusion as in the process of exocytosis.

There is increasing evidence that cholesterol has a more intimate interaction with certain proteins in membranes, especially G protein-coupled receptors. For example, it is essential for the stability and function of the β2-adrenergic receptor, rhodopsin and the (Na+-K+)-ATPase.

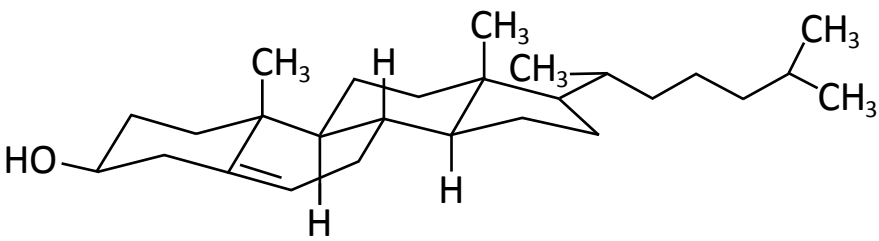


Fig. 2. Cholesterol's tetracyclic ring structure

# Professional Pathways

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

*George Smith is a research fellow at Huntsman Performance Products, where he manages the home and personal care technology group. George is the editor-in-chief for the* Journal of Surfactants and Detergents *(*JSD*) and a past chairman for the S&D division. His research focuses on the use of bio-based raw materials in cleaning products for home and personal care applications.*

## Why did you join AOCS?

My boss at Henkel asked me to give a talk at the 1995 AOCS annual meeting in Atlanta, Georgia, USA, on the low-streaking and filming properties of alkyl polyglycosides in hard-surface cleaning applications. Since then, I think I have missed only one AOCS meeting. It's great to see old friends every year and hear the latest trends in the soaps and detergent industry.

## Describe your career path.

After obtaining a Ph.D in physical chemistry from the University of Oklahoma, my first industrial job was in the chemical products division of Union Camp Corporation in Princeton, New Jersey, USA, working on aqueous dispersions of dimer-based polyamide resins for

adhesive and graphic art applications. After five years, I joined the corporate R&D group at Henkel Corporation in Ambler, Pennsylvania, USA, were I worked on resin-supported emulsion polymers for flexographic printing applications. In 1998, I joined the Huntsman Corporation in Austin, Texas, USA, working in the surfactant applications group. Over the next 16 years, I moved from bench chemist to research fellow managing the surfactant application group for the Americas.

## What do you love about your job?

My job allows me to travel all over the world to meet customers and give presentations at scientific conferences on applied surfactant chemistry. I think it's great to experience different cultures and see new places.

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

I see increasing use of bio-based materials in cleaning products. As stewards for the planet, it behooves us to develop more sustainable, ecologically friendly ingredients to help protect the environment for future generations.

## Describe memorable job experiences.

Some of my most memorable job experiences involve trying to solve really tough technical problems and the flash of inspiration that hits you in the middle of the night. You can't wait to get in the lab the next day and run the experiment to see if it works. When you finally solve the problem, the buzz stays with you for several days.

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

I first learned about surfactants from my organic chemistry professor in undergraduate school. After he described the hydrophobic effect and surfactant self-assembly, I was pretty much hooked for life. 35 years later I am still fascinated about the behavior of surfactants and the endless applications for these materials.

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

Stay active in professional societies like the American Chemical Society and AOCS, and give lots of papers at scientific meetings. Even if you are not comfortable speaking in front of people, the more you practice the easier it becomes.

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

Not that it hasn't been a fantastic ride so far, but I would have taken more classes in biotechnology. I see great potential in the use of microorganisms and biological processes for producing bio-based products.

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

In industrial world, I see a lot of people wanting to go into management or commercial roles. I think staying in the lab is much harder in terms of career advancement but can be more rewarding in terms of the self-satisfaction you get from solving tough technical challenges and the freedom you have to follow your natural curiosity. The main thing is to be passionate about what you do and to never surrender.

## How would you describe the culture in your field, and how has it developed?

The soaps and detergents industry has become increasing commoditized over the last 20 years. Ever-increasing downward pressure on raw material pricing has not been good for innovation. The trick is to recognize that this isn't likely to change, and to focus on using lower-cost raw materials and maximize process efficiency as a way to stay competitive.

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

Personally I think it is better to be well-rounded. Seeing the interconnections between different ideas and application areas allows you to be flexible and try different approaches to solving a problem or developing innovative new products.

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

As an industrial chemist, you definitely need an advanced degree if you want to have the freedom to pursue your own research ideas.

# PATENTS

## Encapsulation of oxidatively unstable compounds

Hendrickson, W.A., *et al.*, Aveka, Inc., US8741337, June 3, 2014

An encapsulated material containing an oxidation-sensitive core is covered by at least a dried phospholipid layer, and contains at least one phytosterol in the core, the phospholipid layer or in a further layer or layers. By using microencapsulation, oxidatively unstable materials may be provided with a synthetic protective barrier and rendered less susceptible to oxidative degradation.

## Method for stabilizing diesel engine lubricating oil against degradation by biodiesel fuel

Habeeb, J.J., *et al.,* ExxonMobil Research and Engineering Co., US8748357, June 10, 2014

The lubricating oil used to lubricate diesel engines is stabilized against the detrimental degradation effects of biodiesel fuel by the addition to the lubricating oil of an additive concentrate comprising a premix of a first antioxidant, a second antioxidant of a type different from the first and an organometallic compound.

## Ultrasonic and megasonic method for extracting palm oil

Goodson, J.M., and L.T. Kheng, Megasonic Sweeping Inc., US8748642, June 10, 2014

A process for extracting palm oil includes an ultrasonic horn press and a megasonic clarifier. The ultrasonic horn press uses ultrasonic vibrations to rupture and heat the palm fruit. After pressing and filtering the palm oil from the ultrasonic horn press, the megasonic clarifier applies megasonic vibrations to clarify the palm oil.

## Methods for improving tolerance, digestion, and lipid soluble nutrient absorption in an infant, toddler, or child

Lai, C.-S., *et al.*, Abbott Laboratories, US8754126, June 17, 2014

Disclosed are nutritional formulations including predigested fats that can be administered to preterm infants, infants, toddlers, and children for improving tolerance, digestion, and absorption of nutrients and for reducing the incidence of necrotizing enterocolitis, colic, and short bowel syndrome. The predigested fats include fatty acid-containing monoglycerides and/or a fatty acid component.

## Degradable perforation balls and associated methods of use in subterranean applications

Luo, H., and D.D. Fulton, Halliburton Energy Services, Inc., US8757260, June 24, 2014

Methods and compositions that include a method of treating a subterranean formation comprising the steps of providing a carrier fluid comprising degradable balls that comprise a carboxylic acid, a fatty alcohol, a fatty acid salt, a fatty ester, a fatty acid salt, or a combination thereof, and introducing the carrier fluid to the subterranean formation during a treatment.

## Method for obtaining a fraction enriched with functionalized fatty acid esters from seeds of oleaginous plants

Piccirilli, A., *et al.*, US8759556, June 24, 2014

The invention relates to a method for the selective extraction of functionalized fatty acid esters from seeds of oleaginous plants, wherein said method includes: (i) at least one step of extracting fatty acid esters that comprises simultaneously feeding into a reactor containing said seeds a light anhydrous alcohol, a basic catalyst, and an extraction solvent nonmiscible with said light alcohol and in which said functionalized fatty ester is not soluble in order to obtain a mixture of esters and glycerol; (ii) and at least one step of selectively extracting hydroxylated fatty acid esters by feeding into the reactor said extraction solvent in a backflush direction relative to the light alcohol in order to obtain an alcohol phase enriched with fatty acid esters, a glycerol phase, and a cake. The invention can be used for obtaining a fraction having a high concentration of hydroxylated or epoxidized functionalized fatty acid esters, and a solvent phase containing the other nonfunctionalized fatty acid esters directly from the seeds of oleaginous plants.

## Heat transfer fluid, additive package, system and method

Yang, B., *et al.*, Prestone Products Corp., US8771542, July 8, 2014

Disclosed herein is a heat transfer fluid, comprising a hydroxylated carboxylic acid of formula $(OH)_x(R_1)(COOH)_y$, wherein $x$ is 2 to 10, $y$ is 3 to 10, and $R_1$ is a C2–50 aliphatic group, a C6–50 aromatic group, or a combination thereof; and wherein the hydroxylated carboxylic acid comprises the hydroxylated carboxylic acid, an ester thereof, a salt thereof, an anhydride thereof, or a combination thereof. A heat transfer system comprises an aluminum component, a magnesium component,

or an aluminum component and a magnesium component; and the foregoing heat transfer fluid.

## Process for making thermoplastic polyesters

Bashir, Z., Saudi Basic Industries Corp., US8772436, July 8, 2014

The invention relates to a process for making a thermoplastic polyester, which comprises contacting at least one carboxylic acid-based compound and at least one alcohol-based compound in esterification and subsequent polycondensation reactions, in the presence of certain exfoliated inorganic nanolayered titanates acting as a catalyst.

## Safflower oil emulsion as dietary supplement and preparation thereof

Fujiwara, K., *et al.*, Shiseido Co., Ltd., US8778363, July 15, 2014

To provide an oil-in-water emulsion skin care cosmetic composition which, without the addition of a pharmaceutical agent and a film-forming agent or the like thereto, effects an excellent elastic or resilient feeling to skin and is excellent in non-stickiness and stability. An oil-in-water emulsion skin care cosmetic composition, comprising (a) a paraffin wax and/or a polyethylene wax, (b) a microcrystalline wax, and (c) an animal/plant-derived wax which contains, as the main ingredient thereof, an ester of a higher fatty acid having from 20 to 32 carbon atoms and an alcohol having from 28 to 34 carbon atoms, and has a melting point of from 75 to 100 ˚C, in which the ratio of component (a) to component (b) is from 70/30 to 95/5 (by mass).

## Method of making nutritional emulsions containing process-encapsulated oils

Walton, J.E., *et al.*, Abbott Laboratories, US8778439, July 15, 2014

Disclosed is a method of making nutritional emulsions, comprising: (a) heating and blending together an emulsifying agent having a melt point above about 25 ˚C and oil having hydrophobic off-notes (e.g. non-encapsulated polyunsaturated fatty acid) in a weight ratio of at least about 1:15; (b) adding the heated blend to a fat, protein, and carbohydrate mixture comprising a maltodextrin (DE of about 10 or less), in a weight ratio of the maltodextrin to the oil having hydrophobic off-notes of at least about 1:2; and (c) homogenizing, and then cooling the combination below the melt point of the emulsifying agent to form a nutritional emulsion comprising from about 0.01 percent to about 5 percent by weight of process-encapsulated polyunsaturated fatty acid. The resulting nutritional emulsions effectively mask off-notes commonly associated with certain oils, e.g., polyunsaturated fatty acids, soy oil, beta-hydroxy-beta-methylbutyrate oils.

## Method for concentrating lipids

Yoshikawa, K., Nippon Suisan Kaisha Ltd., US8784921, July 22, 2014

As a method for an efficient concentration of lipid components from food materials, a method for concentrating lipids contained in a crustacean, which comprises heating squeezed liquid prepared by squeezing the whole crustacean or a part thereof and separating the heated squeezed liquid into solids containing lipid components and liquid containing water-soluble components. Those are useful as the method by which lipids abundantly containing the phospholipid are prepared easily and at a low cost. Furthermore, the solids containing the lipids prepared by said method or a dried product thereof, lipids extracted therefrom and a composition abundantly containing the useful lipids derived from crustaceans are useful as materials for pharmaceuticals, ingredients for foods or feed, etc.

## Toughening cross-linked thermosets

Lascala, J. J, *et al.*, Drexel University, U.S. Government represented by Secretary of Army, US8785547, July 22, 2014

Grafted triglycerides comprising an acrylated triglyceride grafted with a fatty acid residue containing 4 to 28 carbon atoms. Also described are methods for making a grafted triglyceride and for curing a material selected from vinyl esters and unsaturated polyesters and mixtures thereof and optionally a reactive diluent. The method includes the steps of mixing a grafted triglyceride of the present invention with a material selected from vinyl esters, unsaturated polyesters and mixtures thereof to form a mixture, and curing the mixture to form a cured resin system. A cured resin system comprising a cured product obtained by the foregoing method and composites containing the cured product and a filler or reinforcing material are also disclosed. This method also includes use of the grafted triglycerides to make toughened resin and composite systems with reduced hazardous air pollutants without significantly reducing the glass transition temperature and significantly increasing the viscosity.

## Controlled-release fertilizers made from cross-linked glyceride mixtures

Maruvada, S., *et al.*, Agriium Advanced Technologies, US8790437, July 29, 2014

A controlled release fertilizer material comprising a particulate plant nutrient surrounded by a coating which is the reaction product of a mixture including a cross-linked polyol, an isocyanate and a wax is described. The cross-linked polyol is a

CONTINUED ON PAGE 272

# EXTRACTS & DISTILLATES

## Frank D. Gunstone—teacher, researcher, and writer

Marcel, S.F. and L.K. Jie, *Eur. J. Lipid Sci. Techn. 117*: 135–140, 2015, http://dx.doi.org/10.1002/ejlt.201400465.

This article is an extension of a lecture to celebrate the 90th birthday of Professor Frank D. Gunstone of the University of St. Andrews, Scotland, UK, which was delivered at the 7th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry held in Karlsruhe, Germany in March, 2014. The author is greatly honored by this task and privileged to collate some of the pioneering and great works of a "giant" in lipid chemistry. Frank Gunstone is not just a great teacher, who taught the world about fats and oils, but spent a lifetime to investigate the nature of lipid molecules. He shared his vast knowledge of the subject with the chemical world through over 400 publications, including research papers, review articles, and books. He retired on October 27th, 2013, the day when he celebrated his 90th birthday at home with his family in St. Andrews, Scotland, after serving "on the job" for 70 years. Frank was born in Chadderton (Lancashire), which is located in the metropolitan borough of Oldham in Greater Manchester, England. At the turn of the century, Chadderton was a town thriving on the cotton industry and had one of the largest cotton mills in the UK. The mill was driven by a Parson steam turbine, which drove the mill by ropes. His childhood was spent in Chadderton until 1936 when the family moved to Liverpool.

## Fatty acid profiles and antioxidants of organic and conventional milk from low- and and high-input systems during outdoor period

Kusche, D., *et al., J. Sci. Food Agric. 95*: 529–539, 2015, http://dx.doi.org/10.1002/jsfa.6768.

Intensification of organic dairy production leads to the question of whether the implementation of intensive feeding incorporating maize silage and concentrates is altering milk quality. Therefore the fatty acid (FA) and antioxidant (AO)

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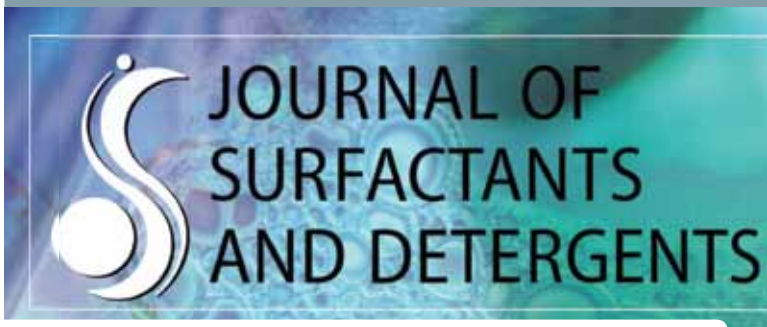


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- Jatoi, A.W., Z. Khatri, F. Ahmed, and M.H. Memon, Effect of silicone nano, nano/micro and nano/macro-emulsion softeners on color yield and physical characteristics of dyed cotton fabric
- Uner, A. and F. Yilmaz, Efficiency of laundry polymers containing liquid detergents for hard surface cleaning
- Chauhan, S., R. Singh, K. Sharma, and K. Kumar, Interaction study of anionic surfactant with aqueous non-ionic polymers from conductivity, density and speed of sound measurements
- Che, Y., *et al.*, Synthesis, characterization and aqueous properties of a new hybrid fluorocarbon cationic surfmer
- Negm, N.A., A.S. Mohamed, S.M. Ahmed, and M.A. El-Raouf, Polymer-cationic surfactant interaction: 1. surface and physicochemical properties of polyvinyl alcohol (PVA)-s-alkyl isothiouronium bromide surfactant mixed systems
- Khanmohammadi, M., H. Rezaee Rudmianeh, A. Bagheri Garmarudi, and K. Ghasemi, Evaluating the performance of detergent powder formulations containing nano alumina using diffuse reflectance infrared spectroscopy and pattern recognition techniques
- Meshram, S.U., U.R. Khandekar, S.M. Mane, and A. Mohan, novel route of producing zeolite A resin for quality-improved detergents
- Vecino, X., G. Bustos, R. Devesa-Rey, J.M. Cruz and A.B. Moldes, Salt-free aqueous extraction of a cell-bound biosurfactant: a kinetic study
- Sarac, N., A. Ugur, R. Boran, and E.S. Elgin, The use of boron compounds for stabilization of lipase from *Pseudomonas aeruginosa* ES3 for the detergent industry
- Chai, J., *et al.*, Comparison of the composition and structural parameters of w/o microemulsions containing gemini imidazoliums with those containing monomeric analogues
- Xu, H., B. Liu B., P. Kang, and X. Bao, Properties of a binary system containing anionic and cationic gemini surfactants
- Zhou, M., *et al.*, Synthesis of new salt-resistant sulfonate gemini surfactants with hydroxyl groups
- Negm, N.A., S.M. Tawfik, M.I. Abdou, E.A. Badr, and F.M. Ghuiba, Evaluation of some nonionic surfactants derived from tannic acid as additives for water-based mud
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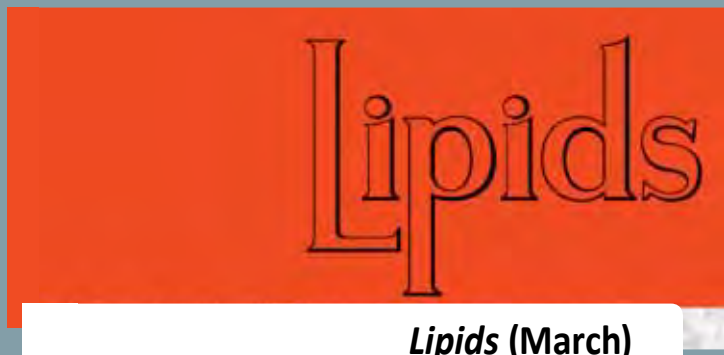
- Behr, A.M., C.J. Tucker, and E.E. Daugs, Performance of new biodegradable di-sulfonate surfactants as hydrotropes in high-temperature and salinity environments

- Glaubitz, J. and T.C. Schmidt, Analytical characterization and comparison of tristyrylphenol ethoxylates used in agrochemical formulations
- Zgoła-Grzes´kowiak, A., T. Grzes´kowiak, and A. Szyman´ski, Biodegradation of nonylphenol monopropoxyethoxylates
- Zhang Q., Y. Sun, L. Zhi, Y. Zhang, and M. Di Serio, Properties of ethoxylated castor oil acid methyl esters prepared by ethoxylation over an alkaline catalyst


## *Journal of the American Oil Chemists' Society* (March)

- Ruschel, C.F.C., *et al.*, Environmentally friendly determination of quality parameters of biodiesel/diesel blends using fourier transform infrared spectra
- Tokay, F. and S. Bağdat, Determination of iron and copper in edible oils by flame atomic absorption spectrometry after liquid–liquid extraction
- Ramaley, L., L.C. Herrera, and J.E. Melanson, Quantitative analysis of TAG in oils using lithium cationization and direct-infusion ESI tandem mass spectrometry
- Shyamsundar, M., S.Z.M. Shamshuddin, and C.U. Aniz, Cordierite honeycomb monoliths coated with zirconia and its modified forms for biodiesel synthesis from *Pongamia glabra*
- Kaymak, H.C., Profile of (*n*-9) and (*n*-7) isomers of monounsaturated fatty acids of radish (*Raphanus sativus* L.) seeds
- Görgün, S. and G. Zengin, Determination of fatty acid profiles and esterase activities in the gills and gonads of *Vimba vimba* (L., 1758)
- Xu, H., L. Zhu, J. Dong, Q. Wei, and M. Lei, Composition of *Catalpa ovata* seed oil and flavonoids in seed meal as well as their antioxidant activities
- Xin, C.M., Y. Zhao, L. Yao, W. Wang, and T. Wang, Stability and oxidizing effect of membraneless electrolyzed water
- Vyssotski, M., K. Lagutin, A. MacKenzie, and Y. Itabashi, Chemical synthesis and gas chromatographic behavior of ã-stearidonic (18:4*n*-6) acid
- Chia, S.L., *et al.*, Effect of subcritical carbon dioxide extraction and bran stabilization methods on rice bran oil
- Oliveira, I.P., A.F. Souza, C.H. Lescano, A.R.L. Caires A.R.L., and R.M. Muzzi, Thermal oxidation analysis of forage turnip (*Raphanus sativus* L. var. *oleiferus* Metzg.) oil
- Akil, E., *et al.*, Oxidative stability and changes in chemical composition of extra virgin olive oils after short-term deep-frying of french fries
- Alves Sobrinho, R.C.M., *et al.*, FAME production and fatty acid profiles from moist *Chlorella* sp. and *Nannochloropsis oculata* biomass
- Jang, Y. and K. Li, An all-natural adhesive for bonding wood
- Cegla-Nemirovsky, Y., A. Aserin, and N. Garti, Oleogels from glycerol-based lyotropic liquid crystals: phase diagrams and structural characterization
- Allı, S., R.S. Tığlı, A. Allı, and B. Hazer, Biodegradable poly(å-caprolactone)-based graft copolymers via poly(linoleic acid): in vitro enzymatic evaluation 449




## *Lipids* (March)

- Köpke, S., T. Buhrke, and A. Lampen, miRNA expression in human intestinal caco-2 cells is comparably regulated by *cis*- and *trans*-fatty acids
- Liu Y.-W., *et al.*, Octacosanol enhances the proliferation and migration of human umbilical vein endothelial cells via activation of the PI3K/Akt and MAPK/Erk pathways
- Michael, D.R., T.S. Davies, L. Laubertová, H. Gallagher, and D.P. Ramji, The phosphoinositide 3-kinase signaling pathway is involved in the control of modified low-density lipoprotein uptake by human macrophages
- Han, H., *et al.*, Lutein prevents high fat diet-induced atherosclerosis in ApoE-deficient mice by inhibiting NADPH oxidase and increasing PPAR expression
- Tian,Y., *et al.*, Association of L-FABP T94A and MTP I128T polymorphisms with hyperlipidemia in chinese subjects
- Vasconi M., *et al.*, Fatty acid composition of freshwater wild fish in subalpine lakes: a comparative study
- Lagutin, K., A. MacKenzie, K.M. Houghton, M.B. Stott, and M. Vyssotski, Novel long-chain diol phospholipids from some bacteria belonging to the class *Thermomicrobia*
- Ntumba, J.K., L. Collard, K.M. Taba, and R. Robiette, Isolation of a series of fatty acid components of *Ongokea gore* Seed (isano) oil and their detailed structural analysis
- Baptist, M., C. Panagabko, J.D. Nickels, J. Katsaras, and J. Atkinson, 2,2'-bis(monoacylglycero) PO4 (BMP), but not 3,1'-BMP, increases membrane curvature stress to enhance α-tocopherol transfer protein binding to membranes

profiles of milk on 24 farms divided into four system groups in three replications ($n = 71$) during the outdoor period were analyzed. In this system comparison, a differentiation of the system groups and the effects of the main system factors 'intensification level' (high-input *versus* low-input) and 'origin' (organic *versus* conventional) were evaluated in a multivariate statistical approach. Consistent differentiation of milk from the system groups due to feeding-related impacts was possible in general and on the basis of 15 markers. The prediction of the main system factors was based on four or five markers. The prediction of 'intensification level' was based mainly on CLA *c*9,*t*11 and C18:1 *t*11, whereas that of 'origin' was based on n-3 PUFA. It was possible to demonstrate consistent differences in the FA and AO profiles of organic and standard conventional milk samples. Highest concentrations of nutritionally beneficial compounds were found in the low-input organic system. Adapted grass-based feeding strategies including pasture offer the potential to produce a distinguishable organic milk product quality.

## Effects of stearidonic acid on serum triacylglycerol concentrations in overweight and obese subjects: a randomized controlled trial

Pieters, D.J.M. and R.P. Mensink, *Eur. J. Clin. Nutr. 69*: 121–126, 2015, http://dx.doi.org/10.1038/ejcn.2014.193.Top of page

Eicosapentaenoic acid (EPA), which may reduce the risk for coronary heart disease (CHD), can be synthesized at low rates from α-linolenic acid (ALA). The rate-limiting step for this conversion is the Δ6-desaturation of ALA into stearidonic acid (SDA). Thus providing oils rich in SDA may increase endogenous synthesis of EPA, which may subsequently lower serum triacylglycerol concentrations, an effect frequently observed after EPA supplementation. We therefore studied the effects of Echium oil on serum triacylglycerol concentrations and the omega-3 index, which correlate negatively with the risk for CHD. A randomized, double-blind, placebo-controlled cross-over trial was conducted, in which 36 healthy overweight and slightly obese subjects daily received 10 g of Echium oil (providing 1.2 g of SDA) or a high oleic acid sunflower oil (HOSO) as control for 6 weeks, with a washout period of at least 14 days. Four subjects dropped out. Differences between periods were tested for statistical significance ($P<0.05$) using a paired *t*-test. Serum triacylglycerol and other lipid concentrations were not significantly affected by consumption of Echium oil compared with HOSO. Echium oil significantly increased percentage of EPA in red blood cell (RBC) membranes with 0.14±0.25% (mean±s.d.) compared with HOSO ($P=0.02$). No significant effects on docosahexaenoic acid in RBC membranes or on the omega-3 index were found. In healthy overweight and slightly obese subjects, an increased intake of SDA from Echium oil does not lower serum triacylglycerol concentrations. Despite an increase in the percentage of EPA in RBC membranes, the omega-3 index was not changed.

## Isomer-specific effects of conjugated linoleic acid on HDL functionality associated with reverse cholesterol transport

Nicod, N., *et al., J. Nutr. Biochem. 26*: 165–172, 2014, http://dx.doi.org/10.1016/j.jnutbio.2014.10.002.

High-density lipoproteins (HDLs) are atheroprotective because of their role in reverse cholesterol transport. The intestine is involved in this process because it synthesizes HDL, removes cholesterol from plasma and excretes it into the lumen. We investigated the role of selected dietary fatty acids on intestinal cholesterol uptake and HDL functionality. Caco-2 monolayers grown on Transwells were supplemented with either palmitic, palmitoleic, oleic, linoleic, docosahexaenoic, eicosapentaenoic, arachidonic or conjugated linoleic acids (CLAs): c9,t11-CLA; t9,t11-CLA; c10,t12-CLA. Cells synthesized HDL in the basolateral compartment for 24 h in the absence or presence of an antibody to SR-BI (aSR-BI), which inhibits its interaction with HDL. Free cholesterol (FC) accumulated to a greater extent in the presence than in the absence of aSR-BI, indicating net uptake of FC by SR-BI. Uptake's efficiency was significantly decreased when cells were treated with c9,t11-CLA relative to the other fatty acids. These differences were associated with lower HDL functionality, since neither SR-BI protein expression nor expression and alternative splicing of other genes involved lipid metabolism were affected. Only *INSIG2* expression was decreased, with no increase of its target genes. Increasing pre-β-HDL synthesis, by inducing ABCA1 and adding APOA1, resulted in reduced uptake of FC by SR-BI after c9,t11-CLA treatment, indicating reduced functionality of pre-β-HDL. Conversely, treatment with c9,t11-CLA resulted in a greater uptake of FC and esterified cholesterol from mature HDL. Therefore, Caco-2 monolayers administered c9,t11-CLA produced a nonfunctional pre-β-HDL but took up cholesterol more efficiently via SR-BI from mature HDL.

## Comparative lipidomic profiling of two *Dunaliella tertiolecta* strains with different growth temperatures under nitrate-deficient conditions

Kim, S.-H., *et al., J. Agric. Food Chem. 63*: 880–887, 2015, http://dx.doi.org/10.1021/jf502967k.

The metabolic changes that occur in *Dunaliella tertiolecta* upon exposure to low temperatures and nitrate deficiency were analyzed by exploring the fatty acid composition and lipid profile of two strains that were acclimated to different temperatures. The results indicate that the levels of linolenic acid (C18:3) and diacylglyceryl-*N*,*N*,*N*-trimethylhomoserine (DGTS) were significantly higher in the low-temperature

(15 °C) strain (SCCAP K-0591) than in a strain grown at 21 °C (UTEX LB999). In addition, DGTS accumulated in LB999 under nitrate-deficient conditions, while the levels of most lipids, including DGTS, remained almost consistent in K-0591. The higher levels of DGTS in K-0591 suggest that DGTS could play a role in adaptation to low temperatures and nitrate deficiency in this organism. The results of this research could be applied to the development of new microalgal strains with tolerance of low temperature and nitrate deficiency by metabolic engineering targeted to DGTS species.

## Alpha-linolenic acid (ALA) is inversely related to development of adiposity in school-age children

Perng, W., *et al., Eur. J. Clin. Nutr. 69*: 167–172, 2015, http://dx.doi.org/10.1038/ejcn.2014.210.

Studies in adults indicate that dietary polyunsaturated fatty acid (PUFA) composition may play a role in development of adiposity. Because adipocyte quantity is established between late childhood and early adolescence, understanding the impact of PUFAs on weight gain during the school-age years is crucial to developing effective interventions. We quantified N-3 and N-6 PUFAs in serum samples of 668 Colombian schoolchildren aged 5–12 years at the time of recruitment into a cohort study, using gas–liquid chromatography. Serum concentrations of N-3 (alpha-linolenic acid (ALA), eicosapentaenoic acid, docosahexaenoic acid) and N-6 PUFAs (linoleic acid, gamma-linolenic acid, dihomo-gamma-linolenic acid, arachidonic acid) were determined as percentage total fatty acids. Children's anthropometry was measured annually for a median of 30 months. We used mixed-effects models with restricted cubic splines to construct population body mass index-for-age *z*-score (BAZ) growth curves for age- and sex-specific quartiles of each PUFA. N-3 ALA was inversely related to BAZ gain after adjustment for sex, baseline age and weight status, as well as household socioeconomic level. Estimated BAZ change between 6 and 14 years among children in the highest quartile of ALA compared with those in the lowest quartile was 0.45 (95% confidence interval: 0.07, 0.83) lower (*P*-trend=0.006). N-3 ALA may be protective against weight gain in school-age children. Whether improvement in PUFA status reduces adiposity in pediatric populations deserves evaluation in randomized trials.

## The Danish tax on saturated fat: why it did not survive

Vallgårda, S., *et al., Eur. J.Clin. Nutr. 69*: 223–226, 2014, http://dx.doi.org/10.1038/ejcn.2014.224.

Health promoters have repeatedly proposed using economic policy tools, taxes and subsidies, as a means of changing consumer behavior. As the first country in the world, Denmark introduced a tax on saturated fat in 2011. It was repealed in 2012. In this paper, we present arguments and themes involved in the debates surrounding the introduction and the repeal. An analysis of parliamentary debates, expert reports and media coverage; key informant interviews; and a review of studies about the effects of the tax on consumer behavior.

Results: A tax on saturated fat had been suggested by two expert committees and was introduced with a majority in parliament, as a part of a larger economic reform package. Many actors, including representatives from the food industry and nutrition researchers, opposed the tax both before and after its introduction, claiming that it harmed the economy and had no positive influence on health, rather the contrary. Few policy actors defended the tax. Public health had a prominent role in the politicians' arguments for introducing the tax but was barely mentioned in the debate about the repeal. Shortly after the repeal of the tax, research was published showing that consumption of saturated fat had declined in Denmark. The analysis indicates that the Danish tax on fat was introduced mainly to increase public revenue. As the tax had no strong proponents and many influential adversaries, it was repealed. New research indicates that the tax was effective in changing consumer behavior.

## Light intensity regulates LC-PUFA incorporation into lipids of *Pavlova lutheri* and the final desaturase and elongase activities involved in their biosynthesis

Guihéneuf, F., *et al., J. Agr. Food Chem. 63*: 1261–1267, 2015, http://dx.doi.org/10.10.1021/jf504863u.

The microalga *Pavlova lutheri* is a candidate for the production of omega-3 long-chain polyunsaturated fatty acid (LC-PUFA), due to its ability to accumulate both eicosapentaenoic (EPA) and docosahexaenoic acids. Outstanding questions need to be solved to understand the complexity of n-3 LC-PUFA synthesis and partitioning into lipids, especially its metabolic regulation, and which enzymes and/or abiotic factors control their biosynthesis. In this study, the radioactivity of $^{14}$C-labeled arachidonic acid incorporated into the total lipids of *P. lutheri* grown under different light intensities and its conversion into labeled LC-PUFA were monitored. The results highlighted for the first time the light-dependent incorporation of LC-PUFA into lipids and the light-dependent activity of the final desaturation and elongation steps required to synthesize and accumulate n-3 C20/C22 LC-PUFA. The incorporation of arachidonic acid into lipids under low light and the related Δ17-desaturation activity measured explain the variations in fatty acid profile of *P. lutheri*, especially the accumulation of n-3 LC-PUFA such as EPA under low light conditions.

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## Tocopherol and tocotrienol contents of different varieties of rice in Malaysia

Shammugasamy, B., *et al.*, *J. Sci. Food Agr. 95*: 672–678, 2015, http://dx.doi.org/10.1002/jsfa.6742.

The present study examined the contents of tocopherols and tocotrienols and their distribution in 58 different varieties of whole rice cultivated in Malaysia. The analytical method used was saponification of samples followed by dispersive liquid–liquid microextraction and reverse phase high-performance liquid chromatography. The total vitamin E contents of different varieties of whole rice ranged between 19.36 and 63.29 mg $kg^{-1}$. Contents of vitamin E isomers varied among rice varieties both within and between grain color groups. Black-pigmented rice showed significantly higher mean contents of $\alpha$-tocopherol, $\beta$-tocopherol and $\alpha$-tocotrienol than non-pigmented rice and red-pigmented rice. Red-pigmented rice had significantly lower mean contents of $\gamma$-tocotrienol and total vitamin E than non-pigmented rice. The mean contents of $\delta$-tocotrienol and total vitamin E in non-pigmented rice, however, were similar to those in black-pigmented rice. $\gamma$-Tocotrienol was the predominant form of vitamin E isomer in all analyzed varieties. The Pearson correlations among vitamin E isomers and total vitamin E content of whole rice were also studied. This study provides information on vitamin E content of different rice varieties that would be beneficial for decision making in genetic breeding of bioactive compound-rich rice varieties.

## A correlation between tocopherol content and antioxidant activity in seeds and germinating seeds of soybean cultivars

Lee, Y.Y., *et al.*, *J. Sci. Food Agr. 94*: 819–827, 2015, http://dx.doi.org/10.1002/jsfa.6963.

Tocopherols are crucial lipid-soluble antioxidants and essential nutrients. There is increasing interest in the biofortification of crops with vitamin E for reducing micronutrient malnutrition. However, relatively little is known about the development of soybean cultivars with high levels of tocopherol through combined breeding. Tocopherol contents of seeds and germinating seeds of 28 Korean soybean cultivars were analyzed and evaluated for health-promoting activities. Total tocopherol concentrations ranged from 203.9 to 503.1 μg $g^{-1}$ in seeds and from 20.1 to 230.1 μg $g^{-1}$ in germinating seeds. The traditional landraces of HaNagari (HN, 503.1 μg $g^{-1}$), Orialtae (OL, 486.6 μg $g^{-1}$), SuMoktae (SM, 476.5 μg $g^{-1}$) and SoRitae (SR, 475.5 μg $g^{-1}$) showed high levels of tocopherol content. The contents of the four isomers of tocopherol in seeds and germinating seeds were correlated with lipid peroxidation. The $\gamma$- and $\delta$-tocopherol contents in seeds were related to 1,1-diphenyl-2-picrylhydrazyl free radical scavenging activity (0.434; $P < 0.01$ and 0.373; $P < 0.05$). Total tocopherol content was higher in soybean landraces as compared with modern cultivars developed by cross-breeding. These results suggest that soybean breeding is necessary to increase tocopherol levels. © 2014 Society of Chemical Industry

## Carnosic acid attenuates obesity-induced glucose intolerance and hepatic fat accumulation by modulating genes of lipid metabolism in C57BL/6J-*ob/ob* mice

Park, M-Y. and M.-K. Sung, *J. Sci. Food Agri. 95*: 828–835, 2015, http://dx.doi.org/10.1002/jsfa.6973.

Carnosic acid (CA), a major bioactive component of rosemary (*Rosmarinus officinalis*) leaves, is known to possess antioxidant and anti-adipogenic activities. In this study it was hypothesized that CA would ameliorate obesity-induced glucose intolerence and hepatic fat accumulation, and possible mechanisms are suggested. It was observed that a 0.02% (w/w) CA diet effectively decreased body weight, liver weight and blood triglyceride (TG) and total cholesterol levels ($P < 0.05$) compared with the control diet. CA at 0.02% significantly improved glucose tolerance, and hepatic TG accumulation was reduced in a dose-dependent manner. Hepatic lipogenic-related gene (*L-FABP*, *SCD1* and *FAS*) expression decreased whereas lipolysis-related gene (*CPT1*) expression increased in animals fed the 0.02% CA diet ($P < 0.05$). Long-chain fatty acid content and the ratio of C18:1/C18:0 fatty acids were decreased in adipose tissue of animals fed the 0.02% CA diet ($P < 0.05$). Serum inflammatory mediators were also decreased significantly in animals fed the 0.02% CA diet compared with those of the obese control group ($P < 0.05$). These results suggest that CA is an effective anti-obesity agent that regulates fatty acid metabolism in C57BL/6J-*ob/ob* mice.

## Health benefits of maternal supplementation with docosahexaenoic acid, folic acid, vitamin D, and iodine during pregnancy and lactation for fetal and infant brain development and function

Morse, N., *Lipid Technology 27*: 31–35, 2015, http://dx.doi.org/10.1002/lite.201500001.

Dietary deficiencies of nutrients critical for fetal/infant brain development and function are increasingly being

reported in scientific literature. Maternal supplementation with these nutrients within safe intake recommendations during pregnancy and while breast-feeding has the potential to prevent many brain and central nervous system abnormalities and could enhance brain development and function in their children.

## Synthesis and refining of sunflower biodiesel in a cascade of continuous centrifugal contactor separators

Abduh, M.Y., *et al.*, *Eur. J. Lipid Sci. Techn. 117*: 242–254, 2015, http://dx.doi.org/10.1002/ejlt.201400206.

The synthesis of fatty acid methyl esters (FAME) from sunflower oil and methanol was studied in a continuous centrifugal contactor separator (CCCS) using sodium methoxide as the catalyst. The effect of relevant process variables like oil and methanol flow rate, rotational speed and catalyst concentration was investigated and modelled using non-linear regression. Good agreement between experiments and model were obtained. At optimised conditions (oil flow rate of 31 mL/min, rotational speed of 34 Hz, catalyst concentration of 1.2%w/w and a methanol flow rate of 10 mL/min), the FAME yield was 94 mol% at a productivity of 2470 kg $_{FAME}$/$m^3_{reactor}$.h. Proof of principle for the synthesis and subsequent refining of FAME in a cascade of two CCCS devices was also obtained. Relevant properties of the refined FAME obtained using this technology were determined and were shown to meet the ASTM specifications.

## Characterization of phospholipids by two-dimensional liquid chromatography coupled to in-line ozonolysis–mass spectrometry

Sun, C., *et al.*, *J. Agr. Food Chem. 63*: 1442–1451, 2015, http://dx.doi.org/10.1021/jf5049595.

In this study, the characterization of phospholipids (PL) was achieved by using a combination of LC/MS/MS and two-dimensional LC/MS. A HILIC LC column was used for PL class separation, while the further molecular species separation of each PL class was achieved by using online HILIC × C18 LC. The double bond positions along the fatty acyl chains of these PL molecular species were also obtained by using the combination of 2D-LC and in-line ozonolysis–MS analysis. The ozonolysis device is composed of a gas-permeable, liquid-impermeable Teflon tube passing through a glass chamber filled with ozone gas, which is then placed in-line between the 2D-LC and the mass spectrometer. The eluting PL molecules in the LC mobile phase passed through the device where they rapidly reacted with the ozone that penetrated through the tubing wall. The ozonolysis products were then detected by MS in real-time, which allowed the localization of the double bonds along the fatty acyl chains in these PL molecular species. This comprehensive method was successfully applied to an egg yolk PL extract, which revealed the detailed structures of the PL molecules.

## Microalgae lipid characterization

Yao, L., *et al.*, *J. Agric. Food Chem. 63*: 1773–1787, 2015, http://dx.doi.org/10.1021/jf5050603.

To meet the growing interest of utilizing microalgae biomass in the production of biofuels and nutraceutical and

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Celebrating 50 Years 50 Years Publishing Lipid Research

Lipids

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## No. 3 on the "fab 5" list

In celebration of the 50th volume of the AOCS journal *Lipids*, we are featuring one paper each month from a list of five pivotal original papers representing the broad areas of research from the first 49 volumes of the journal. All five articles are available free of charge at http://tinyurl.com/Lipids-Fab-5.

This month's paper—No. 3 on the "Fab 5" list—was written by William A. Pryor, J.P. Stanley, and E. Blair at Louisiana State University in Baton Rouge. It appeared in 1976, has been cited more than 500 times, and is titled "Autoxidation of polyunsaturated fatty acids: II. A suggested mechanism for the formation of TBA-reactive materials from prostaglandin-like endoperoxides."

"This paper helped form the foundation in the literature that polyunsaturated fatty acids (PUFA) are subject to free radical-initiated autoxidation and form endoperoxides," notes *Lipids* Editor-in-Chief Eric J. Murphy, which are now recognized as an important part of the pathophysiology of numerous human diseases, including atherosclerosis and cancer. By using several mass spectrometric techniques, the researchers determined that oxidation of methyl linolenate results in endoperoxide formation and that these products go on to form malonaldehyde. By extension, other PUFA would be subject to autoxidation to form endoperoxides and are the source of the TBA-reactive [thiobarbituric acid] materials in autoxidation systems, now known to contain mainly malondialdehyde formed via PUFA autoxidation.

# Scientific activism for cosmetic chemists

- **The best science supports the notion that modern cosmetics are safe to use. Unfortunately, misinformed and fear-mongering groups are learned in the ways of PR, the media finds scare stories more interesting than legitimate science, and there are not a lot of scientists offsetting inaccuracies with reliable information.**
- **The best way to combat misinformation about cosmetic and chemical safety is to publish your own accurate content and participate in scientific activism.**
- **This article describes ways you can do that.**

**Perry Romanowski**

At the Lake Erie Society of Cosmetic Chemists meeting in 2014 [1], Joe Schwarcz, director of the Office for Science & Society at McGill University in Montreal, Quebec, Canada, made some great points about a number of hot button issues including lead in lipstick, parabens, phthalates, and more. The basic message is that non-governmental organizations like the Environmental Working Group (EWG) have it wrong. One of the speaker's main messages was that the public is being misinformed by fear-mongering groups, and it is up to scientists to set the record straight. I've given this a lot of thought and put together what I believe scientists can do to combat the unscientific nonsense that is pushed daily by misinformed groups.

## WHY IS THIS A PROBLEM

But before we cover what to do, it's helpful to discuss why this is a problem cosmetic chemists should care about. First, miseducated consumers will influence market research which could make your marketing folks demand that you avoid disparaged ingredients. You may lose control over which ingredients you can use, but you won't lose the responsibility for the results of those decisions. There is no upside for formulators who are restricted in their ingredient choice for no scientific reason.

Next, your company may lose sales and may be targeted for negative publicity for no good reason. Johnson & Johnson was compelled to reformulate perfectly fine formulations due to unfounded claims by consumer groups. You will likely find that reformulating functional products takes away resources that should go into creating innovative new products. This kind of fear mongering inhibits cosmetic innovation.

Finally, as a formulator you should be educated about the safety of ingredients you use in your formulations. You should be the expert people turn to when they have questions about cosmetics.

## WHAT CAN YOU DO?

The reasons that so much misinformation gets out in the public and takes hold is because groups that spout this nonsense are learned in the ways of public relations, the media finds scare stories more interesting, and there are not a lot of scientists offsetting lies with the truth. You can do your part to start combating these lies about cosmetic and chemical safety by publishing your own truthful content. Participate in scientific activism. Here are 10 ways you can do that.

## SCIENTIFIC ACTIVISM

### 1. LEARN WHAT'S TRUE.

In starting a blog or answering questions about these topics you should be well-versed on what is true. How many of you know about the safety profile of parabens? What would you tell people about the levels of lead in lipstick? As a formulator, you should have ready, science-based answers to these questions. The way to learn what science has to say is to do some research in reliable, science-based sources. The FDA Cosmetics site at http://www.fda.gov/Cosmetics/ is a great place to start. The Cosmetic Ingredient Review (http://www.cir-safety.org/) is also good as is Personal Care Truth (http://personalcaretruth.com/). And, you can learn a lot from the cosmetic science discussion forum in Cosmetic Chemists Corner, a website written for cosmetic chemists by cosmetic chemists [2].

### 2. KNOW YOUR COMPETITION.

While you're trying to get the correct information out about cosmetic products, you should know who the misinformation groups are and what they are saying. Some of the key groups that have wrong things to say about cosmetic products include:

- the Campaign for Safe Cosmetics (CFSC) [3],
- the Environmental Working Group (EWG) [4], and
- the David Suzuki Foundation [5].

### 3. START A BLOG.

People learn about things from the Internet and doing Google searches. Having a blog is a great way to get your information to show up when someone does a search. At the time I wrote this article, a search for the term "sunscreen" pulled up the EWG 2014 sunscreen guide. This is junk information filled with untruths and misunderstandings of science. The first mostly unbiased result was the 5th spot on the search page, an article by WebMD. The FDA showed up in the 7th & 8th spot, but scientifically valid information from the American Academy of Dermatology didn't even show up on the front page. Similarly, junk information about parabens is the first thing you see when you search for it on Google. This should not be. Starting a blog and writing about sunscreen, parabens, or other cosmetic topics important to consumers will help move these junk peddlers off the front page of the search results. It's easy to start a blog. Go to WordPress.com or Blogger.com to get started for free.

### 4. LINK TO GOOD INFORMATION.

When you write about topics, be sure to include links to sites with supporting information using the appropriate words. Do a search for the term keywords to understand better what I'm talking about, but, basically, Google ranks websites based on the number of other websites that link to them. So the reason that the CFSC ranks high for the term "parabens" is because there are a lot of websites that use the word "paraben" then link it to the CFSC webpage that talks about parabens. To get the FDA's website higher for the search term "paraben," you should link the word "paraben" to the FDA website [6]. The way to knock bad information off the front of Google is to replace it with good information.

### 5. WRITE ABOUT THE RIGHT THINGS.

When you are writing your blog, you should make a list of topics that you want to help change the public's perception about. I would suggest things like parabens, preservatives, pthalates, sulfates, sunscreens, or any of the other vilified cosmetic ingredients. The more you write about these things, the greater the chance your page will show up in a search result—and the more likely someone will find out what is true.

### 6. PARTICIPATE IN SOCIAL MEDIA.

Having a blog is great, but many of these conversations are happening on social media sites like Twitter, Facebook, and LinkedIn. You should set up your own accounts on these websites and start producing content. You could just repeat things from your blog, but you could also respond to what other people are putting out. Getting a digital conversation going is the best way to combat misinformation. There are more social media sites beyond the ones I've suggested, but those are the main ones. YouTube is also a great place to produce content if you want to make videos.

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# INFORMATION

[1] www.lescc.com
[2] chemistscorner.com/cosmeticsciencetalk
[3] www.safecosmetics.org
[4] ewg.org
[5] www.davidsuzuki.org
[6] www.fda.gov/cosmetics/productsingredients/ingredients/ucm128042.htm
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[8] rbutr.com
[9] www.rachaelrayshow.com/tips/10236_the_brains_behind_the_beauty_industry/index.html
[10] personalcaretruth.com/2011/03/personal-care-truth-under-attack

## 7. CORRECT WIKIPEDIA.

Wikipedia is an excellent source for many topics, but for controversial ones it is less reliable. Since anyone can update a Wikipedia entry you should go through and update topics that are filled with misinformation. I know I had to fix the cosmetics entry because it was filled with inaccuracies that seemed to have been placed there by the EWG. There is an art to updating a Wikipedia page, however, so be sure to following best practices guidelines [7].

## 8. REBUT BAD INFORMATION.

There is a skeptical plug-in called Rbutr [8] which you can update on any page you find that has misinformation. Start using it to correct things that are mistaken on the web. It is not having a huge impact at the moment but it may in the future.

## 9. STAY INFORMED.

Stay informed about new findings in the cosmetic area. When there is new information about the safety of parabens or sunscreens or anything else, you should know about it. Don't be afraid to reverse your opinion either based on new evidence. We are scientists and it is ok to be wrong. It is not ok to be wrong and not correct your mistakes when you discover you've made one. Information is always changing. If something you wrote a few years back is no longer applicable, be sure to set the record straight. This is the primary difference between fear-mongering groups like the EWG and scientists. The EWG will never reverse its opinion on parabens despite the fact that science has demonstrated that they are safe.

## 10. FOLLOW THE FOLLOWING PUBLISHING TIPS FOR WORKING SCIENTISTS.

- *Watch your behavior*. Remember that anything you write on the Internet will potentially be there forever. Avoid calling people names, being insulting, swearing or writing or producing anything that you will regret in the future. If you are searching for a job now or in the future, potential employers will look at your online activity and use that in their assessment of whether they want to hire you. If you use your blog to mock natural product formulators, don't be surprised if it is harder for you to find employment with one of those producers. Some people may not worry about this, but you might not want to add this extra hurdle in your way of future job prospects.
- *Don't let emotional drain get you down.* Being more visible on the Internet will open you up to more criticism. Even if what you say is true there will be critics who will call you names, question your ethics, question your intelligence, and call you evil. I learned this after being on the Rachel Ray show [9] and getting highly criticized in their comments section. They seem to have removed it now, but there were some mean things said about me. You can read a recap by another blogger [10]. But don't be discouraged. People will say things to you or about you on the Internet that they would never say to you in real person.
- *Don't waste your time and energy.* You'll need to learn to let some arguments go. Avoid the temptation to be the one to finish an argument. Respond once or twice to someone then move on. People are not really interested in having their minds changed. You respond to effect people who may be lurking and reading the discussion, but don't ever think you are going to change the mind of the person you're directly communicating with. Most likely, you won't—no matter how good your information is. There are people in this world who will never believe that humans cause global warming or that parabens are safe to use as preservatives.
- *Know your company's policies.* Perhaps most important is that you should know your company's online policy. If your company doesn't have one, assume that anything you write will be seen as representing what your company is saying. A disclaimer along the lines of "thoughts and opinions expressed are those of the author and the author alone and do not represent those of any past, present or future employers" may help, but some companies don't want you to write about cosmetics at all. In these cases, I would encourage you to post using a pseudonym. I did that for years on the Beauty Brains until I was able to leave my corporate job. As the employee of a corporation, you are not really free to write what you want without possible repercussions. This is true of a blog, social media accounts, and forums. If you are not independent, be very careful about what you say or start writing anonymously.

Well, that's all I have for the moment. I hope some of you take some of these suggestions and start fighting the tide of unscientific nonsense that has swept through the Internet. Perhaps we can fight the fear mongers and use the truth to remove them from the limelight.

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# Busting myths about personal care products

Catherine Watkins

- **The Internet is filled with myths parading as fact.**
- **Many myths about consumer products arise because of chemophobia.**
- **Below, *Inform* examines eight pernicious Internet rumors about personal care products.**

Some of the oddest rumors—many with the potential to cause harm—circulate endlessly via the Internet. Unfortunately, most people who receive crackpot emails or funky Facebook posts forget to verify them on Snopes.com or other such myth-debunking sites, which can lead to public relations nightmares for entire industries. A case in point: the damaging email first collected by Snopes in 2001 claiming that canola oil is toxic.

Among the most enduring myths are those dealing with personal care products and cosmetics. Many consumers distrust manufacturers and are deeply chemophobic. Most do not realize that absolutely everything is composed of chemicals, which allows unscrupulous "greenwashing" marketers to play upon consumers' fears and misconceptions.

In service to the personal care industry and consumers, *Inform* decided to research eight pervasive myths. Each has its own unique ratio of fact to fiction. Can you guess which ones—if any—are true?

## 1. Mascara is made with bat feces.

The cosmetics industry can thank a US reality television show star for starting this rumor, according to Snopes. Billy Bretherton, aka "Billy the Exterminator," told his viewers that the bat feces on an attic floor in a bat-infested house he was exterminating would become an ingredient in mascara.

Billy was wrong. His confusion stems from the similarity of the Spanish word *guano*—which means fertilizer or dung—and *guanine*—a purine base ($C_5H_5N_5O$) that is a fundamental constituent of DNA and RNA. A crystalline form of guanine is widely used in the cosmetics and toiletries industries, according to the Personal Care Products Council (PCPC). Guanine functions as a colorant and as a shimmering or light-diffusing agent in products such as fragrances, hair conditioners, lipsticks, shampoos, and skincare products.

PCPC—a trade association based in Washington, DC, USA—notes that guanine is approved by the US Food and Drug Administration (FDA), which regulates cosmetics in the United States. "By law, guanine must be derived from fish scales," PCPC spokesperson Irene Malbin told Snopes. "It is not derived from guano. In addition, there are no guano- or feces-based ingredients used in any cosmetics."

## 2. Anesthetics such as Novocain or Lidocaine are the secret behind "no tears" baby shampoos.

This certifiably false rumor has been around since at least 1994. The mild nature of baby shampoos comes from the use of long-chain surfactants or an ionic polymer, both of which alleviate stinging if the product gets into the eyes, and not from anesthetics.

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## 3. Lead in lipstick is dangerous.

No one disputes that lead is present in lipstick . . . as well as in drinking water and food. In fact, lead occurs naturally in the Earth's crust at an average level of 13 parts per million (ppm), according to www.cosmeticsinfo.org, a website produced by the PCPC and member companies.

There is disagreement, however, over just how much lead is in lipstick. A well-publicized report released in 2007 by the Campaign for Safe Cosmetics (CSC; San Francisco, California, USA) stated that more than half of 33 lipsticks the group tested contained levels of lead ranging from 0.03 to 0.65 ppm. CSC represents a consortium of consumer activist and environmental groups working to eliminate chemicals linked to cancer, reproductive harm, and other adverse health impacts from cosmetics and personal care products.

In 2009, FDA scientists published an article in the *Journal of Cosmetic Science* (http://tinyurl.com/FDA-lead) detailing the highly sensitive method they had developed and validated to analyze total lead content in lipsticks. The team evaluated the same selection of lipsticks tested by CSC and found levels ranging from 0.09 ppm to 3.06 ppm, with an average value of 1.07 ppm and an estimated detection limit of 0.04 ppm.

So now comes the question: Are these levels safe?

There is no specific limit for lead in personal care products and cosmetics. There are, however, limits on the level of lead permitted in the colors used in formulating foods, drugs, and cosmetics. Those allowed levels range from 10 to 20 ppm, which is well above the amount of total lead characterized in the FDA study.

FDA conducted an expanded survey of 400 lipsticks in 2010 that returned similar results, and concluded: "Lipstick, as a product intended for topical use with limited absorption, is ingested only in very small quantities. We do not consider the lead levels we found in the lipsticks to be a safety concern."

## 4. The anionic surfactants sodium lauryl sulfate (SLS; also known as sodium dodecyl sulfate) and sodium laureth sulfate (SLES), found in many personal care products such as toothpaste and shampoo, cause cancer.

Many independent distributors of "natural" personal care products spread this myth on their websites and through emails. Although the compounds are known irritants—which is why they aren't used in baby shampoos—they are not known or suspected carcinogens, according to the International Agency for Research on Cancer (IARC; Lyon, France).

One potential byproduct of the manufacture of these surfactants through ethoxylation is classified as a probable human carcinogen (1,4-dioxane). Some products with SLS/SLES have been found to contain traces of up to 279 ppm of 1,4-dioxane, according to FDA research. The FDA has monitored 1,4-dioxane in cosmetic and personal care products since the late 1970s by assessing products and raw materials. Based on that monitoring, the agency says that levels of 1,4-dioxane in personal care products ". . . do not present a hazard to consumers." FDA also has noted that the levels of 1,4-dioxane in cosmetic and personal care products have declined significantly over the years due to the vacuum stripping process used in manufacturing. (See http://tinyurl.com/FDA-Dioxane.)

## 5. Mineral oil, which is a petrochemical, contains carcinogenic polyaromatic hydrocarbons (PAHs).

Mineral oil has been a mainstay in personal care product formulations for dry skin for a number of reasons: It is inexpensive, fragrance free, does not oxidize, and provides a particularly effective protective layer for the skin. It is true that some grades of industrial mineral oils can contain PAHs; however, cosmetic-grade mineral oil has been purified and so does not.

Colin Sanders, a formulator of cosmetics and topical pharmaceuticals who writes the Colin's Beauty Pages blog at http://colinsbeautypages.co.uk, notes that a rumor persists that mineral oil is banned in the European Union. "The origin of this story is elusive," he says, adding that it is "easily disproved simply by looking on the EU's Cosing database." (See http://tinyurl.com/EU-Cosing.)

In short: "There is absolutely no evidence that cosmetic-grade mineral oil causes cancer," according to Perry Romanowski, a cosmetic chemist and Area II Director of the Society of Cosmetic Chemists, writing for the personalcaretruth.com blog.

## 6. "Natural" chemicals produced solely by nature without human intervention are more healthful than compounds produced via chemical synthesis.


There is a saying in advertising that "perception is everything." The idea that synthetic chemicals are innately more dangerous or unhealthful than chemicals as found in nature is a case in point.

Most consumers do not have the scientific sophistication to understand why this myth is false.

Perhaps the most ridiculous claim made by marketers when attempting to manipulate chemophobic buyers is that a given product is "chemical free." The very fact that many shoppers do not realize how preposterous such claims are suggests that the scientific community needs to do a better job of educating them.

Toward that end, Sense about Science, with funding from the Royal Society of Chemistry, has published *Making Sense of Chemical Stories*, which aims to help bridge the disconnection between lifestyle reporting by journalists and chemical realities. (See http://tinyurl.com/Sense-Science.)

As this 16-page guide points out, "the chemical reality is that whether a substance is manufactured by people, copied from nature, or extracted directly from nature, tells us nothing much at all about its properties. In terms of chemical safety, 'industrial,' 'synthetic,' 'artificial,' and 'man-made' do not necessarily mean damaging and 'natural' does not necessarily mean better. For example, the dye henna can cause allergic reactions, untreated water can kill, and poor food hygiene can result in toxins that make people very ill, yet these are all natural."

In summary, the biological activity of a chemical is a function of its structure rather than its origin, and the perception of risk often is not consistent with actual risk. An analysis of compounds identified as human carcinogens by IARC found that 62% occur naturally: 16 are natural chemicals, 11 are mixtures of natural chemicals, and 10 are infectious agents (*Food Safety and Food Quality*, http://dx.doi.org/10.1146/annurev.en.39.010194.002421, 2001).

Another point made in the booklet is that natural products are "inherently variable." The chemical composition of plants often changes with the season; manufacturers often produce very different botanical preparations in terms of strength and purity because of a lack of standardization. "It is worth noting that, although it's popular to complain about 'all those synthetic chemicals,' this contrasts with increasing demand for them in and around the home, e.g., [in] oral contraceptives, mouthwash, and decorating materials, and for gadgets [that] are manufactured using them, [such as] mobile phones, computers, and CDs," says toxicologist Andrew Cockburn of Toxico-Logical Consulting Ltd. in Albury, Hertfordshire, UK.

## 7. A corollary of the preceding myth is that the fewer ingredients used in formulating personal care products, the safer the product will be.

"Formulating any kind of product to the fewest number of ingredients is a truly bizarre and wholly irrational goal," writes *Inform* Contributing Editor Dave McCall, a chemist and formulator with Vaughan Industries in Detroit, Michigan, USA. As he pointed out in a letter to the editor of *Chemical & Engineering News*, "Mother Nature doesn't hold herself to such an unrealistic goal."

McCall's letter was in response to a news item about Charlie's Soap, a laundry detergent marketed to chemophobic consumers. The manufacturer claims that textiles washed in the detergent will be "residue-free" because of the product's simple formula, which consists of water, sodium carbonate, sodium metasilicate, and C12-15 pareth-2, a coconut oil-based surfactant.

"It has always been true and will always be true that as time goes on we will find alternative ingredients that

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biodegrade faster and have lower toxicity profiles," says McCall. "However, this doesn't mean the older ingredient was toxic. Why would I use something that poisons me and my customers?"

Formulators don't add compounds without a reason, he adds, noting that "if we use 13 ingredients, that is because each one adds to the performance of the product."

## 8. Trans fatty acids (TFAs) in personal care products are as dangerous as TFAs in foods.

This idea, which can be found on various websites and blogs including an entry at OrganicConsumers.org, at first seems laughable. As it turns out, however, concern could be warranted. There simply isn't enough research to be sure, one way or the other.

Partially hydrogenated vegetable oils—the primary source of industrially produced TFAs—are used in a variety of personal care products. In most products, though, the concentration is low and the dose so small that the TFA content likely would not reach dangerous levels. As a reminder, in the case of dietary TFAs, the World Health Organization suggests that dietary consumption of 5 g/day is associated with a 23% increase in the risk of coronary heart disease.

Unlike products used on only a small area of skin, body butters and lotions are slathered over the entire body, where they remain until the person next bathes. Because fatty acids are used as skin penetration enhancers for drug delivery, there is no doubt that they are absorbed through the skin. Further, a study out of India's University of Pune concluded that topically applied vegetable oil is absorbed in neonates "and is probably available for nutritional purposes" (*Indian Pediatrics 42*:998–1005, 2005). Additional findings from this study suggest, "the fatty acid constituents of the oil can influence changes in the fatty acid profiles of the massaged babies."

All of this leads to an unanswerable question: Would the absorption and metabolism of TFAs in a body butter rise to toxic levels? Only further research can answer that question.

Is this an issue that the FDA is likely to be concerned about, given that the agency has made a preliminary determination that partially hydrogenated vegetable oils are no long Generally Recognized as Safe in foods?

Although cosmetics sold in the United States are required to be safe for consumers when used under labeled or customary conditions, cosmetic products and ingredients, other than color additives, do not need FDA approval before they go on the market, and the law does not require cosmetic companies to share their safety information with FDA.

"There is no regulation prohibiting or restricting the use of trans fatty acids in personal care products," an FDA spokesperson told *Inform* in an email. "Cosmetic products are generally meant to work on or near the surface of our skin. However, some cosmetic ingredients have the potential to be absorbed through the skin surface, and skin penetration of ingredients is something that FDA considers when evaluating cosmetic safety."

This brings us back to the idea that perception is reality. If enough consumers object to TFAs in their skincare products and mount a Facebook or Twitter campaign against manufacturers who use partially hydrogenated oils in their products, the FDA will not have to act. If such a consumer revolt occurs, it won't be the first or the last time that the marketplace will drive formulation.

## INFORMATION

- **www.thebeautybrains.com**
- **www.cosmeticsinfo.org**
- **www.ewg.org/skindeep**
- **http://personalcaretruth.com**
- **http://tinyurl.com/Sense-Science**
- **www.snopes.com**

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# Cleaning up a **solvent problem**

Michael McCoy

Anyone pulling a really old bottle of Windex or Formula 409 spray cleaner from the back of the pantry is in for a pleasant surprise. The stuff still works great—perhaps better than a recently purchased bottle-cleaning windows and walls easily and drying quickly with no streaking or smearing.

Until about a decade ago, Windex, Formula 409, and many other hard-surface cleaners owed much of their cleaning power to ethylene glycol monobutyl ether, or EGBE, a glycol ether solvent renowned for its ability to cost-effectively remove both water-soluble soils and water-insoluble oils and greases.

"It is a tremendous solvent. It's magic," says Martin Vince, a chemist who runs LizMar, an Ontario-based formulation consultancy.

EGBE came under fire for health rea sons, including its ability to cause red blood cell breakage when inhaled, and consumer goods makers largely removed it. But the ingredients substituted for EGBE were often volatile organic compounds (VOCs) or presented other environmental problems. Sometimes they just didn't clean very well. And EGBE continues to be used in many industrial and institutional cleaning products.

Now, a new round of solvent replacement is taking place in laundry detergents, spray cleaners, and other cleaning products for home and industry. Multiple solvents are being added or removed for performance, environmental, and human health reasons.

For chemical makers, the upheaval means a business boom. Over the past year, companies, often the very ones that make glycol ethers and other traditional solvents, have come out with a flurry of new products.

They run the gamut from biobased to synthetic, from solvent to surfactant, but they are all intended to help customers in the cleaners business create formulas that are robust, cost-effective, and green. As a result, these are busy times for

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- **Performance, environmental, and human health concerns are causing multiple solvents to be added or removed from laundry detergents, spray cleaners, and other cleaning products for home and industry.**
- **Chemical makers have responded by introducing a flurry of new products to help customers in the cleaners business create formulas that are robust, cost-effective, and green.**
- **This article describes some of the current offerings.**

Reprinted with permission from *Chem. Eng. News*, January 10, 2015, *93*(3), pp 16–19.

formulation chemists at cleaning product companies across the U.S.

Last October, two icons of corporate America—Procter & Gamble and DuPont—announced plans to use cellulosic ethanol as a solvent in Tide Coldwater Clean, a member of P&G's flagship laundry detergent family. The cold-water version of Tide is marketed to consumers seeking to reduce energy consumption.

At present, ethanol derived from com kernels helps keep Tide Coldwater's myriad ingredients together in solution. DuPont is building a plant in Iowa that will make ethanol from corncobs and stalks in stead. Blending this cellulosic ethanol into Tide Coldwater will repurpose more than 7,000 tons of agricultural waste a year, the partners say, and in the process save the energy needed to do all the clothes washing in homes across California for a month.

For DuPont, the agreement with P&G is part of a growing focus on the home and fabric care market, according to Simon Herriott, DuPont's global business director for biomaterials. For about five years the company also has been marketing 1, 3-propanediol, another biobased chemical in its portfolio, to the household products industry.

Propanediol's main use is as a raw material for DuPont's Sarona brand fiber. One of its next-largest markets, Herriott says, is household care, where it has a lot of room to grow as a solvent, stabilizer, and enzyme carrier. Propanediol is found, for example, in a spray cleaner and a concentrated laundry detergent marketed by Method, a purveyor of environmentally friendly cleaning products.

Herriott is happy with this business, but he sees the potential for DuPont's solvents to go beyond the niche market served by Method. "Mainstream consumers are increasingly concerned about the impact their own personal actions have on the environment," he says, and this trend is influencing home care product firms." We're at an inflection point between the green pioneers and major mainstream formulators."

Another new solvent taken up by both Method and Seventh Generation, a competitor in the green consumer goods space, is ethyl levulinate glycerol ketal, manufactured by the biobased chemicals start-up Segetis. The ketal is found in the Method laundry detergent and in specialty spray cleaners from both Method and Seventh Generation.

For Clement Choy, senior director of advanced innovation at Seventh Generation, the ketal is a welcome addition to a woefully small arsenal of solvents his environmentally rigorous company can use. Choy, a chemist, is familiar with the wider world of solvents. Before joining Seventh Generation in 2008 he spent more than a quarter-century at Clorox and P&G, which had more liberal criteria for choosing solvents.

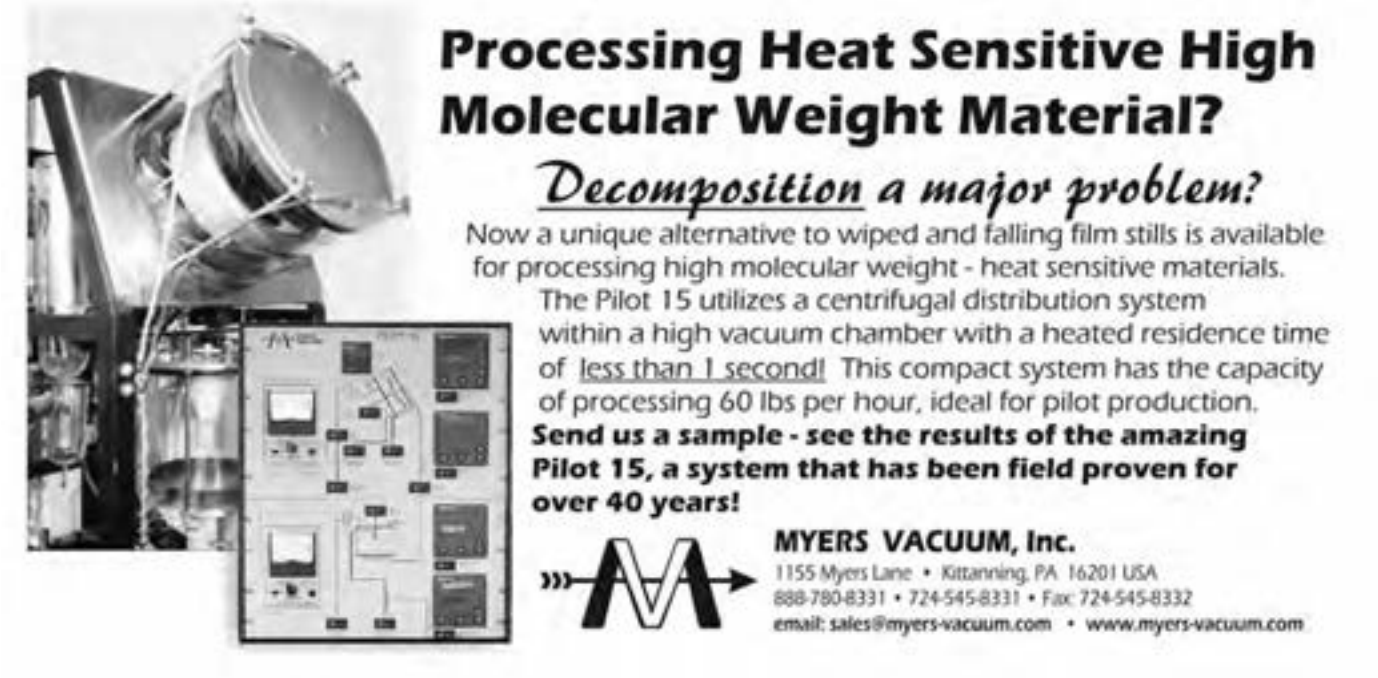
"We are definitely more selective and more restrictive," Choy says about his current employer. For Seventh Generation, glycol ethers are verboten, and synthetics are avoided whenever possible.

The company also won't use VOCs, a restriction that eliminates "a fair number of products out there," Choy says.

Seventh Generation began working with Segetis in 2011. The following year it formulated ethyl levulinate glycerol ketal into a new line of spray cleaners for stone, wood, and stainless steel. Its main role in these products isn't so much to dissolve soil or grease but to help solubilize fragrance oils and keep the overall cleaning formula stable.

Method hooked up with Segetis even earlier, coming out with the laundry detergent and a ketal-containing tub and tile cleaner in March 2011. In addition to ethyl levulinate glycerol ketal, the bathroom cleaner includes ethyl levulinate propylene glycol ketal. The two solvents work together to dissolve stains and soap scum, according to Kaj Johnson, a product development director at Method who goes by the title green chef.

And for the laundry detergent, which is superconcentrated, Method relies on a system of four solvents: propanediol, ethyl levulinate glycerol ketal, glycerin, and methyl esters. In addition to



providing cleaning power, the system makes the formula compatible, flowable, and phase stable under extreme storage conditions.

Like Choy, Johnson is happy to have a growing family of sustainable solvents at his disposal when formulating products. But that's not enough, be cautions.

"If sustainability were all we were concerned about, we would have a very simple task," Johnson says. In addition, human safety, effective cleaning, compatibility, stability, degradability, and surface safety all need to be considered. To best achieve these goals, he still seeks non-VOC solvents with broad surface safety, a broader portfolio of solubility parameters, and broad pH and heat stability.

Johnson works with non-VOC, biobased ingredients because Method's upscale, environmentally conscious customers demand it. For Joe Zhou, vice president of R&D at Misco Products, a Pennsylvania based maker of cleaners for the commercial and industrial markets, the demands aren't so lofty. His customers are janitorial firms seeking products that clean quickly, effectively, and economically.

That means Misco continues to use EGBE in many of its traditional products, such as its MPC brand concentrated glass cleaner for the maintenance market. ''EGBE is a very, very good solvent and very cost-effective," Zhou says. "It's like a Chevrolet–a dependable workhorse."

But for its Elements glass cleaner, part of a line it calls "environmentally responsible maintenance solutions,"Misco has replaced EGBE with a blend of diethylene glycol monobutyl ether and propylene glycol mono *n*-butyl ether. Unlike EGBE, these glycol ethers aren't readily absorbed by the skin and aren't associated with blood cell breakage, the firm says.

Misco is using propylene-based glycol ethers—so-called P-series glycol ethers—to replace EGBE in most of the new products it develops, according to Zhou. The catch, he says, is that there's no one drop-in replacement for EGBE. The company often must tailor blends out of propylene glycol monopropyl ether, dipropylene glycol monopropyl ether, propylene glycol mono *n*-butyl ether, and dipropylene glycol mono *n*-butyl ether.

Vince, the formulation chemist, also must get creative for customers that come to him seeking to replace EGBE. Sometimes those firms are developing green formulas to appeal to municipal buyers with a mandate to purchase cleaners bearing an eco-label.

Other times, customers need to remove VOCs to make their product comply with US Environmental Protection Agency laws or with state regulations that started in California but are now spreading across the United States. Canada, where Vince's form is based, will soon enact similar rules.

"In the past, companies would label their products 'Not for sale in California,'" Vince says. "Now, as more and more states adopt the California standard, having two distribution channels doesn't wash anymore."

And soon to affect cleaning product manufacturers is the United Nations Globally Harmonized System of Classification & Labelling of Chemicals, or GHS, which will make chemical hazard information more transparent on product labels and safety

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data sheets. The Occupational Safety & Health Administration wants US manufacturers to be in compliance by June 1.

Vince notes that GHS requires the use of pictograms to convey hazards. The health hazard symbol, which depicts a human figure with a starlike light on its chest, is particularly forbidding. "It's something you don't want on your product," he says.

For BobStahurski, chief executive of the industrial cleaners firm Nyco Products, it was mostly the threat of new VOC regulations that prompted the creation of a line of ready-to-use spray cleaners based on butyl 3-hydroxybutyrate, a cleaning solvent developed by Eastman Chemical.

Before the solvent, named Omnia, was launched last year, coming up with EGBE replacements wasn't easy, according to Stahurski. "We were looking for the trifecta of a safe solvent, a product with exceptional performance, and a low-vapor-pressure VOC," he recounts. ''Traditionally we could only get two out of three."

The company formulated some cleaning products with other glycol ethers but found they were expensive and not always compatible with the rest of the formula. It also encountered flammability problems. So when a representative from Eastman's solvents sales team approached Stahurski about being a sounding board and development partner for the firm's new solvent, he was all ears.

Eastman, a major manufacturer of glycol ethers, had embarked on the search for an effective but environmentally friendly solvent several years ago, according to Carol Perkins, head of Eastman's industrial and household care business.

The company tackled the problem methodically, starting with a database of some 3,000 molecules with potential as cleaning solvents and whittling it down to one through a combination of in silica and wet-lab testing.

Since launching Omnia, Eastman has been "overwhelmed by sample requests," Perkins says, both from companies moving away from solvents such as EGBE and from firms that have already reformulated but aren't happy with the results. "They come saying, 'Please help us get that performance back,'" she says.

Also claiming robust customer interest in new solvents is Elevance Renewable Sciences, which converts vegetable oils into specialty chemicals with olefin metathesis technology invented by Nobel Laureate Robert H. Grubbs.

The Illinois-based company was formed in 2008.Two years later it started pursuing surfactants based on Elevance feedstocks in cooperation with the surfactants manufacturer Stepan.

The result, according to Andy Corr, head of consumer and industrial ingredients for Elevance, is a surfactant called Steposol MET-10U, which Stepan launched early last year as a replacement for solvents such as *n*-methylpyrrolidone and methylene chloride in adhesive removers and paint strippers. The surfactant also can be used in household and industrial cleaners in place of glycol ethers.

Soon after Stepan debuted its surfactant, Elevance came out with its own product, Elevance Clean 1200,a heavy-duty degreasing solvent aimed at manufacturing, food processing, and transportation maintenance customers looking for ingredients that are considered low vapor pressure by California and have a low enough vapor pressure or enough carbon atoms to be exempt from EPA's VOC designation.

Clean 1200 is being marketed as a replacement for aromatic hydrocarbons and D-limonene, a citrus-derived VOC. In addition, the new product can provide a performance boost to dibasic esters and soy methyl esters, solvents that are VOC compliant but can have performance short comings, Corr says.

Elevance and Stepan already have some early customers and others with high interest in the new products, according to Corr. Customers are divided roughly equally between ones that are confronting solvent replacement for the first time and ones that switched but aren't satisfied. Some in the later category "have had to give up a hell of a lot of performance," he says.

That's not the view of Zhou, the R&D head at Misco, who has done his share of solvent replacement for the firm's Elements line of cleaners. In some products, Zhou says, Misco replaced EGBE with P series glycol ethers from Dow Chemical. In others it replaced petroleum solvents and D-limonene with soy methyl esters and ethyl lactate, two biobased solvents. Zhou says both Elevance and Eastman have asked him to try their new products but that at present he is happy with the solvent choices he has.

Those are comforting words to executives at Dow, a leader in glycol ethers and related cleaning product ingredients, including polyethylene glycols and propylene glycol.

The firm considers EGBE to be safe when used appropriately. Steve Vogler, global marketing director for Dow's home, institutional, and personal care solutions business, argues that EGBE has been tarred by association with glycol ethers such as ethylene glycol methyl ether, which has been shown in lab animals to have adverse reproductive effects.

Dow sells EGBE to companies that want it, even as it acknowledges that other products have more favorable toxicity profiles. "We have a pretty good track record of defending E-series glycols," Vogler says, ''but overall people are looking for things on the propylene glycol side, so when concerns come up we just automatically run to the P-series."

That line includes about 10 products, several of which are low-vapor-pressure VOCs and thus EPA exempt. Dow's newest P-series product, launched last year, is dipropylene glycol phenyl ether. According to Vogler, it manages to be a low VOC while providing minimal streaking. Another new solvent from Dow is Diamosolv323,a plant-derived ester aimed at degreasing applications.

Vince, the consultant, says it's going to take all the new products from Dow and its competitors to replace EGBE and other unwanted solvents in industrial and institutional cleaners. He doesn't see any single winner but rather modest market inroads by all of them as cleaning product companies reformulate.

The reformulation is a boon both for experts such as Vince and for people who work in industrial environments. ''It means business for me, but more importantly it means a healthier and safer workplace," Vince says. "The products these guys are going to be using day in and day out will be safer, and people will live longer."

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*Michael McCoy is an assistant managing editor for* C&EN *in New York City.*

# Preventive Controls for Animal Food: **understanding what processors need to do**

**David Smith**

- **The proposed rules under FSMA for the Preventive Controls for Animal Food, which are expected to become effective in August 2015, will affect processors of oilseed meal as well as processors of dried distiller's grain with solubles.**
- **Affected facilities will have one year from the date that the rule becomes effective to develop and implement their programs.**
- **This article summarizes the two primary components (Current Good Manufacturing Practices and a Food Safety Program) and requirements that will need to be addressed.**

The US Food and Drug Administration (FDA), as authorized by the Food Safety Modernization Act (FSMA), has proposed rules for the Preventive Controls for Animal Food. These rules, which are expected to become effective in August 2015, will affect processors of oilseed meal as well as processors of dried distiller's grain with solubles.

Preventive Controls for Animal Food is a management system for assuring the safety of feed ingredients. As with other management systems, such as Process Safety Management and environmental management, significant program documentation will be required.

The new rules are intended for facilities that process animal food, which includes feed ingredients, to be more proactive in providing safe feed products. The emphasis of the program is on assessing and controlling the risks associated with maintaining safe feed ingredients. The focus of this program is on three key elements:

- the health of animal food and in turn the health of animals,
- the health of humans who are exposed to animal food, and;
- the safety of animal derived products that are for human consumption.

There are some exemptions to this rule. However, if you are an oilseed processor producing meal intended as an animal food ingredient, and your facility has more than $2.5 million in total annual sales, then you will likely be covered.

Each affected facility will have one year from the date that the rule becomes effective to develop and implement their program. So, if the requirements become effective in August

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## ADDITIONAL RESOURCES

- For additional information, visit the FDA Food Safety Modernization Act web site at: http://www.fda.gov/Food/GuidanceRegulation/FSMA/ucm366510.htm .
- The original proposed rule may be found at this website: http://www.regulations.gov/#!documentDetail;D=FDA-2011-N-0922-0002

2015 as expected, then processors will have until August 2016 to complete and fully implement their programs. Although this date seems to be far into the future, there are many time-consuming tasks that must be completed.

There are two primary components of this management system to be developed and implemented:

1. Current Good Management Practices (cGMPs)
2. Food safety Program (FSP)

## CURRENT GOOD MANUFACTURING PRACTICES

The process of complying with the requirements of cGMP guidelines is considered by many FDA-regulated companies to be a time-consuming and expensive ordeal. In fact, the opposite is true: Not complying with cGMP guidelines is potentially more time-consuming and expensive.


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In the FDA's view, cGMP guidelines are intended to ensure that products are consistently produced in a controlled environment with quality standards guiding their intended use. cGMPs include operational aspects such as good hygiene practices, proper cleaning and maintenance of facilities and grounds, pest control, proper use and storage of toxic cleaning compounds, applying adequate sanitation principles, and properly labeling ingredients and finished animal food.

cGMPs provide for systems that assure proper design, monitoring, and control of manufacturing processes. Adherence to the cGMP requirements assures the quality and purity of animal feed products by requiring that manufacturers adequately control their manufacturing operations. This includes establishing quality management systems, obtaining appropriate quality raw materials, establishing robust operating procedures, detecting and investigating product quality deviations, and maintaining reliable testing procedures. This formal system of controls, if adequately put into practice, helps to prevent instances of contamination, mix-ups, deviations, failures, and errors. It also assures that animal feed and feed ingredients meet their quality standards.

The cGMP requirements were designed to be flexible so that each processor can decide individually how best to implement the necessary controls by using sound process design, processing methods, and testing procedures. The flexibility in the requirements also allows companies to use modern technologies and innovative approaches to achieve higher quality through continual improvement. Accordingly, the "c" in cGMP stands for "current," requiring companies to use technologies and systems that are up-to-date. in order to comply with the regulations. Systems and equipment that may have been considered "top-of-the-line" for preventing contamination, mix-ups, and errors 10 or 20 years ago may be less adequate today.

It is important to note that cGMPs are minimum requirements. Many feed ingredient producers are already implementing comprehensive, modern quality systems and risk management approaches that exceed these minimum standards.

The cGMP provisions require covered facilities to:

- establish sanitation and housekeeping procedures in buildings and facilities;
- train and ensure that personnel follow proper hygienic practices;
- establish guidelines for the proper operation, maintenance and sanitation of processes;
- review and enhance equipment design and use;
- establish proper maintenance and preventive maintenance procedures;
- establish effective process controls; and
- provide safe warehousing and distribution equipment and storage.

## FOOD SAFETY PROGRAM

A Food Safety Program (FSP) is the second part of the requirements for feed ingredient producers. This program requires producers of feed ingredients to identify food safety and adulteration risks associated with their foods and processes, to implement controls to minimize those risks, to verify that the controls are working, and to design and implement corrective actions to address any deviations from the controls that might

arise. Everything in the FSP must be properly documented and must conform to FDA standards and definitions as they apply to facilities, controls, hazards, and the adulteration of foods. An animal food facility should document all aspects of its FSP, periodically review the plan, constantly maintain the FSP, and document its verification steps

The Food Safety Program (FSP) requires the following to be developed and implemented.

- Identify one or more Qualified Individuals (QI) to develop, implement, and maintain the written FSP.
- Perform a Hazard Analysis on the process, referred to as a Hazard Analysis of Risk-based Preventive Controls (HARPC).
- Create and implement preventive controls based upon the HARPC findings.
- Monitor the program and adjust the program as necessary.
- As problems and issues with the FSP are identified, develop and implement corrective actions to address the program issues.
- Verify through an audit and inspection program that the FSP is being implemented as written.
- Reanalyze and revise the program as needed.

The following steps are recommended for developing and implementing the FSP. These steps are best performed by a team comprised of facility personnel:

1. Identify the Qualified Individual(s).
2. Identify the animal feed ingredient that is covered by the FSP.
3. Create a flow diagram of the facility food process from the beginning to the end.
4. Identify all known or reasonably foreseeable hazards.
5. Evaluate the identified hazards.
6. Develop preventive controls that address the identified hazards.
7. Validate preventive controls and establish parameters.
8. Implement and monitor the controls for effectiveness.
9. Take corrective actions where needed and adjust the program.
10. Verify that the monitoring and corrective actions are taking place and are effective.
11. Develop and implement a recall plan.

Taking steps now to begin planning how you will develop your cGMP and FSP will help to assure that you have a working program in place by the compliance date. Although the rules are not final, they are not expected to vary significantly from the proposed rules. Significant time will be needed to develop, implement and document the program. Begin today to determine what needs to be done, which team members will develop the programs, and a schedule for completion.

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*David Smith is a licensed professional engineer and the Principal of PROJECTS Inc., Fort Wayne, Indiana, USA. Smith has 35 years of oilseed processing experience in the areas of operations, engineering, quality, safety and environmental management. He can be contacted at DBSmith@projects-inc.com.*

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# Fish feed optimization **still needs some work**

Domanique P. Bureau

In a context of significant competition and low profit margins, aquaculture feed manufacturers are required to formulate to increasing lower or narrower nutritional specifications ("specs") in order to minimize feed cost. Decreasing specs for certain nutrients (e.g. lysine, methionine, DHA, available phosphorus) can significantly reduce the cost of feeds. The formulation of cost-effective aquaculture feeds adequately meeting the nutrient requirements of animals, while not being too wasteful, can be a very delicate balancing act. Perhaps a relatively unique feature of aquaculture feeds is that they are characterized by a wide range of nutritional specifications. This is expected given the very large number of fish and crustacean species produced around the world using feed-based production systems.

**Formulating feed for aquaculture is challenging due to the large number of fish and crustacean species that are produced around the world. This article discusses:**

- **the need to define the essential nutrient requirements of commercially important species, the factors affecting those requirements, and the potential of nutritional modeling;**
- **alternatives to marine ingredients; and**
- **the need for quality assurance when sourcing from multiple countries, manufacturers, and brokers.**

However, the protein, lipid, starch, and digestible energy contents of feeds can significantly vary not only as a function of species and life stages for which they are formulated (trout vs. tilapia feed, starter vs. grower vs. finisher feed), but also as a function of a myriad of other factors, such as production systems, farmers' or feed manufacturers' preferences, environmental constraints, and socio-economic conditions (e.g., fish price, access to credit, degree of risk).

Most fish feed manufacturers have to serve a large client base cultivating numerous fish and invertebrate species in very different production systems (ponds vs. cages, marine vs. freshwater environment, etc.) and socio-economical contexts (small farmers vs. large vertically integrated corporations). Formulating "on the edge" is therefore very complicated in this complex sector.

## MORE FISH SPECIES

Significant efforts have been invested over the past six decades on the definition of the nutrient requirements of numerous fish and crustacean species, and the body of knowledge is growing significantly every year. Reviews of the literature and nutritional recommendations are provided on a relatively regular basis by different groups of researchers or committee of experts. The relatively new NRC (2011) "Nutrient Requirements of Fish and Shrimp" and other reference documents are providing feed manufacturers with a reasonably good basis for the formulation of feeds meeting the requirements of many of the commercially important aquaculture species. However, the number of fish and crustacean species studied by different investigators is staggering and this leads to dilution of research efforts.

Globally, there is need for significant improvements in the focus of nutritional studies, and the scope and quality of the experimental efforts invested in the definition of essential nutrient requirements of commercially important species. It would be recommendable to increasingly focus the research efforts on the 15 or so fish and crustacean species (e.g., Chinese carps, Indian major carps, Nile tilapia, Pangasid catfish, Atlantic salmon, Pacific white leg shrimp, etc.) that represent the bulk of the global farmed fish and crustacean production. Studies have suggested that some of these nutrients, such as phospholipids, cholesterol, nucleotides and arachidonic acid (ARA, 20:4 *n*-6), abundant in fish meal and other animal feedstuffs, are essential to some species and/or for the larval stage of certain species. Nonetheless, there is mounting evidence that most fish and crustacean species can be considered "obligate carnivores" (of sort) and that some nutrients rich in animal products may often be overlooked in formulation and nutritional requirement studies.

## FACTORS AFFECTING REQUIREMENTS

Estimates of requirements are generally derived from studies with young fish fed diets containing purified and chemically defined ingredients that are highly digestible and, generally, represent minimum nutrient concentrations required for maximizing performance of these young animals under laboratory conditions.

While this type of approach and definition of "requirement" may sound relatively simple and straightforward, reality is a lot more complicated. Significant differences may exist in the experimental conditions (diet composition, experimental design, duration of study, fish trains, life stages), measured parameters (live weight gain, protein gain, enzyme activity, body stores, histological changes), performance achieved (growth rate, feed efficiency), and methods of analysis of the results for "similar" studies. Consequently, very different "estimates" of requirement can be derived from similar studies.

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Moreover, the same dataset (e.g. data from one single study) can also be interpreted in very different ways through the use of different mathematical models to analyze data or by simply putting more emphasis on different parameters (body stores vs live weigh gain vs enzyme activity). Moreover, how requirements evolve with changes in the genetic, weight, growth rate or feed conversion achieved, or health status of the animal is something that, in my humble opinion, has not been adequately studied for aquaculture species.

Defining a nutrient requirement value is clearly not a straightforward thing and yet published estimates of requirements are too often taken at face value and/or misunderstood. It must be recognized that published estimates of nutrient requirement are derived from consensus among "experts" and are thus very much products of opinion and not some sort of unchallengeable truth. Feed formulators should ideally dig in the primary research literature for the real data and develop their own opinion. Feed manufacturers should also focus a significant part of their R&D efforts toward verifying the adequacy and suitability of their nutritional specifications.

## CONSIDERING SAFETY MARGINS

The mode of expression of requirement is an issue that has not received sufficient attention. There are numerous diverging opinions with regards to appropriate modes of expression of essential nutrient requirements. It is especially the case for essential amino acid (EAA) for which very different modes of expression of requirement are used, often interchangeably, in the literature.

These different modes of expression are based on different, often diametrically opposed, assumptions. In practice, the use of different modes of expression of EAA requirement can often result in dramatically different nutritional recommendations. Individual EAA levels deemed adequate may be very different depending on the mode of expression adopted and the composition of the diet formulated. This is a significant issue since feeds for a given species are formulated to widely different protein, lipid, starch, and digestible energy levels.

The root cause of these conflicting views is our limited understanding of how endogenous and dietary factors affect EAA utilization and requirements of fish. Finally, requirements are generally amount of nutrient in a biologically available form that needs to be delivered to the animal. It is important in this context to consider a reasonable safety margin to account for potentially lower digestibility or bioavailability of nutrients in practical ingredients, for losses of nutrients during manufacturing and storage of the feed, and for potential "changes" in nutrient requirements imposed by various environmental or endogenous factors. What represents a reasonable safety margin is again something up for discussion.

## THE POTENTIAL VALUE OF MODELLING

Decades of use in different animal production (dairy, beef, swine, poultry) sectors have demonstrated the value of nutritional modeling as an effective way of compiling, integrating, and interpreting available information (research-based or farm-specific information) and enabling the development of practical and reliable tools for feed formulation and /or production, feeding, and waste outputs management.

A relatively large number of nutritional models have been developed for fish and crustaceans over the past four decades (Bureau, *et al.*, 2002; Dumas, *et al.*, 2010). However, the nutritional models developed so far for fish all present important limitation and are not sufficiently flexible and reliable to be applied to a wide range of conditions (Bureau, *et al.*, 2002; Dumas, *et al.*, 2010). More comprehensive and pragmatic frameworks that incorporate the latest information in terms of nutrient requirements and utilization by fish and crustaceans need to be developed (Hua, *et al.*, 2010; 2012). Future nutritional models need to be robust and increasingly mechanistic and rational.

## ALTERNATIVES TO MARINE INGREDIENTS

Up to about 10 years ago, fish meal and fish oil represented about 70% of the weight of most commercial salmon and marine fish and crustacean species feeds sold worldwide. Their use is declining and fish meal is not a major ingredient any more. Manufacturers have been relying on the use of an increasingly diverse array of alternative feedstuffs of plant, terrestrial animal or microbial origins, each of which having their own characteristics and limitations.

While a number of research trials have shown that feeds can be formulated without fish meal provided the feed is formulated with high-quality ingredients (including ingredients of animal origin and various nutritional supplements), several studies have shown that formulating fish feeds without fish meal is not always an easy feat. Accurate assessment of nutritive value of feed ingredients is extremely important for the formulation of cost-effective feeds with lower levels of high-quality fish meal. Better characterization of the nutrient composition of feedstuffs is essential to improve their "valorization" by leastcost feed formulation programs.

More efforts need to be invested in systematically investigating the effects of numerous factors that can affect the nutritive value of feed ingredients. Studies have suggested that some of these nutrients provided by fish meal and other feedstuffs of animal origins (eg. phospholipids, cholesterol, and arachidonic acid) may be essential or conditionally essential for some species or at specific life stages of some species.

Recent studies have shown significant benefits from supplementing plantbased "grower" fish feeds with cholesterol, taurine, and hydroxyproline, three nutrients also abundant in fish meal and other animal products. More research needs to be carried out to determine if these nutrients are truly essential or under what circumstances they are required or beneficial. Nonetheless, replacing fish meal may also means paying attention to once overlooked nutrients present in animal products.

## DEALING WITH VARIABILITY IN QUALITY

Sourcing an increasing diverse array of raw materials from different suppliers can also results in greater probability for significant variations in the quality of the raw materials purchased. The high price of certain feedstuffs may also incite unscrupulous suppliers to adopt deceptive practices, such as product adulteration.

In this context, the sector needs to have to invest significant resources in the characterization of the nutritive value of different feedstuffs (and batches thereof) and in quality assurance. Larger manufacturers often need to source the required high volumes

of certain raw materials from multiple suppliers. Small manufacturers due to their lesser needs may be able to source from single suppliers but, at the same time, may be even more at the mercy of capriciousness of the markets. The production of highly nutritious and cost-effective feeds with an increasingly wide array of feed ingredients obtained from different suppliers is clearly not an easy task.

This is certainly keeping some feed formulators awake at night. Sourcing of raw materials from different countries, manufacturers, or brokers arguably results in greater probability for significant variations in the quality of the raw materials purchased. The high price of certain feedstuffs (for example fish meal) may also incite (unscrupulous) suppliers to adopt deceptive practices, such as product adulteration (for example blending less expensive raw materials with more expensive raw materials). Feedback from the field indicates that variability in the nutritive quality and adulteration of feedstuffs are not a thing of the past. In this very complex context, quality assurance (QA) plays an extremely important role. QA usually involves the definitions of specifications for the purchasing of the raw materials and for the inspection and analysis of these raw materials as they are received at the feed mill.

Most, if not all, aquaculture feed manufacturers have adopted some sort of QA process and invest very significant financial and staff resources in this. The main emphasis of QA systems in place is on chemical composition, mainly on proximate analysis (crude protein, crude lipids, crude fiber, etc.), of the raw materials. Relatively little emphasis is placed on direct measurements of individual nutrient or contaminant levels due to the often prohibitive cost of this type of analysis.

Near Infrared Reflectance Spectroscopy (NIRS) is widely used by most aquaculture feed manufacturers around the world to obtain rapid and generally accurate estimation of the proximate and individual nutrient levels of batches of raw materials. However, measurements obtained with these technologies must be calibrated carefully against diet characteristics that are biologically meaningful, such as content and bioavailability of nutrients, bioactives, and contaminants.

## GOOD DIET STARTS WITH KNOWLEDGE

It is not easy to formulate fish diets. Fish meals, feather meals, meat and bone meals and distiller's dried grains with solubles (DDGS) often come to mind as ingredients that can vary quite significantly in terms of digestibility and nutritional quality. It is therefore important to pay more attention to accurately characterizing of the nutritive value of the different types of ingredients (and batches thereof) available on the market, with increasing emphasis on minor nutrients and chemical components.

Also, more research needs to be carried out to determine if these nutrients are truly essential or under what circumstances they are required or beneficial for different fish species.

More data would really help guide QA efforts of aquaculture feed manufacturers. For example, NIRS is highly dependent on the availability of high-quality raw data on the composition and nutritive value (for example amino acid digestibility) of different raw materials so that reliable calibration of the instruments can be done. This is one area where academic research groups could play a very important role and yet are virtually absent.

Other rapid but more direct ways of assessing the nutritive value of different batches of raw materials are also required. Pepsin digestibility is probably one of the most widely used tests to estimate digestibility of protein. However, there is some controversy as to the proper concentration of pepsin to be used and the applicability of this type of tests to different aquatic animal species and different raw materials. There is very limited published experimental (animal) studies examining the reliability of pepsin digestibility assays and defining their limitations.

Other *in vitro* tests, such as pH-stat protein digestion assays have been developed but they also suffer from a lack of standardization and lack of validation. Right now, efforts are really disparate and different groups are proposing very different approaches.

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*Dominique P. Bureau is an animal nutritionist, aquaculture scientist, and professor in the animal and poultry science department at the University of Guelph in Guelph, Ontario, Canada. He can be contacted at dbureau@uoguelph.ca.*

This article was reprinted from *AllAboutFeed 22*: 30–32, 2014, www.allaboutfeed.net. References available from author upon request.

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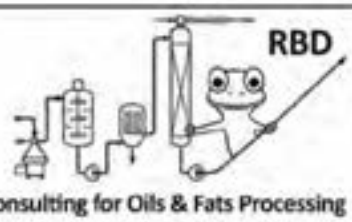


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# AOCS 2015 **award recipients announced**

AOCS celebrates ingenuity and collaboration by honoring those individuals and teams who have taken the industry to the next level, who have advanced the quality and depth of the profession, and who have leveraged their knowledge for the benefit of the society.

These individuals from around the world will be recognized during the 106th AOCS Annual Meeting and Industry Showcases to be held May 3–6, 2015, in Orlando, Florida, USA. The following list includes awards for whom recipients had been named by the deadline for this issue of *Inform*.


Dunford

## SOCIETY AWARDS

### Award of Merit

**NURHAN T. DUNFORD**, Associate Professor, Oklahoma State University, USA

**A plaque**

The Award is presented for productive leadership service that has advanced the prestige, standing, or interests of AOCS, and for services not otherwise specifically recognized.


Kemper


Marangoni


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### AOCS Fellows

**TIMOTHY G. KEMPER**, Desmet Ballestra North America, USA

**ALEJANDRO G. MARANGONI**, University of Guelph, Canada

**DELAND J. MYERS**, North Dakota State University, USA

**SUK-HOO YOON**, Woosuk University, Republic of Korea

**A plaque and Fellow membership status**

Fellows are selected in recognition of their notable and valuable contributions to the sciences or technology of lipid chemistry to support our mission and serve the Society.

## SCIENTIFIC AWARDS

### Supelco/Nicholas Pelick–AOCS Research Award


List

**GARY R. LIST**, Consultant, retired US Department of Agriculture, USA

**$10,000 honorarium, $1,500 travel stipend, and a plaque**

The Supelco/Nicholas Pelick–AOCS Research Award is for accomplishment of outstanding original research in fats, oils, lipid chemistry, or biochemistry, the results of which have been presented through publication of technical papers. The award is funded by Supelco Inc., a subsidiary of Sigma-Aldrich, and Nicholas Pelick, an AOCS past president.

### Stephen S. Chang Award


Bornscheuer

**UWE T. BORNSCHEUER**, University of Greifswald, Germany

**$1,500 honorarium and a jade horse**

The Stephen S. Chang Award recognizes a scientist, technologist, or engineer who has made decisive accomplishments in basic research for the improvement or development of products related to lipids. The award was established by former AOCS President Stephen S. Chang and his wife, Lucy, for individuals who have made significant contributions through a single breakthrough or through an accumulation of publications.

### AOCS Young Scientist Research Award


Rogers

**MICHAEL A. ROGERS**, University of Guelph, Canada

**$1,000 honorarium, $1,500 travel stipend, and a plaque**

The AOCS Young Scientist Research Award recognizes a young scientist who has made a significant and substantial research contribution in one of the disciplines represented by AOCS Divisions. Vijay K.S. Shukla and the International Food Science Centre A/S of Denmark sponsor the award.


Turner

## DIVISION AWARDS

### Analytical Division: Herbert J. Dutton Award

**CHARLOTTA TURNER**, Lund University, Sweden

**$1,000 honorarium, $1,000 travel stipend, and a plaque**

The award is presented for significant contribution to the analysis of fats and oils or to improvement in the understanding of the processes used in the fats and oils industries. The award is named for Dr. Dutton, a long-time research leader at the US Department of Agriculture facility in Peoria, Illinois, USA.

### Edible Applications Technology Division: Achievement Award

**DAVID A. PINK**, St. Francis Xavier University, Canada

**$500 honorarium, and a plaque**

The award recognizes outstanding research in the edible fats and oils community. Through their involvement they have made significant contributions to the knowledge, technology, and history of the industry.

### Timothy L. Mounts Award

**YEONHWA PARK**, University of Massachusetts Amherst, USA

**$750 honorarium and a plaque**

The award is for either basic or applied research accomplishments relating to the science, technology, or application of edible oils in food products. It memorializes the former AOCS president, who was a distinguished research scientist with the US Department of Agriculture. The award is sponsored by Bunge North America.


Park

### Student Award

**EBENEZER A. IFEDUBA**, The University of Georgia, USA

**$500 travel stipend and a certificate**


Ifeduba

### Health and Nutrition Division: Ralph Holman Lifetime Achievement Award

**PHILIP C. CALDER**, University of Southampton, United Kingdom

**$500 honorarium, $1,000 travel stipend, and an orchid print**

The award recognizes outstanding performance and meritorious contributions to the health and nutrition interest

CONTINUED ON NEXT PAGE


Calder

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Malomo

area. The award is named after Ralph Holman in recognition of his lifetime service to the study of essential fatty acids.

## Student Award

**SUNDAY A. MALOMO**, University of Manitoba, Canada

**$500 honorarium and a certificate**


Dumeignil
© photos : Sébastien JARRY

## Industrial Oil Products Division: ACI/NBB Glycerine Innovation Award

**FRANCK DUMEIGNIL**, University Lille 1 of Science & Technology, France

**$5,000 honorarium and a plaque**

The ACI/NBB Glycerine Innovation Award, sponsored by the American Cleaning Institute and the National Biodiesel Board, recognizes achievements in research relating to new applications for glycerine, particularly those with commercial viability.


Hasselberg

## Student Award

**JENNIFER HASSELBERG**, Technische Universität, Germany

**$500 travel stipend and a certificate**


Kellens

## Processing Division: Distinguished Service Award

**MARC J. KELLENS**, Desmet Ballestra, Belgium

$1,000 travel stipend and a certificate

The award recognizes outstanding, meritorious service to the oilseed processing industry or to the Division over a substantial amount of time.

## Protein and Co-Products Division: ADM Best Paper Award

***Chemistry/Nutrition***

*Lipid Co-oxidation of Proteins: One Size Does Not Fit All* (*Inform* 25:134–139)

**KAREN M. SCHAICH**

Rutgers University, USA

***Engineering/Technology***

*Physicochemical Properties Improvement of Soy Protein Using Divalent Ions During a Two-Step Fractionation Process* (*JAOCS* 91:1235-1245)

**NA-NA WU[1], ER-LI ZHENG[1], BIN TAN[2], ZI TENG[3], XIAO-QUAN YANG[1],** and **ZHI-MING GAO[1]**

[1]South China University of Technology, P.R. of China; [2]Academy of State Administration of Grain, P.R. of China; and [3]University of Maryland, USA

**Plaque and certificates for all authors**

The awards are presented annually for the outstanding paper related to protein and co-products appearing in an AOCS publication during the previous year. Archer Daniels Midland Company sponsors the awards.

## Surfactants and Detergents Division: Samuel Rosen Memorial Award


Hammond

**CHARLES E. HAMMOND**, CESI Chemical USA

**$2,000 honorarium and a plaque**

The award recognizes a significant advance in, or application of, the principles of surfactant chemistry by a chemist working in the industry. The award is sponsored by Milton Rosen in honor of his father, Samuel, who worked as an industrial chemist on the formulation of printing inks for more than four decades.

## American Cleaning Institute (ACI) Distinguished Paper

*Trends to Attain a Lower Interfacial Tension in a Revisited pure Alkyl Polyethyleneglycol Surfactant–Alkane–Water Ternary System. Basic Concepts and Straightforward Guidelines for Improving Performance in Enhanced Oil Recovery Formulations.* (*JSD* 17:199–213)

**JEAN-LOUIS SALAGER, LISBETH MANCHEGO, LAURA MÁRQUEZ, JOHNNY BULLÓN,** and **ANA FORGIARINI**

Universidad de Los Andes, Venezuela

**Glass plaques for all authors**

The award is presented annually to the authors of the best technical paper published during the preceding year in the *Journal of Surfactants and Detergents*. The award is sponsored by the American Cleaning Institute (ACI).


Muñoz

## Student Award

**SILVIA E. ZARATE MUÑOZ**, University of Toronto, Canada

**$500 travel stipend and a certificate**

Moreau

## SECTION AWARDS

### USA Section: Alton E. Bailey Award

**ROBERT E. MOREAU**, US Department of Agriculture, USA

**$750 honorarium and a plaque**

The award recognizes outstanding research and exceptional service in the field of lipids and associated products. The medal commemorates Alton E. Bailey's great contributions to the field of fats and oils as a researcher, as an author of several standard books in the field, and as a leader in the work of the Society. Archer Daniels Midland Company and Kraft Foods Inc. sponsor the award.

Wu

### Hans Kaunitz Award

**BICHENG WU**, University of Massachusetts Amherst, USA

**$1,000 honorarium, $500 travel allowance, and a certificate**

The award recognizes the outstanding performance and merit of a graduate student within the geographical boundaries of the USA Section.

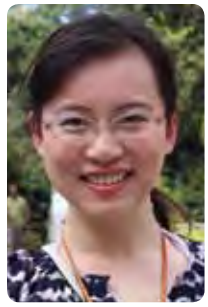
## STUDENT RECOGNITION

### Thomas H. Smouse Memorial Fellowship Award

**BICHENG WU**, University of Massachusetts Amherst, USA

**$10,000 scholarship, $5,000 research funding, and bookends**

The Archer Daniels Midland Foundation, the AOCS, the AOCS Foundation, and the family and friends of Dr. Smouse have established and assisted in funding a fellowship program designed to encourage and support outstanding graduate research in a field of study consistent with the areas of interest to the AOCS.



Wu

### AOCS Foundation Honored Student Awards

The award recognizes graduate students at any institution of higher learning who are conducting research in any area of science dealing with fats and lipids and who are interested in the areas of science and technology. Supported by contributions from members as well as companies in the industry.

**Travel stipend and a certificate**

### Manuchehr (Manny) Eijadi Award

The Eijadi Award recognizes outstanding merit and performance by an AOCS Honored Student. The award, established by Mr. Eijadi, is intended to help the recipient finance his or her studies.

**$1,000 scholarship and a certificate**

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Mintec

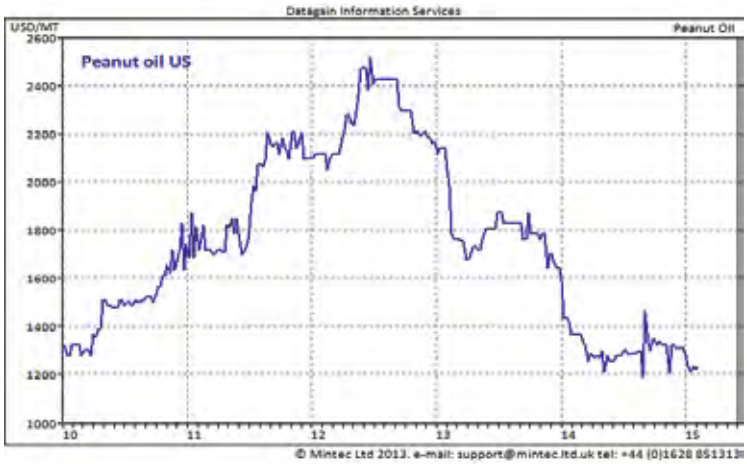
## STATISTICAL ANALYSIS FROM MINTEC

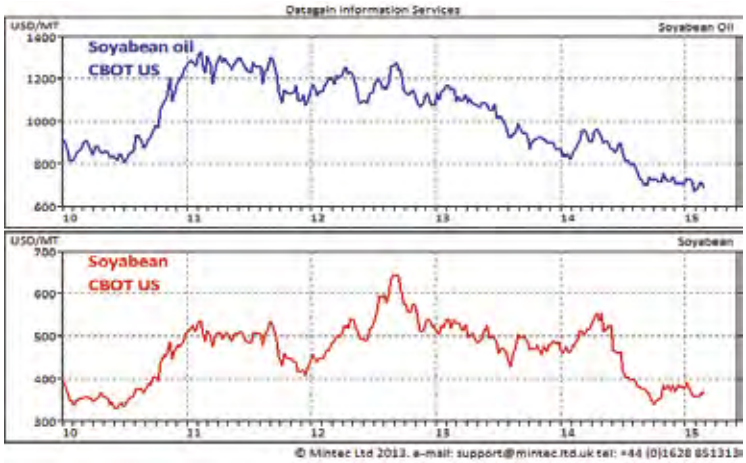
Abigail Green

Global soybean production is expected to rise by 11% year-on-year to reach a record 315.1 million metric tons (MMT) in 2014/15. US production will rise by 18% to 108.0 MMT with exports expected to rise by 9% year-on-year to 48.7 MMT, helped by an expected increase in demand from China which is set to import a near record 74.0 MMT of soybeans.

Global soybean oil production is expected to rise 5% year-on-year to a record 47.4 MMT. Production is expected to increase in the four major producers: China, the United States, Argentina, and Brazil following good output and good growing conditions in all countries. Consumption is expected to rise but at a slower rate than output, up 3% year-on-year to 46.6 MMT, resulting in a forecast increase in ending stocks, up 10% year-on-year to 3.5 MMT.

In 2014/15, groundnut production is forecast to fall to 39.0 MMT, down 0.5% year-on-year. Due to this fall, global groundnut oil production is expected to fall to 5.5 MMT, down 1% on the 2013/14 season. High supplies in 2013/14 led to a drop in prices for groundnut oil. Consumption in 2014/15 is also forecast to fall, down 2% year-on-year to 5.5 MMT, and supply is forecast to marginally exceed consumption.

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## Peter and Clare Kalustian Award

The Kalustian Award recognizes outstanding merit and performance by an AOCS Honored Student. The award is supported by the Kalustian estate.

**$1,000 scholarship and a certificate**


Bandara


Hayyan


Malomo

**NANDIKA P. BANDARA**, University of Alberta, Canada

**ADEEB HAYYAN**, University of Malaya, Malaysia [*Manuchehr Eijadi Award*]

**SUNDAY A. MALOMO**, University of Manitoba, Canada

**FERNANDA PEYRONEL**, University of Guelph, Canada [*Peter & Clare Kalustian Award*]


Peyronel

## Ralph H. Potts Memorial Fellowship Award


Komaiko

**JENNIFER KOMAIKO**, University of Massachusetts Amherst, USA

**$2,000 scholarship, travel stipend, and a plaque**

The Ralph H. Potts Award is presented annually to a graduate student working in the chemistry of fats and oils and their derivatives. The award is sponsored by AkzoNobel to memorialize Ralph Potts, a pioneer in research on industrial uses of fatty acids. ■

# Extracts & Distillates (cont. from 247)

pharmaceutical lipids, we need suitable analytical methods and a comprehensive database for their lipid components. The objective of the present work was to demonstrate methodology and provide data on fatty acid composition, lipid class content and composition, characteristics of the unsaponifiables, and type of chlorophylls of five microalgae. Microalgae lipids were fractionated into TAG, FFA, and polar lipids using TLC, and the composition of fatty acids in total lipids and in each lipid class, hydrocarbons, and sterols were determined by GC-MS. Glyco- and phospholipids were profiled by LC/ESI-MS. Chlorophylls and their related metabolites were qualified by LC/APCI-MS. The melting and crystallization profiles of microalgae total lipids and their esters were analyzed by DSC to evaluate their potential biofuel applications. Significant differences and complexities of lipid composition among the algae tested were observed. The compositional information is valuable for strain selection, downstream biomass fractionation, and utilization.

## Impact of iron, chelators, and free fatty acids on lipid oxidation in low-moisture crackers

Barden, L., *et al.*, *J. Agric. Food Chem. 63*: 1812–1818, 2015, http://dx.doi.org/10.1021/jf5048018.

This research strove to understand the relationship between physical structure and oxidative stability in crackers since mechanisms of lipid oxidation are poorly understood in low-moisture foods. Confocal microscopy showed that lipids formed a continuous matrix surrounding starch granules, and starch–lipid, lipid–air, and protein–lipid interfaces were observed. Unlike bulk oils, meats, and emulsions, lipid hydroperoxides exhibited greater stability in low-moisture crackers as hexanal formation was delayed >20 d. Iron, added at 10 times the concentrations normally found in enriched flour, did not increase oxidation rates compared to the control. EDTA may reduce endogenous iron activity but not as greatly as in other matrices. Addition of fatty acids up to 1.0% of total lipid weight did not statistically affect lipid oxidation lag phases. The unique structure of low-moisture foods clearly affects their resistance to metal-promoted lipid oxidation.

## How the multiple antioxidant properties of ascorbic acid affect lipid oxidation in oil-in-water emulsions

Uluata, S., *et al.*, *J. Agric. Food Chem.*, *63*: 1819–1824, 2015, http://dx.doi.org/10.1021/jf5053942.

Lipid oxidation is a serious problem for oil-containing food products because it negatively affects shelf life and

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nutritional composition. An antioxidant strategy commonly employed to prevent or delay oxidation in foods is to remove oxygen from the closed food-packaging system. An alternative technique is use of an edible oxygen scavenger to remove oxygen within the food. Ascorbic acid (AA) is a particularly promising antioxidant because of its natural label and multiple antioxidative functions. In this study, AA was tested as an oxygen scavenger in buffer and an oil-in-water (O/W) emulsion. The effects of transition metals on the ability of AA to scavenge oxygen were determined. Headspace oxygen decrease less than 1% in the medium-chain triacylglycerol (MCT) O/W emulsion system (pH 3 and 7). AA was able to almost completely remove dissolved oxygen (DO) in a buffered solution. Transition metals ($Fe^{2+}$ and $Cu^{+}$) significantly accelerated the degradation of AA; however, iron and copper only increased DO depletion rates, by 10.6–16.4% from day 1 to 7, compared to the control. AA (2.5–20 mM) decreased DO in a 1% O/W emulsion system 32.0–64.0% and delayed the formation of headspace hexanal in the emulsion from 7 to over 20 days. This research shows that, when AA is used in an O/W emulsion system, oxidation of the emulsion system can be delay by multiple mechanisms.

## Microbial oils: a customizable feedstock through metabolic engineering

Ledesma-Amaro, R., *Eur. J. Lipid Sci.Techn. 117*: 141–144, 2015, http://dx.doi.org/10.1002/ejlt.201400181.

In addition to animal fats and vegetable oils, microbial oils are gaining importance as a renewable feedstock for the chemical industry. One of the main advantages in the use of microorganisms to produce oils is the versatility and malleability of the microbial metabolism, which make it more easily manipulated. Thereby, the composition and properties of microbial oils can be designed through metabolic engineering. Consequently, the required chemical steps to synthesize a market product may be significantly reduced, together with the production costs. Accordingly, microorganisms have been engineered to: i) accumulate a high amount of lipids; ii) tune lipid composition; and iii) facilitate lipid extraction. Finally, microbial oils can be used as feedstock by the chemical industry to produce a huge variety of commodities, such as lubricants, polymers, fuels, coatings or surfactants. Microbial oils are considered promising alternatives to fossil fuels as feedstock for the chemical industry. Additionally they present advantages over vegetable oils and animal fats since microorganisms can be easily engineered: i) to accumulate high amount of lipids; ii) to be enriched in a desired kind of lipid; and iii) to facilitate the extraction of the oil from the cells. This short article is intended to present the concept of microbial oils to the general reader, taking into special consideration the malleability of microbial oils by metabolic engineering.

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*Extracts & Distillates is compiled by Robert Moreau, a research chemist with the US Department of Agriculture in Wyndmoor, Pennsylvania, USA. Contact him at robert.moreau@ars.usda.gov.*

# **Patents** (cont. from 241)

reaction product of a polyhydroxyl compound, such as glycerol, and a triglyceride and the monoglyceride and/or diglyceride products are cross-linked with sulfur, oxygen and/or a peroxide cross-linking moiety, or are directly cross-linked at unsaturated sites in the monoglycerides and/or diglycerides.

## Chocolate with agglomerate structure and the method for preparing thereof

Mendez, P.S., T *et al.*, Natra Cacao SL Unipersonal, US8790737, July 29, 2014

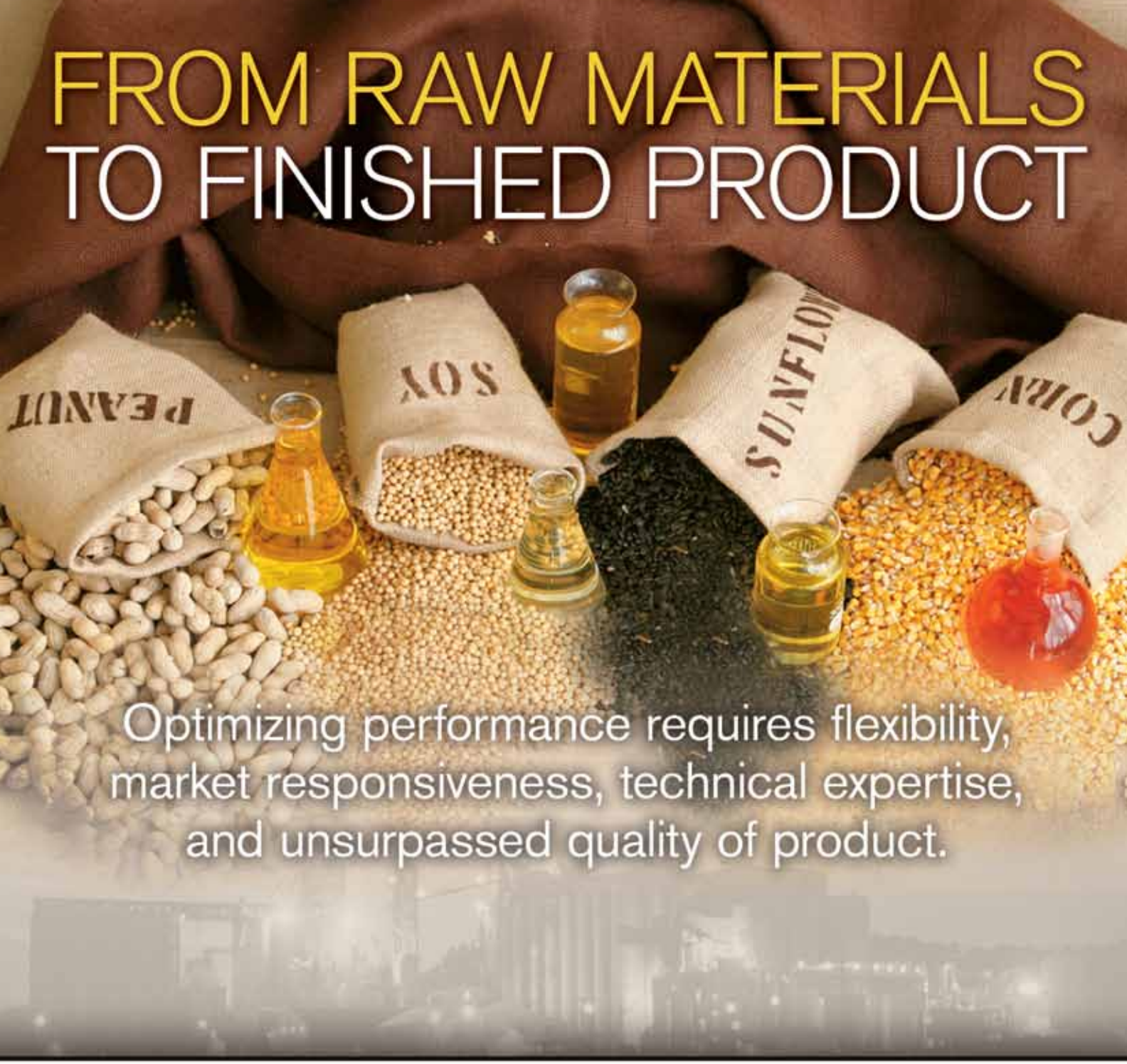
The present invention relates to a method for preparing chocolate with agglomerate structure. It also relates to the chocolate obtained by said method characterized in that has the organoleptic characteristics of the conventional chocolate, it is physico-chemically stable at a temperature greater than or equal to 40 degrees centigrade, maintains its flowability at a temperature of up to 50 ˚Cμ and is crunchy.

## Process for fractionating refined triglyceride oil

Yeoh, C.B. and C.L Chong, Malaysian Palm Oil Board, US8791283, July 29, 2014

The present invention relates to a process for fractioning refined triglyceride oil. The process according to the present invention attains a reproducible crystallization by introducing a controlled temperature profile and ensuing crystal development that reduce the amount of entrapped olein inside the crystals or crystal aggregates. The process of the present invention may be used to fractionate refined and or refined, bleached and deodorized vegetable oils especially refined and or refined, bleached and deodorized palm oil.

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

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