



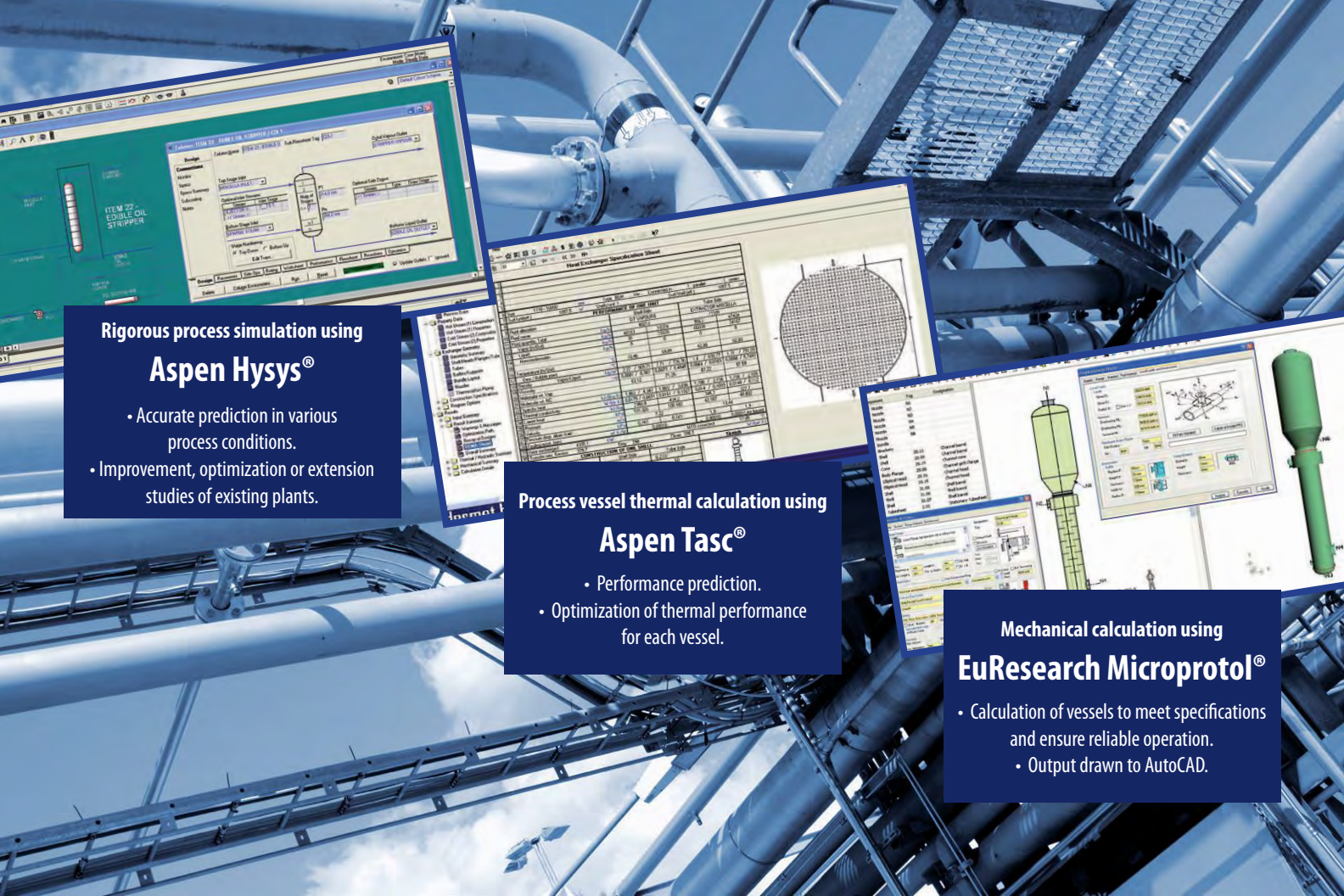
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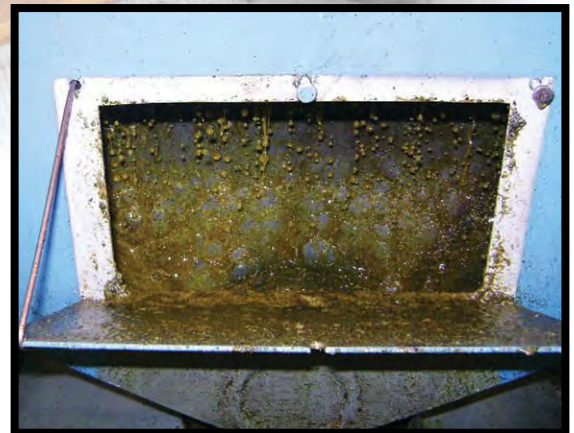
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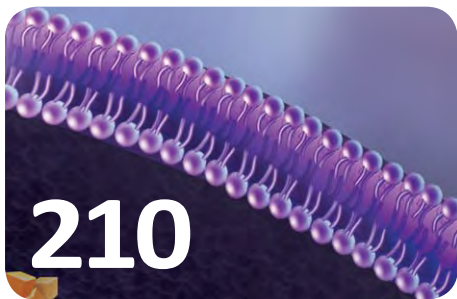
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Letter from the president

About one year has transpired since I began my term as AOCS president in May of 2012. In my speech as incoming president, I talked about the importance of AOCS in my professional career and why I believe that AOCS is a relevant and important professional scientific organization: first, because it provides current scientific and industry information about fats and oils and related materials; and second, because it offers career development opportunities to all professionals whether they work in industry, academia, or government. I also listed the challenges the Society faces as it endeavors to maintain its strength and relevance in a rapidly changing world. These included: i) identifying ways to meet the needs of global partners and members; ii) utilizing new communication technologies; and iii) finding new markets for our programs and services. During my tenure as AOCS president, I believe we have put programs in place that are meeting the aforementioned challenges. We have also laid the groundwork for additional programs that will ensure our continued success.

The first step was to continue to implement the strategic plan by reorganizing the AOCS Governing Board structure. Our new CEO, Pat Donnelly, has provided excellent leadership in this effort. He has challenged us to think more broadly about who we are as an organization and to identify the opportunities we have to expand our products and services in existing and new markets. To accomplish this, our strategic working groups within the Governing Board (Strategic Planning, Governing Board Operations, Constituent Relations, and Finance/Tracking) are becoming the vehicles for generating ideas that the Governing Board can then consider. Moreover, other members with expertise in their respective areas are now providing initial input through three Value Centers (Networking, Content, and Technical Services). These teams met for the first time and are already starting to

provide the excellent information, insight, and direction that will assist the leadership of the Society in making key decisions that will ensure our success in meeting the challenges outlined above.

More specifically, during my tenure, AOCS implemented several initiatives that will help us meet the needs of members and markets globally. Pat and AOCS Senior Director of Programs Jeff Newman traveled to various parts of the world to participate in joint meetings for which AOCS played a significant leadership role, such as the AOCS World Conference on Fabric and Home Care meeting in Singapore, and to plan future meetings and collaborations. I personally had the opportunity to travel with Pat to Japan and India. In Nagasaki, Japan, we represented AOCS at the World Congress on Oleo Science and 29th ISF Congress and participated in the 60th anniversary celebration of the Japanese

CONTINUED ON NEXT PAGE



I personally want to thank Pat Donnelly, the AOCS staff, and you, the membership, for your patience and support during my term as president.

Oil Chemists' Society. In India, we attended the 67th Annual Convention of the Oil Technologists' Association of India in Mumbai. While attending these events, we met members as well as academic and industry leaders who informed us how we can better meet their needs and helped us to identify new opportunities to collaborate with other organizations in these regions.

With respect to communications technology, efforts are still underway for the development of *Inform|Connect*, an Internet-based resource for market information, product development solutions, technical expertise, and collaboration that will be available to anyone who is interested in oils, fats, and the disciplines represented by the AOCS membership. The Society is also increasing its presence on social network sites such as Facebook, Twitter, and LinkedIn to strengthen communications among members, AOCS headquarters, and persons interested in communication and information about fats, oils, and related materials.

In an effort to expand programs and membership, Pat has been attending major meetings and conferences outside of

AOCS and meeting with corporations to benchmark, network, and promote the Society. We are also reviewing membership recruitment and retention policies and practices, especially as they relate to young professionals seeking opportunities in the Society for professional growth. Technical Services is exploring opportunities for expanding the Certified Reference Material program in conjunction with the US Food Safety Modernization Act. These are just some of the activities and initiatives during my tenure as president that I believe will continue to grow the organization and increase our visibility, both nationally and internationally. I personally want to thank Pat Donnelly, the AOCS staff, and you, the membership, for your patience and support during my term as president. It has been an honor to serve you, and I am sure that under the guidance of incoming President Tim Kemper and the help of AOCS staff and Board members, the Society is poised for a bright future.

Deland J. Myers
AOCS President 2012–2013



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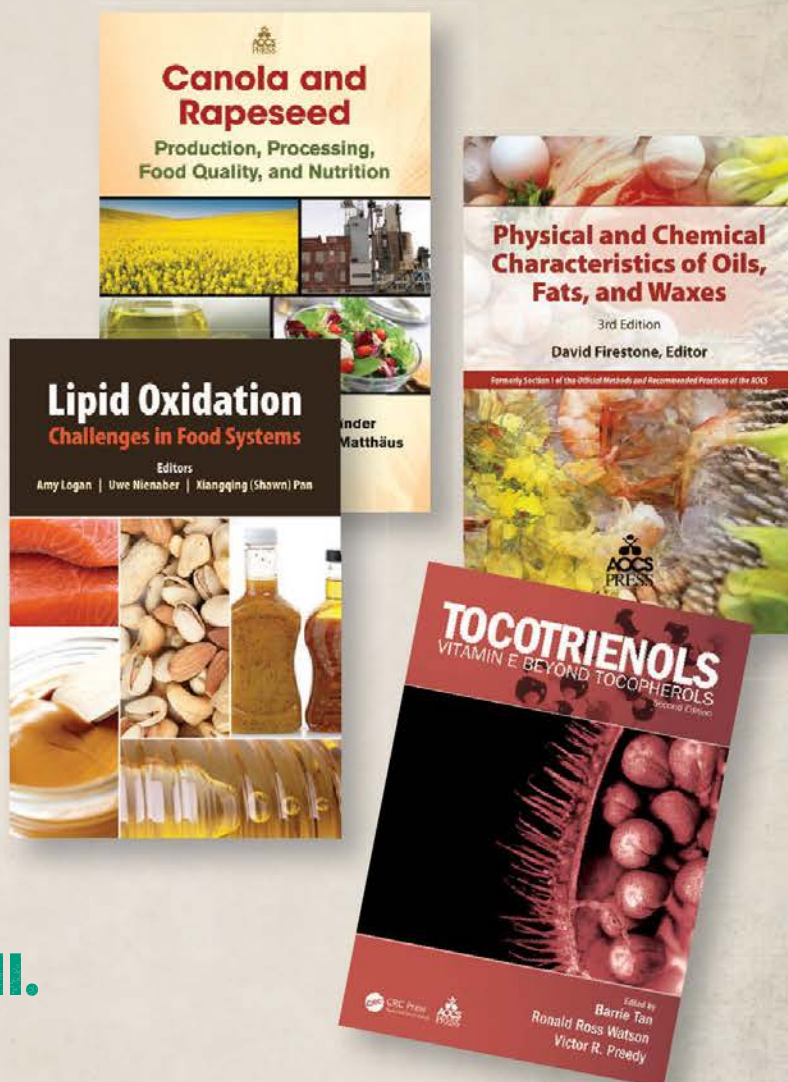
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President's profile: Timothy G. Kemper

It is a tremendous honor for me to be the next president of AOCS. When I look back at the names of past presidents I am humbled to be in such company. AOCS is driven by a talented and diverse membership. As your next president, I will do all I can to uphold the image and value of our society around the world. With the help of our members, governing board, CEO, and staff, we will collectively continue our progress of guiding AOCS to an even brighter future, reaching a diverse audience with high quality technical content, global networking opportunities, and specialized technical services.

My experience in the oilseeds business began at a very young age. I grew up on a grain farm in western Ohio (USA), where we primarily raised soybeans. At age 10, when I was tall enough to press in the clutch and still touch the tractor seat, I started plowing, tilling, planting, and cultivating. A couple of years later I was operating our Gleaner combine and harvesting the crop. By age 14, I was old enough to take loads of grain to the local elevator, and was entrusted to carry those big embossed grain checks back to the farm. Little did I know that 40 years later I would still be working with soybeans.

When I was in high school, my grandfather rented me land and equipment so I could try my hand at farming. I made good money the first three years raising soybeans, then switched to wheat for crop rotation. I was introduced to army worms when it was too wet, cutworms when it was too dry, then learned a cruel lesson about the farming business: What could be earned in three years could be lost in only one. That hard reality motivated me to go on to college and find a career that was less financially dependent on good weather.

I attended the University of Cincinnati (Ohio), where I studied mechanical engineering. As a requirement of that program, I spent every other semester doing cooperative education (internship). My advisor connected me with The French Oil Mill Machinery Company (Piqua, Ohio). During a co-op term there, I designed oilseed-crushing equipment, worked in the pilot plant and analytical lab, and had the opportunity to visit



Timothy Kemper and his wife Joyce, a special education teacher, have been married for 26 years. Since their daughters Molly and Morgan left the nest, they enjoy Atlanta Braves baseball games and rooting for the University of Georgia football team at the 50 yard line. Reprinted with permission from CLIX Studios ©.

crush plants. I officially caught the contagious desire to stay in the oilseed business and after graduation went to work for The French Oil Mill Machinery Company.

Shortly after college, I married Joyce, my girlfriend since high school. Joyce is a special education teacher with the tireless patience needed to educate children with special needs, and the patience needed to live with me and all my traveling. In the early 1990s, we were blessed with two wonderful daughters: Molly and Morgan. Molly has since graduated from college and

CONTINUED ON NEXT PAGE

is working for the Pepperdine School of Law in Malibu, California. Morgan is a sophomore at the University of Georgia and an avid Bulldog football fan. Having spent many years shuttling our daughters around to their activities, Joyce and I are now in the "empty-nest" mode. After 26 years of marriage, I could not ask for a better partner.

At French, I spent a good bit of my first year after graduation starting up solvent extraction equipment, then went into technical sales. At that time, Dan French, chairman and president of the company, introduced me to AOCS and suggested I become a member. I thank Dan for my start in AOCS in 1988 and the great opportunities it has brought me since.

My years in technical sales allowed me to start traveling the world. I have been fortunate to continue those travels, which have taken me to 51 different countries and counting. It is a wonderful experience to meet people from all different ethnic and cultural backgrounds. The lesson I learned over time is that the world is full of remarkable people.

In the 1990s, I moved to managing engineering and R&D at French, where I designed oilseed-crushing equipment and developed new oilseed-crushing technologies. Some of my notable developments were the Reflex® Extractor and Dimax™ Desolventizer, two popular technologies used around the world. My boyhood idol was the inventor, Thomas Edison. I still enjoy

inventing new and improved approaches and thus far have been an inventor on seven US patents.

In 1999, Desmet Ballestra purchased the solvent extraction product line from French, and I moved from Ohio to Georgia to join Desmet Ballestra. Shortly thereafter, I was named president & CEO of Desmet Ballestra's North American operations. Once with Desmet Ballestra, in addition to oilseed crushing, I had the opportunity to learn about the edible oil refining industry and the biodiesel industry. To facilitate my profit and loss responsibilities I went back to college and earned an online Master's in Business Administration from Indiana Wesleyan University in 2002. I then joined Vistage (www.vistage.com), a continuous learning organization to enable executives to stay on the leading edge.

In 2011, I transitioned to a new role at Desmet Ballestra: Global Technical Director, Solvent Extraction. Today I work for our oils and fats headquarters, directing the effort to globally standardize our solvent extraction technology and develop new and improved oil extraction technologies for the future.

In addition to working in the oils and fats industry, I love anything to do with sports. I play basketball at the YMCA from 6:00–7:30 a.m. before going to work. It's much more effective than a cup of coffee to wake me up! My wife and I go to a number of Atlanta Braves baseball games each summer, and we have season tickets on the 50 yard line to root for the University of Georgia football team. We are also active with our church, and I volunteer each year with Habitat for Humanity to help build houses for those in need. As time allows, I enjoy genealogy and have traced my family roots back to 1600 in Germany.

During the past 25 years, I have also had the opportunity to volunteer with AOCS. I have served as a frequent technical presenter at meetings, an author of articles, a session chairperson, a division board member, and as a governing board member. On the governing board, I served as a member at large, then treasurer, then vice president before being considered for the position of president. While on the governing board I have seen AOCS flirt with bankruptcy, make tough decisions, and change its approach to be financially stable. Under the guidance of a number of talented presidents, I have seen the AOCS governing board develop into a working board with defined subcommittees, develop a strategic planning process, and hire an outstanding CEO (Pat Donnelly) to help lead us into the future.

Today, we find ourselves in an era when technology is creating an unprecedented rate of change in how we communicate and learn. Many societies have become less relevant as a result. 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, and executed through our strategic plan.

Thanks for the opportunity to be your next president. I look forward to the challenges and rewards that lie ahead. ■

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POINT–COUNTERPOINT: omega-3 fatty acids and oxidative stress



Michael Logli

For many years, long-chain omega-3 (n-3) fatty acids have been touted for their health benefits. Eicosapentaenoic acid (EPA; 20:5n-3) and docosahexaenoic acid (DHA; 22:6n-3) have been found to lower the risk of cardiovascular disease and improve mental health, among other positive health effects. But could omega-3 fatty acid supplementation—when taken as part of a diet already high in omega-6 fats—actually cause oxidative stress, particularly in the elderly?

Findings from a study in mice that appeared in the *British Journal of Nutrition* (doi:10.1017/S0007114512005326, 2013) suggest just that conclusion. Researchers led by Sanjoy Ghosh and Deanna Gibson at the University of British Columbia–Okanagan campus (UBC; Kelowna, Canada) fed three groups of two-year-old mice differing amounts of omega-6 fatty acids: a “normal” diet with fat at 9% daily energy, a high-fat diet with fat at 40% daily energy, and a high-fat diet (also 40% daily energy) that included EPA + DHA.

Ghosh, in a UBC news release, said: “Our hypothesis is that levels of omega-6 are so high in our bodies that any more unsaturated fatty acid—even omega-3, despite its health benefits—will actually contribute to the negative effects omega-6 PUFA [polyunsaturated fatty acids] have on the heart and gut.”

In their study, aged mice on a diet high in n-6 PUFA experienced bacterial overgrowth, weight gain, and changes in the gut microbiota. Based on results from the high-fat supplemented with EPA + DHA diet, the addition of n-3 fatty acids apparently countered these changes, reducing weight gain and inflammation. However, the combined n-3 and n-6 diet also led to the creation of a product of lipid peroxidation—4-hydroxynonenal—in the intestines, potentially signifying oxidative stress, which can damage a cell’s ability to recover and communicate with other cells.

The Global Organization for EPA and DHA Omega-3 (GOED), a trade group based in Salt Lake City, Utah, USA, took issue with the study results. GOED Executive Director Adam Ismail and Vice President of Regulatory and Scientific Affairs Harry Rice responded to press reports of the study, critiquing its methods and conclusions. Bruce Holub, professor emeritus of the University of Guelph in Ontario, Canada, provided additional comments. Emailed correspondence among *Inform*, the GOED team, and Ghosh and his team delineated the following points of contention.

POINT

- It is not clear what role oxidative stress in the small intestine plays in the pathogenesis of small intestinal diseases in old mice, not to mention humans. Numerous human trials have supported the cardiovascular benefits of omega-3 fatty acids in fish oil, and the American Heart Association advises supplementary n-3 fatty acids daily for those with coronary heart disease. According to Holub, the fish oil, while yielding more oxidation, actually reduced the infiltration by inflammatory cells in the intestines of these mice when they were fed maize [corn] oil (high in n-6 fatty acids).
- Within the last two years, both the European Food Safety Authority (EFSA; <http://tinyurl.com/EFSA-UL>) and the Norwegian Scientific Committee for Food Safety (VKM; <http://tinyurl.com/VKM-n-3>) published safety evaluations of n-3 long-chain PUFA and reported no evidence that they induce changes in lipid peroxidation [that] might raise a concern with respect to risk for any disease.
- According to Holub, quality fish oil supplements with omega-3 fatty acids are in encapsulated form to protect the omega-3 from oxidation. They are not administered as liquid, unprotected fish oil added to a dry diet, as was the case in the study in mice.
- Methods used to assess lipid peroxidation in tissue samples are indirect, and the evidence that the methods actually reflect lipid peroxidation *in vivo* is limited. Due to the lack of validation of lipid oxidation or oxidative stress end points as biomarkers for disease or health-compromised states, or risk thereof, it is not possible to interpret the present results in old mice to determine any potential hazard to health in humans from ingestion of EPA + DHA.

COUNTERPOINT

- Although the influence of oxidative stress to small intestinal problems is speculative at this moment, it is important to note that increased oxidative stress in human intestines alters the intestinal gene expression profile, which can have long-term effects in humans [1]. With regard to fish oil decreasing inflammation, this was indeed true and would be potentially beneficial for anyone suffering from chronic inflammatory conditions.

However, we question whether the entire population, including susceptible populations such as infants and the elderly, should be consuming unregulated amounts of omega-3 fatty acids, considering another recent study of ours published in *PLOS ONE*, Fish oil attenuates omega-6 PUFA-induced dysbiosis and infectious colitis but impairs LPS [lipopolysaccharide] dephosphorylation activity causing sepsis (<http://dx.plos.org/10.1371/journal.pone.0055468>), where we found that fish oil supplementation led to sepsis and increased mortality in mice due to impaired inflammatory responses when faced with an intestinal bacterial pathogen. Safety documents from the EFSA and the VKM reports agree that no tolerable upper limit could be established for n-3 PUFA intake due to lack of data. We would like to emphasize that the lack of information does not equate to safety.

- In studies presented in the VKM (page 36) and EFSA (page 22) reports, vitamin E was incorporated along with fish oil to diminish oxidative stress and establish safety. Thus, it seems to be well known that oxidative modification of fish oil can be actually harmful, but yet, in 2012, GOED has deemed the practice of adding antioxidants to fish oil supplements as optional (page 21, last paragraph, EFSA document).

Both the VKM and EFSA documents conclude safety of fish oil pills based primarily on the presence of two oxidative markers, F2 isoprostanes and low-density lipoprotein (LDL) oxidation, in human n-3 PUFA supplementation studies. But we find determining plasma or urinary F2 isoprostanes as a marker for lipid peroxidation in n-3 PUFA supplementation to be inadequate. F2 isoprostanes are produced specifically from arachidonic acid (ARA; 20:4n-6) and not n-3 PUFA. Because EPA/DHA replace ARA in membranes, it is expected that F2 isoprostanes will not rise or be decreased following n-3 PUFA supplementation. Peroxidation

CONTINUED ON NEXT PAGE

of α -linolenic acid (18:3n-3), EPA, and DHA produces F1, F3, and F4 isoprostanes [2,3], which were never measured in any of these trials on which the safety assumptions are based. Although the exact roles of these novel isoprostanes are yet unclear, a positive correlation between F4 and F1 isoprostane levels has been suggested in patients with Alzheimer's disease and in immune modulation [4–6]. In fact, one of the earlier groups who reported a lack of F2 isoprostanes with fish oil supplementation (Barden 2004, EFSA) later reported an increase in F1 phytoprostanes with flaxseed supplementation in humans [7]. Such evidence contradicts the assumption that lipid peroxidation is not increased after n-3 PUFA supplementation. It could simply be that the wrong biomarkers (i.e., F2 isoprostanes derived from ARA) were used to measure lipid peroxidation in n-3 PUFA supplementation studies in humans. This was even recognized as a potential confounding factor in the VKM publication (page 37, comment section).

TABLE 1. Reported adverse events related to EPA and DHA as drugs, from the WHO Adverse Drug Events Database (accessed April 1, 2010)^a

Adverse events	Frequency
Nausea	23
Blood triglyceride increase	21
Eructation	20
Abdominal distension	17
Rash	17
Chest pain	16
Pruritus	15
Diarrhea	13
Dizziness	13
Blood glucose increase	12
Constipation	12
Abdominal discomfort	10
Flatulence	10
LDL-cholesterol increase	10
SUM	209

^aAdapted from Frøyland *et al.*, Evaluation of negative and positive health effects of n-3 fatty acids as constituents of food supplements and fortified foods, Report by the Norwegian Scientific Committee for Food Safety (VKM), published June 28, 2011; <http://tinyurl.com/VKM-n-3>, accessed February 15, 2013.

n-3 PUFA supplements are (usually) taken by middle-aged to elderly persons with various chronic diseases who—in North America—are presumably on a high omega-6 PUFA diet. The antioxidant levels necessary to combat the oxidative effects of n-3 PUFA are much lower in these patients, leading to a chance for higher lipid peroxidation. If we consider the data presented in the VKM document (see Table 1), we see that a number of adverse effects have been reported with high n-3 fatty acid intakes in humans. Interestingly, a vast majority of these events are associated with gut-related phenomena such as diarrhea, nausea, constipation, abdominal discomfort, and flatulence, which can be related to oxidative stress. Therefore, our findings in the small intestine of mice on a high omega-6 PUFA diet are consistent with results demonstrated in humans.

We additionally wonder: If it has been deemed optional to stabilize n-3 PUFA, how can we guarantee that fish oil we consume has not been altered? Because these pills are covered in a gelatin shell, consumers cannot identify whether rancidity has occurred during the manufacturing process. Moreover, the labels of most fish oil supplements do not indicate peroxide values to ascertain their state of stability or vitamin E incorporations, required to stabilize the n-3 PUFA.

- Eating fish and supplementing with fish oil are two different strategies. Most human studies demonstrate problems with supplementation but not fish intake. Human populations consuming fish do not naturally ingest high levels of omega-6 PUFA. We believe that the oxidizability of fish oil pills and a concomitant presence of high doses of omega-6 PUFA are at play in causing increased lipid peroxidation.
- It is true that direct measurement of free radicals is often not feasible in clinical studies. However, oxidative stress biomarkers have been implicated in various diseases ranging from Alzheimer's disease to diabetes. We are not claiming that intakes of fish are harmful; but instead we want to highlight the risk for fish oil supplementation and unregulated addition of n-3 PUFA in common food items such as bread and yogurt. In light of recent negative data on the efficacy of such supplementation strategies in various chronic diseases [8–10], in people who are again presumably on a high n-6 PUFA diet, we are concerned with the total content of n-3 fatty acids in the current food supply, the quality of fish oil used in supplements without antioxidants, and especially on the effect of the background high n-6 PUFA that may negate beneficial and/or exacerbate the harmful effects of fish oil pills.

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Omega-3s: Fishing for a Mechanism

Ethan J. Anderson and David A. Taylor

Four decades ago, Danish medical students Jørn Dyerberg and Hans Olaf Bang traveled west across the Greenland ice sheet on dog-sleds to test a theory. For many years prior to their journey, there had been anecdotal reports that Greenland Eskimos had an extremely low incidence of heart disease, and Dyerberg and Bang speculated that this was linked to the high levels of polyunsaturated fatty acids (PUFAs) in the fish the native people consumed on a daily basis. After collecting and analyzing scores of blood samples, their hypothesis was borne out, and ever since, the medical and scientific community has been on a quest to determine exactly how PUFAs impart protective effects, and what amount must be ingested in order to achieve such benefits. Nearly 40 years and thousands of published studies later, however, these questions remain largely unanswered.

Cardiovascular disease continues to have an enormous impact on the world's health and economy, making it all the more urgent that health-care practitioners find and implement low-cost prevention strategies. Dietary intake of PUFAs, specifically the n-3 PUFAs found in fish (commonly known as omega-3s), could serve as a perfect solution, but the lack of understanding of how PUFAs work—and continuing controversy over whether they really do work—has made it nearly impossible to properly implement their use in the clinic. Thus, a coordinated effort is needed to establish a mechanism for how n-3 PUFAs function

- Despite abundant evidence supporting the ability of fish oil–derived fatty acids to help prevent and treat cardiovascular disease, their therapeutic effectiveness remains controversial.
- The greatest limitation to properly evaluating the results of many clinical trials is that they vary so widely in the type of n-3 PUFA given, dose, formulation (e.g. capsules or oil), and duration of intake.
- A better understanding of exactly how these compounds act in the body could inform the development of relevant and proper dosing strategies for n-3 PUFA use in clinics.

in normal metabolism in order to develop proper therapeutic paradigms and to clarify their effectiveness in the prevention and treatment of cardiovascular disease.

THE PUFA MYSTERY

Cardiovascular disease can affect any part of the circulatory system, from the heart and major arteries to veins and capillaries. Its causes are diverse, as are its treatments, which include compounds that exert vasodilating, anti-inflammatory, anti-thrombotic (reducing the formation of blood clots), anti-arrhythmic (suppressing abnormal heart rhythms), and heart rate–lowering effects. PUFAs from PUFA-rich foods and dietary supplements have shown therapeutic promise in virtually all of these areas. One of the more intriguing therapeutic potentials for n-3 PUFAs is in the treatment and prevention of heart failure. (1)

CONTINUED ON PAGE 212

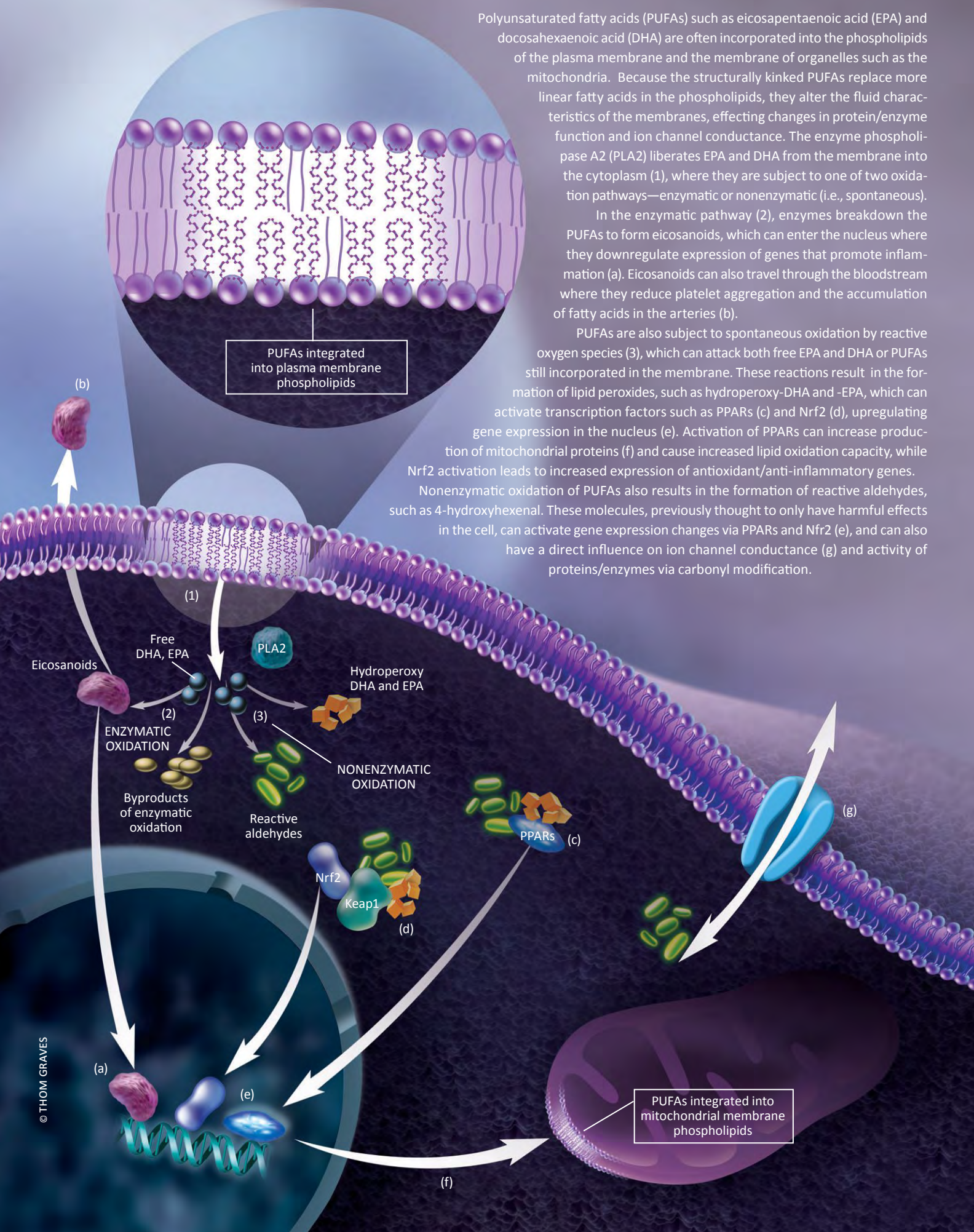
The many actions of PUFAs:

Polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are often incorporated into the phospholipids of the plasma membrane and the membrane of organelles such as the mitochondria. Because the structurally kinked PUFAs replace more linear fatty acids in the phospholipids, they alter the fluid characteristics of the membranes, effecting changes in protein/enzyme function and ion channel conductance. The enzyme phospholipase A2 (PLA2) liberates EPA and DHA from the membrane into the cytoplasm (1), where they are subject to one of two oxidation pathways—enzymatic or nonenzymatic (i.e., spontaneous).

In the enzymatic pathway (2), enzymes breakdown the PUFAs to form eicosanoids, which can enter the nucleus where they downregulate expression of genes that promote inflammation (a). Eicosanoids can also travel through the bloodstream where they reduce platelet aggregation and the accumulation of fatty acids in the arteries (b).

PUFAs are also subject to spontaneous oxidation by reactive oxygen species (3), which can attack both free EPA and DHA or PUFAs still incorporated in the membrane. These reactions result in the formation of lipid peroxides, such as hydroperoxy-DHA and -EPA, which can activate transcription factors such as PPARs (c) and Nrf2 (d), upregulating gene expression in the nucleus (e). Activation of PPARs can increase production of mitochondrial proteins (f) and cause increased lipid oxidation capacity, while Nrf2 activation leads to increased expression of antioxidant/anti-inflammatory genes.

Nonenzymatic oxidation of PUFAs also results in the formation of reactive aldehydes, such as 4-hydroxyhexenal. These molecules, previously thought to only have harmful effects in the cell, can activate gene expression changes via PPARs and Nrf2 (e), and can also have a direct influence on ion channel conductance (g) and activity of proteins/enzymes via carbonyl modification.



PUFAs in fish oil, in particular docosahexaenoic acid (DHA), have been shown in several animal models of heart failure to improve cardiac function and the efficiency with which the organ pumps blood. These findings have been supported recently by placebo-controlled clinical trials showing that daily intake of DHA and another fish-oil PUFA, eicosapentaenoic acid (EPA), for at least a year improved left ventricular function and exercise capacity in patients with established heart failure. (2) Furthermore, clinically significant changes in left ventricular function have been reported as early as 3 months after initiating n-3 PUFA treatment. (3)

Despite these promising outcomes, the results of large-scale meta-analyses and clinical trials involving PUFAs and heart-disease risk have been mixed, raising concerns that initial evidence regarding their effectiveness was misleading. A review published in September in *The Journal of the American Medical Association*, for example, found that increased PUFA intake failed to reduce the risk of stroke, heart attack, or death. (4) Reasons for this disparity can be attributed to a variety of factors, including studies that lack sufficient statistical power and the use of differing methodologies to determine serum and tissue levels of PUFAs. Probably the greatest limitation to properly evaluating the results of many clinical trials is that they varied so widely in the type of n-3 PUFA given, dose, formulation (e.g. capsules or oil), and duration of intake. This widespread variation reflects the paucity of understanding regarding mechanism. If we better understood exactly how these compounds act in the body, then clinical trials regarding their use

could be vastly improved and designed to be more reproducible. What researchers have learned about mechanisms of n-3 PUFA therapy has led us to propose a novel hypothesis that may help reconcile the controversy, uniting well-characterized n-3 PUFA effects with as-yet unresolved questions.

METABOLIC FATE OF PUFAS

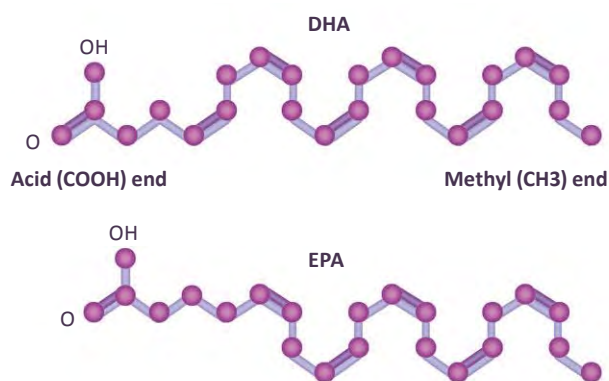
Because long-chain fatty acids are subjected to many different pathways of enzymatic and nonenzymatic metabolism, the identification of exactly how PUFAs are therapeutically effective for cardiovascular ailments has been particularly elusive. Until recently, researchers have focused most of their attention on the incorporation of EPA and DHA into membrane phospholipids, and the enzymatic oxidation of these compounds into signaling molecules called eicosanoids. (See illustration on page 211.) Experimental evidence suggests that increasing levels of EPA/DHA in membranes reduces platelet aggregation and lowers expression of genes that promote inflammation and the accumulation of fatty acids in the arteries.

Further support for eicosanoid-mediated effects of n-3 PUFAs comes from the discovery by Charles Serhan of Harvard Medical School and colleagues of an exciting new family of eicosanoids derived from EPA and DHA. (5) This group of compounds has potent properties that help put out the “fire” of inflammation, leading to their designation as resolvins, and they are currently being studied for their pain-relief potential, among other therapeutic effects. (See “Resolving Chronic Pain,” *The Scientist*, January 2012.) These benefits aside, burgeoning experimental evidence suggests that attributing the benefits of n-3 PUFA therapy for treatment of cardiovascular disease solely to eicosanoid-mediated effects is grossly oversimplistic.

The physiological consequences of n-3 PUFAs becoming incorporated into membrane phospholipids is particularly important in highly oxidative, excitable tissues such as the heart. Here, phospholipid composition is critical for proper membrane structure, thereby ensuring the maintenance of ion channel activity, charge separation, and energy conservation—all necessary for proper cardiac function. Several studies have proposed that EPA and DHA directly modify the exchange of ions through the cardiomyocyte plasma membrane, which may partially explain the PUFAs’ anti-arrhythmic properties.

PUFAs have also been shown to become incorporated into organelle membranes inside the cell. One possible PUFA incorporation site is cardiolipin, a phospholipid unique to mitochondria that helps maintain the electrochemical gradient necessary for oxidative phosphorylation, which generates energy to fuel the cell. Recent findings in animal models of heart failure have demonstrated that altering cardiolipin structure results in increased left ventricular function similar to the effect seen with EPA/DHA treatment. However, it is not yet clear how altering cardiolipin structure by EPA/DHA incorporation would enhance mitochondrial function and improve cardiac energetics.

Finally, aside from eicosanoid synthesis and other well-characterized enzymatic pathways in which PUFAs are known to become oxidized, these compounds are prone to nonenzymatic, spontaneous oxidation because of their highly unsaturated



KINKED STRUCTURES: Polyunsaturated fatty acids (PUFAs) are characterized by the presence of carbon-carbon double bonds (C=C), which give them a kinked structure that makes them prime targets for oxygen or lipid radicals. All PUFAs have two ends—an acid (COOH) end and a methyl (CH₃) end—and the location of the first double bond (counted from the methyl, or omega, end) dictates the molecule’s name. In the case of n-3 PUFAs from fish oil, also known as omega-3s, the first double bond falls after the third carbon atom. Docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) are two common examples of n-3 PUFAs. © THOM GRAVES

structure. (See illustration above, left.) Carbon-carbon double bonds in PUFAs present prime targets for oxygen or lipid radicals. These reactions ultimately form lipid peroxides, reactive aldehydes, and other electrophilic lipids that have very diverse biological effects.

Of all the PUFAs, DHA is the most susceptible to spontaneous oxidation, due to its chemical structure. To date, such nonenzymatic oxidation pathways and their products have been largely ignored by investigators, partly due to the suspicion that the rate of nonenzymatic n-3 PUFA oxidation in vivo is negligible. Also, because the dogma regarding lipid peroxides has always been that they are toxic and undesirable, the possibility that they may be involved in mediating the beneficial effect of n-3 PUFAs is counterintuitive.

But accumulating evidence suggests that spontaneously oxidized PUFAs can be beneficial in many contexts, due largely to the fact that they are highly reactive agonists for certain receptors. For example, recent reports demonstrate that oxidized DHA has a high affinity for the peroxisome proliferator-activated receptor (PPAR) family of transcription factors, which regulate cellular differentiation, development, metabolism, and tumorigenesis. Moreover, oxidized DHA has a greater PPAR-activating effect than any other PPAR ligand tested. (6) These findings could have broad clinical implications because they indicate that DHA peroxidation in vivo could greatly enhance its potency as a PPAR agonist—a class of widely prescribed drugs that treat a variety of ailments, from high cholesterol to type 2 diabetes.

Additionally, beyond the beneficial roles for the oxidized PUFAs themselves, the by-products of PUFA-derived “lipoxidative stress”—the very molecules that are thought to induce harm—could, in fact, be doing the body good.

PUFAS AND STRESS

Mithridates VI, king of Pontus and Armenia Minor in northern Anatolia (now Turkey) from about 120 BC to 63 BC, was a forward-thinking and perceptive individual who understood that a little bit of stress can be a good thing. Terrified of succumbing to the same fate as his father, who was assassinated by poisoning at his own banquet, Mithridates began ingesting sublethal doses of poisons to develop immunity to them, a real-life example of The Princess Bride's Westley.

The benefit of this practice, which in modern times is known as “hormesis,” is believed to stem from the fact that in low, subtoxic amounts, poisons, toxins, and other types of stress will upregulate antioxidants and detoxification enzymes in the liver, heart, and other major organs, thereby augmenting the natural ability of the body to detoxify and protect itself against future exposure to those same toxins. Could that be what's happening with n-3 PUFAs in the heart? Could the highly reactive oxidized products generated from PUFA oxidation cause adaptations in the heart—such as biochemical/biophysical alterations in membranes and the upregulation of cardio-protective genes—that subsequently protect the vital organ against disease and stress?

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It has long been known that 4-hydroxynonenal, an aldehyde formed from the oxidation of n-6 PUFAs (primarily found in corn and vegetable oils and a huge part of our diet), can both help and harm the heart. At subtoxic concentrations ($\leq 10\mu\text{M}$), 4-hydroxynonenal exerts a beneficial "hormetic" effect that activates antioxidant response gene pathways. At higher concentrations, however, 4-hydroxynonenal causes cell death. Yan Zhang of the Keio University School of Medicine in Tokyo and colleagues recently showed that treating cardiomyocytes with small, subtoxic doses ($5\mu\text{M}$) of 4-hydroxynonenal offers protection from subsequent exposure to toxic doses ($\geq 20\mu\text{M}$). (7) This group further showed the physiological relevance of this effect

by pretreating mice with 4-hydroxynonenal prior to restriction of their coronary blood supply, and showed that treated mice fared better: less of the ventricular tissue died following the simulated heart attack.

Scientists are only just beginning to elucidate the molecular mediators of these positive responses to hormesis, but recent studies have pointed to a number of possibilities, including the upregulation of amino acid biosynthesis, increased expression of antioxidant/anti-inflammatory genes, and mitochondrial biogenesis. Some studies, including the one just described by Zhang and colleagues, have specifically implicated the involvement of the transcription factor NF-E2-related factor-2 (Nrf2) in upregulating detoxification and antioxidant genes in response to PUFA oxidation. Furthermore, a recent study in our laboratory showed that mice fed a high-fat diet enriched with n-3 PUFAs showed an increase in n-3 PUFA-derived 4-hydroxyhexenal and upregulation of Nrf2-mediated enzymes in the heart. (8) The net result was a large increase in antioxidant enzyme activity, decreased production of mitochondrial reactive oxygen species (ROS), and augmented levels of the antioxidant glutathione and related enzymes.

A number of other studies in animals have similarly reported increased expression of antioxidant/anti-inflammatory enzymes in the heart following n-3 PUFA dietary supplementation, and clinical studies have shown similar effects in humans. Several trials have reported marked increases in antioxidant enzyme levels in the blood of patients taking n-3 PUFAs, and in some cases, lipid peroxidation was shown to precede the elevation in these enzymes. Furthermore, a small clinical trial conducted by Rodrigo Castillo and colleagues at the University of Chile recently showed that 2 weeks of fish oil and vitamin E treatment before cardiac revascularization surgery augmented antioxidant activity and suppressed the activation of pro-inflammatory transcription factor NF κ B in the myocardium, leading to reduced inflammation and oxidative stress during the procedure. (9) It is further possible that a large part of the electrophysiological effects attributed to n-3 PUFAs may be dependent on their oxidation. An interesting study led by Sébastien Judé of Nutrition, Croissance et Cancer in France showed that the electrophysiological effects of DHA on the transient outward current in cardiomyocytes were only present when the DHA was oxidized with a small amount of hydrogen peroxide; DHA on its own was much less effective. (10) This finding led the authors to speculate that perhaps it is oxidized derivatives of DHA that are responsible for many of the electrophysiological effects of DHA observed to date—primarily in culture dishes, where DHA is exposed to room air and thus likely to be oxidized.

These results point to the idea that the products formed during PUFA oxidation contribute to the cardiac benefits observed so far. If true, this mechanism would be very important from a clinical perspective: low levels of oxidative stress could theoretically protect the heart from a broad array of other stressors, including metabolic disease, infection, aging, and ischemia. So, it seems, Mithridates may not have been original in his idea to build up tolerance by exposing himself to sublethal levels of

poison; the natural biological processes at work in his own body may have already been employing the same strategy.

FUTURE DIRECTIONS

If n-3 PUFA-derived lipoxidative products are indeed at least partially responsible for the therapeutic effects observed, it would follow that any physiological state resulting in sustained oxidative stress—such as cardiovascular or metabolic disease—would drive increased lipoxidative product formation in the presence of EPA and DHA. This hypothesis is controversial because it contradicts existing paradigms regarding the relationship between oxidative stress and disease, but we believe that the evidence presented above certainly seems to challenge those paradigms.

It must be emphasized, however, that 4-hydroxyhexenal, and indeed all n-3 PUFA-derived lipoxidative products, will affect tissues and organ systems differently depending on their ability to adapt positively to mild lipoxidative stress. Thus, the protective effects of these compounds would be manifested to the greatest extent in organs with large antioxidant capacities, such as the heart. Moreover, it is expected that this adaptation would require several days or weeks to become

optimal, a fact that could explain why long-term intake of PUFAs appears to be the most beneficial. These considerations could inform the development of relevant and proper dosing strategies for n-3 PUFA use in clinics. Consequently, the notion that many of the broad effects of n-3 PUFAs in cardiovascular disease can be explained by lipoxidative products derived from them is deserving of rigorous evaluation.

Ethan J. Anderson is an assistant professor and David A. Taylor is a professor and chairman in the Department of Pharmacology and Toxicology at East Carolina University (ECU) in Greenville, North Carolina. Anderson is also an affiliate member of the East Carolina Diabetes and Obesity Institute at ECU.

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University of Iowa researchers Abhinaba Gupta and Ned B. Bowden have developed a nanofiltration membrane technique for separating fatty acids in vegetable oils (doi:10.1021/am3025867, 2013). By modifying them with trialkylamines to form fatty acid-amine salt pairs, the scientists increased the differences in the shapes of the alkyl chain tails. They then made 100- μ m-thick nano-porous membranes from PDCPD (polydicyclopentadiene). Varying the amines and using several membranes together allowed the team to isolate all the fatty acids in a mixture. Their work has implications for the production of oleochemicals on an industrial scale. *Inform* recently asked a roundtable of experts to comment on the ramifications of this research. Their thoughts are available in the supplement to the digital edition, which can be accessed by logging in to read *Inform* at aocs.org/login.

■ ■ ■

Government limits on mold toxins present naturally in grain crops should be expanded to include so-called “masked mycotoxins” that change from harmless to potentially harmful forms in the body, a new study concludes (*Chemical Research in Toxicology*: doi:10.1021/tx300438c, 2013).

Chiara Dall'Asta and colleagues at the University of Parma in Italy explain that these “masked mycotoxins” are not included in current safety regulations because of uncertainty about what happens when people and animals eat them. Their study focused on two of the most widespread mycotoxin contaminants of grain crops—deoxynivalenol (DON) and zearalenone (ZEN). The authors say their results show, for the first time, that bacteria present in the large intestine in people deconjugate or “unmask” DON and ZEN, releasing the original toxic forms.

■ ■ ■

Laval University (Québec, Ontario, Canada), Danone, and Québec's federation of dairy producers are conducting a \$500,000 pilot project to feed flaxseed to cows on 30 farms. They hope to replicate results of studies in Europe, the United States, and Brazil, which found that adding flaxseed reduces the amount of greenhouse gases (principally methane) produced by cows. ■

NEWS & NOTEWORTHY



Nanoparticles found in soybean plants

Two of the most widely used nanoparticles (NP) accumulate in soybeans in ways previously shown to have the potential to adversely affect the crop yields and nutritional quality, a new study has found. It appears in the journal *ACS Nano* (doi:10.1021/nn305196q, 2013).

Jorge L. Gardea-Torresdey and colleagues at the University of Texas at El Paso (USA) cite rapid increases in commercial and industrial uses of NP, the building blocks of a nanotechnology industry projected to put \$1 trillion worth of products on the market by 2015. Zinc oxide and cerium dioxide are among today's most widely used NP. Both are used in cosmetics, lotions, sunscreens, and other products. They eventually go down the drain, through municipal sewage treatment plants, and wind up in the sewage sludge that some farmers apply to crops as fertilizer. Gardea-Torresdey's team previously showed that soybean plants grown in hydroponic solutions accumulated zinc and cerium dioxide in ways that alter plant growth and could have health implications.

The question remained, however, as to whether such accumulation would occur in the real-world conditions in which farmers grow

soybeans in soil, rather than nutrient solution. Other important questions included the relationship of soybean plants and NP, the determination of their entrance into the food chain, their biotransformation, toxicity, and the possible persistence of these products into the next plant generation. The researchers' new study, performed at two synchrotron facilities—the SLAC National Accelerator Laboratory in California and the European Synchrotron Radiation Facility in Grenoble, France, addressed those questions. (A synchrotron is a cyclotron in which the magnetic field strength increases with the energy of the particles to keep their orbital radius constant.)

“To our knowledge, this is the first report on the presence of cerium dioxide and zinc compounds in the reproductive/edible portions of the soybean plant grown in farm soil with cerium dioxide and zinc oxide nanoparticles. In addition, our results have shown that cerium dioxide NP in soil can be taken up by food crops and are not biotransformed in soybeans. This suggests that cerium dioxide NP can reach the food chain and the next soybean plant generation, with potential health implications,” the study notes.

CONTINUED ON NEXT PAGE

The authors acknowledge financial support from the National Science Foundation and the US Environmental Protection Agency.

Omega-3-rich dairy products pass initial tests

New work on the fortification of milk and milk products with medium- and long-chain omega-3 (n-3) fatty acids has brought promising results.

Adding n-3 fatty acids to dairy products can be done in one of two ways: pre-harvest, by altering a cow's diet to include feeds high in n-3 fatty acids; or post-harvest, mixing n-3-rich material into the milk at some point in the processing.

Sue Duncan, registered dietitian and professor of food science and technology at Virginia Polytechnic Institute and State University (VT; Blacksburg, Virginia, USA) and her team used a post-harvest process to blend a food-grade n-3 fatty acid mix—which included anchovy, sardine, canola, and sunflower oils—with dairy products. Their study appeared in the *Journal of Dairy Science* (<http://dx.doi.org/10.3168/jds.2012-5364>, 2012).

The researchers separated fresh raw milk into cream and skim milk. Both were pasteurized and stored overnight in a refrigerator. The cream was churned into butter and buttermilk. These products were then fortified with the n-3 fatty acids—largely eicosapentaenoic (EPA; 20:5n-3) and docosahexaenoic (DHA; 22:6n-3) acids from fish oil—and then frozen until needed. After 35 days, there was no noticeable fish scent in the samples and little to no oxidation had occurred.

The recommended amount of EPA + DHA for patients without heart disease, according to the American Heart Association, is contained in two three-ounce servings of fatty coldwater fish per week. (In the case of wild salmon, this would translate to up to 4 g of EPA + DHA.) By contrast, Duncan's formula contained around 430 milligrams of EPA + DHA per eight-ounce serving (200 mg/100 g). EPA + DHA-fortified dairy products currently on the market generally have between 32 and 50 mg of EPA + DHA per serving.

Duncan said that she and her group plan to conduct taste and consistency tests on their fortified dairy product, adding that she

does not believe pre-harvest techniques will work because they cannot achieve a consistent product. But at Oregon State University (Corvallis, USA), a team led by Gerd Bobe believes they can achieve that consistency by incorporating flaxseed (linseed), which is high in α -linolenic acid (ALA; 18:3n-3), into the diets of cows.

Bobe and his team fed various ratios of extruded and ground flaxseed to 10 pregnant cows in their usual feed for two-week periods. Their aim was to determine the optimal rate of flaxseed supplementation for improving the fatty acid profile without decreasing production characteristics of milk and dairy products. They saw the biggest increase in ALA in the final dairy product when incorporating 2.72 kg of flaxseed, comprising roughly 7% of the total diet.

The group manufactured several products from the pasteurized milk, including mozzarella cheese, butter, and buttermilk. In the dairy products, polyunsaturated acid (PUFA) content rose in average concentration by 82% and ALA levels rose 70%. Saturated fatty acids in the milk dropped 18%, though they still accounted for more than half of the fatty acids in the product, while PUFA took up no more than 9% of the finished product.

The butter consistency was softer than normal. However, the texture and production of the other dairy products were not affected. Levels of ALA per eight-ounce serving (150–175 mg/100 g) of milk reached 350–400 mg.

Bobe said he hopes to continue his research, which appeared in the *Journal of Dairy Science* (96:1177–1188, 2013), and to repeat the experiment on a larger scale.

Innovative products utilize soybean oil

Chances are you have used soybean oil before, whether you have known about it or not. But have you slept on it?

The United Soybean Board (USB; Chesterfield, Missouri, USA) recently released a list recognizing 45 new products that incorporate soy in different forms, including a mattress with soy-based foam.

Foam mattresses are known for their ability to give sleepers back and lumbar support. The new foam mattress from Impact Gel Corp. (Ettrick, Wisconsin, USA) takes a ventilated foam mattress and places the company's trademark product—Impact Gel, which features epoxidized soybean oil-based polyurethane—inside the spaces between the foam of the mattress.

Impact Gel consists of seven main ingredients—soybean oil, a prepolymer, a thermoplastic polymer, a metal catalyst, and other filler ingredients—with different blends featured for different uses, including insoles, sports padding, horse saddles, and mobile phone cases. Impact Gel began as an impact insulator gel in safety devices for the NASCAR (National Association for Stock Car Auto Racing) vehicles before making its way into foam mattresses.

Troy Goodenough, head of Impact Gel's operations, said one of the unique challenges of making the mattresses involved finding the right ratio and positioning of the gel in the foam itself. A mattress containing Impact Gel has all the advantages of foam mattresses and is more durable. The gel also makes the mattress more breathable, Goodenough said, improving air flow in the mattress and keeping it from heating up, a flaw of many foam mattresses.

CONTINUED ON PAGE 220



SUSTAINABILITY WATCH

First mobile app for green chemistry

Mention mobile applications, or mobile apps, and people think of games, email, news, weather, productivity and other software for Apple, Android, and other smart phones and tablet computers. But an app with broader impact—the first mobile application to foster wider use of the environmentally friendly and sustainable principles of green chemistry—is the topic of a report in the new journal, *ACS Sustainable Chemistry & Engineering* (1: 8–13, 2013).

Sean Ekins, Alex M. Clark, and Antony Williams point out that the companies that manufacture consumer products have a commitment to work in a sustainable fashion without damaging the environment. That's the heart of "green chemistry," often defined as "the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products."

Their article describes a guide on doing so for solvents, key ingredients in many manufacturing processes. Some traditional processes (particularly in the manufacture of pharmaceuticals) generate 25–100 times more waste than the chemical they are making. The Green Solvents mobile app version of the guide for Apple devices covers 60 different solvents and is available online at <http://tinyurl.com/Green-Solvents>, and the Lab Solvents app for Android devices is available online at <http://tinyurl.com/Lab-Solvents>.

Chemical industry focuses on sustainability

The chemical industry is increasingly focusing on sustainability, according to a new survey by Genomatica and *ICIS Chemical Business* magazine.

According to the survey, 71% of the over 700 participants indicate that they have a sustainability strategy in place or under development. Almost half of producers (44%) said it was "very important" that they are a front-runner in sustainable chemicals and 72% of producers said their customers have expressed interest in sustainable chemicals. Both producers and users are incorporating sustainability in their current practices and renewable materials have become increasingly important.

One of the most important factors for users is minimal impact on product performance or characteristics; similarly, for producers it is minimal impact on downstream products and customers. Most companies reported that they are taking a pragmatic approach and looking for drop-in or near-drop-in biobased alternatives to petroleum products in an attempt to minimize development time and costs associated with reformulation and re-equipping production facilities.

"We've seen a big shift from several years ago, when increasing sustainability was viewed more as a cost than a benefit," said John Baker, global editor of *ICIS*, and organizer of the survey. "A majority of companies in the chemical industry have now incorporated sustainability into business practices and are looking to it as a way not only to reduce environmental impact but also to lower costs and meet customer requirements. These are all strong drivers toward more sustainable everyday products being made from renewable-based chemicals."

The Genomatica and *ICIS* survey was completed by over 700 *ICIS Chemical Business* readers working globally in the petrochemicals, specialty chemicals, and polymers segments of the chemical industry. The respondents were generally senior executives (27% board level and 24% general manager) and worked mainly in the specialty (22%) and commodity/polymers (30%) sectors, with a further 12% in chemical distribution.

Genomatica develops new technologies for manufacturing intermediate and basic chemicals from renewable feedstocks. The company is based in San Diego, California, USA. ■

"It's a new field for us," he noted. "A customer suggested we try it. We did and it worked pretty well."

Unlike most foam mattresses, the Impact Gel mattress is non-toxic. This is also true of the Real Action Paint Ball Inc. (RAP) Eco-Friendly Field Paintball. The Santa Clara, California, USA, company wanted to find a way to fix some of the problems of standard paintballs, and found soybean oil to be the answer.

For the uninitiated, Wikipedia describes paintball as a game in which players compete, in teams or individually, to eliminate opponents by tagging them with capsules containing water soluble dye and gelatin shell outside (known as paintballs) propelled from a device called a paintball marker (commonly referred to as a paintball gun).

Paintballs are typically made with a combination of polyethylene glycol (PEG), water-soluble solutions that are nontoxic, and dye encapsulated in a gelatin sphere. Breaking on contact, these balls bring a messy payload to whatever they hit. But higher-quality dyes are much harder to remove from clothes, skin, and the playing field, and the paint remains and thickens over long periods of time. Lower-quality paintballs may make paint easier to remove, but the balls themselves are more likely to explode in the gun or not break on contact because of the quality of fill and capsule.

"We've been to some paintball fields that use artificial turf [to cover paint splashes]. When you pull it up, the artificial turf is all goood up," said Mike Lovato, general manager of RAP.

RAP used soy sterol-based-PEG to partially replace the petroleum-based PEG in its Eco Friendly Field Paintballs. The paint fades

quickly in the sun and is washed away in the rain, sinking into the ground without damaging nearby plant or water sources, according to Lovato.

Another item featured in USB's new product list is manufactured by Soy Technologies, LLC (Nicholasville, Kentucky, USA). The company specializes in using soy-based ingredients in cleaning solvents to lower their levels of volatile organic compounds (VOC). Low-VOC nail polish is the latest entry in the company's lengthy product list, said Soy Technologies President Randy Frees.

Nail polish removers typically rely on acetone to break up and dissolve nail lacquer. However, acetone gives off VOC and is a harsh chemical that can damage the nail and cuticle with continued use. Using a soy-methyl-ester-based nail polish remover can actually improve and moisturize the nail and cuticle without giving off a sharp scent, Frees noted. Called the Soyanol NPR-6, the nail polish remover that Soy Technologies sells to private companies in a base formula can be customized for color, scent, and other cosmetic characteristics. The company is now working on an NPR-7 formula that will include moisturizers.

"If you look at soy-based nail polish removers, there's a good chance we're involved," Frees said. "All of these products are much better for the nail and cuticle."

The full list of USB-recognized products can be found at <http://tinyurl.com/USB-45>. USB funds research and market development from the proceeds of the US soy checkoff program, in which farmers invest a mandated amount for each bushel of soybeans sold. ■



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BRIEFS

According to a report by Bloomberg (<http://tinyurl.com/Brazil-EtOH-sugar>), Brazilian sugarcane refineries directed 48.44% of their product to sugar in 2011/12, and 49.59% in 2012/13. At least for the first part of 2013, the percentage directed toward ethanol production is expected to exceed 50%. Gasoline prices have been rising, making ethanol more competitive, and as of May 2013 the government plans to raise the amount of anhydrous ethanol blended into gasoline to 25% from the 20% level at which it now stands.

■ ■ ■

In January 2013, the European Commission, executive body of the European Union (EU), proposed imposing a penalty of 9.5% on imported biofuels from the United States. The EU accused the United States of dumping ethanol, negatively affecting the EU bioethanol industry. The period under consideration for this accusation is October 2010 to September 2011. During this time the US market share of ethanol rose from 1.9% to 15.7% of the EU market. Brazil, which is the only other substantial supplier of ethanol to the EU, saw its market share fall from 30.3% to 4.5%. A decision on the proposal was expected by February 22, 2013.

■ ■ ■

As presented by Environmental Entrepreneurs (E2; www.fuelinggrowth.org), there are now more than 80 advanced biofuel companies, refineries, and related operations located in at least 27 of the United States. California has the most of these facilities, almost 30. Beyond that, the top four states for biofuel companies are Illinois (8), Colorado (6), Texas (5), and Iowa (4). At the E2 website is a searchable map and state-by-state breakdown of companies involved in the advanced biofuels industry. The site also compiles information on how clean fuel companies are driving economic growth. ■

BIOFUELS NEWS



Proposed US Renewable Fuel Standards for 2013

On January 31, 2013, the US Environmental Protection Agency (EPA) announced its proposed 2013 percentage standards for four fuel categories that are part of the agency's Renewable Fuel Standard program (RFS2). These standards are based on gasoline and diesel projections from the Energy Information Administration (EIA). EPA is also required to set the cellulosic biofuel standard each year based on the volume projected to be available during the following year, using EIA projections and assessments of production capability from industry.

This regulatory action proposed standards for (i) cellulosic, (ii) biomass-based diesel, (iii) advanced biofuel, and (iv) total renewable fuels that apply to all gasoline and diesel produced or imported in the year 2013 (Table 1). These volumes represent the minimum that would need to be consumed in the United States. If excess volumes of cellulosic biofuel or biomass-based diesel were

TABLE 1. Volumes used to determine the proposed 2013 percentage standards^{a,b}

Cellulosic biofuel	14 million gallons
Biomass-based diesel	1.28 billion gallons
Advanced biofuel	2.75 billion gallons
Renewable fuel	16.55 billion gallons

^aAll volumes are ethanol-equivalent, except for biomass-based diesel, which is actual. Note: 1.0 billion gallons = 3.8 billion liters.

^bSource: <http://tinyurl.com/EPA-RFS-2013>.

to be so consumed they would count toward the advanced biofuel and total renewable fuel volume requirements.

As part of the rulemaking, the EPA proposed a cellulosic ethanol volume for 2013 of 14 million gallons. This value was developed based on the projected available

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TABLE 2. Proposed percentage standards for 2013^a

Cellulosic biofuel	0.008%
Biomass-based diesel	1.12%
Advanced biofuel	1.60%
Renewable fuel	9.73%

^aSource: <http://tinyurl.com/EPA-RFS-2013>.

cellulosic biofuel plant volumes from four named companies that are farthest ahead in commercializing cellulosic ethanol, namely, Abengoa (Hugoton, Kansas), Fiberight (Blairtown, Iowa), INEOS Bio (Vero Beach, Florida), and KiOR (Columbus, Mississippi).

The EPA also announced it would consider public comments for 45 days (ending date March 17, 2013) before setting the cellulosic standard.

Under the RFS program, four separate percentage standards are required, corresponding to the four separate volume requirements (Table 1, page 221). The percentage standards represent the ratio of renewable fuel volume to nonrenewable gasoline and

diesel volume (Table 2). Thus for 2013 about 10% of all fuel used will be from renewable sources.

The EPA has a web site (<http://tinyurl.com/EPA-RFS-FAQ>) presenting further aspects of the RFS program, including how ethanol equivalents are calculated, as well as responses to frequently asked questions.

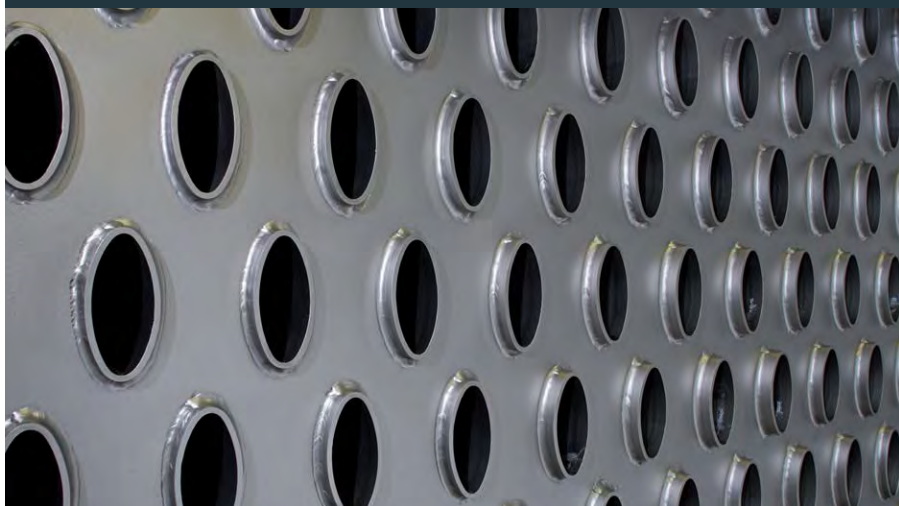
Neste Oil expands renewable inputs

Neste Oil (Porvoo, Finland) increased its use of waste animal fat for production of renewable fuels from 330,000 metric tons (MT) in 2011 to 742,000 MT in 2012. Part of the increase was attributable to the addition of waste fat from the fish processing industry to its feedstock base. The company also commissioned Europe's first pilot plant for producing waste-based microbial oil in 2012.

Neste used a total of 2.1 million metric tons of renewable inputs in 2012 to produce renewable diesel, of which palm oil accounted for 65%, waste and residues 35%, and other vegetable oils under 0.5%. In a company statement, Matti Lehmus, executive vice president, oil products and renewables for Neste, said, "Neste Oil is the world's largest supplier of renewable diesel today and the largest producer of renewable fuels from waste and residues. The amount of renewable diesel that Neste Oil produces from waste

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and residues today is equivalent to the annual fuel consumption of 740,000 cars" (<http://tinyurl.com/Neste-waste-use>).

Producing algae with paper mill wastes

The Swedish government, through its agency for innovation systems, will invest \$624,000 over three years to develop processes to convert micro-algae grown on the waste products of pulp and paper mills into bio-oil. The test facility will be built at a pilot plant scale at the Bäckhammar paper mill outside Kristinehamn.

Altogether, the total budget slightly exceeds \$1.25 million. SP Technical Research Institute is leading the project, with the help of the Paper Province, Nordic Paper Bäckhammar, and 11 other partners from industry, academia, and the public sector.

The intent of the project is to develop a process by which algae can use nutrients in paper mill wastewater and CO₂ from flue gases to synthesize biomass. Oil will be extracted from the algae and refined into products such as biodiesel, bioplastics, and lubricating oil. Waste heat from the flue gases can be used to maintain an optimal temperature for growing the algae. (<http://tinyurl.com/paper-mill-algae>).

US Renewable Fuel Standards for 2012

On January 25, 2013, a federal appeals court threw out the quota set in 2012 by the US Environmental Protection Agency (EPA) for incorporating cellulosic biofuel into car and truck fuels. This ruling was in response to a case brought by the American Petroleum Institute (API), whose members were supposed to comply with the 2012 quota.

The court vacated the cellulosic biofuel standard because it believed that EPA had impermissibly set the volume with the objective of promoting growth in the industry, rather than making an accurate prediction. On the other hand the court rejected API's argument that EPA was not entitled to consider information from cellulosic biofuel producers in setting its projection. The court found that cellulosic producers were "an almost inevitable source of information" for the EPA (<http://tinyurl.com/2012-cell-EtOH-rejected>). The court also rejected API's argument that EPA was required to follow the US Energy Information Administration's projections in setting its own.

Car approved for higher biodiesel blends

In February US car and truck manufacturer General Motors (GM) announced that its 2014 Chevrolet Cruze light-duty diesel passenger car was approved for use with 20% biodiesel blends (B20). The Cruze 2.0 L clean diesel engine will offer an estimated 42 mpg (5.9 L/100 km) highway fuel rating with an automatic transmission and expected best-in-segment range based on testing conducted by GM. According to the company, clean diesels using modern diesel exhaust technology and ultra-low sulfur fuel are over 90% cleaner than older models. In a statement (<http://s.tt/1zAIL>), the National Biodiesel Board said that more than 33 light- and medium-duty diesel passenger cars and trucks, as well as heavy-duty diesel models

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from nearly 20 different brands, will be available in the US market in 2013, and about 80% of manufacturers selling diesel vehicles and equipment in the United States now warranty them for use with B20 biodiesel blends.

Flaxseed as niche feedstock for biodiesel?

Canada produces 56% of the world's supply of flax. Jon Dwyer, an entrepreneur and president of Toronto-based Flax Energy Corp., is exploring possibilities of using flaxseed as a source of biofuel (<http://flaxenergy.ca>). The company, founded in 2008, has been operational since September 2012. It processes about 46 metric tons of flaxseeds daily. The nameplate capacity of its biodiesel unit is 16.4 million liters annually.

Dwyer has filed for a patent for his process of creating biodiesel out of flaxseed. His company uses a cold-pressed process to extract oil from the seeds, rather than solvent. He explained to the Toronto *Globe and Mail* newspaper that seed is fed into food-grade stainless steel turbines. As the turbine spins, it drags the seeds through the machine, crushing them. The process generates heat, which facilitates release of the oil from the seeds (<http://tinyurl.com/flaxseed-to-biofuel>).

The company presently maintains flax farms in Manitoba and in Hamilton, Ontario. Most of the fuel it produces presently is being sold to Toronto-based Steam Whistle Brewing, which

concentrates on making pilsner beer, and to the cities of Brampton and Mississauga. The meal remaining after oil removal is being sold as animal feed.

Malaysia to increase biodiesel usage

Malaysia's Plantation Industries and Commodities (MPOC) Minister Bernard Dompok indicated that the adoption of B10 (10% biodiesel, 90% petrodiesel) in the country by the middle of 2014 should help stabilize declining prices of crude palm oil produced in Malaysia. The country is currently contending with a record-high stock of palm oil, and conversion of some of this to fuel to be used within the country should ease problems with this oversupply.

Dompok told a meeting on "Reach and Remind Friends of the Industry" on February 4, sponsored by the MPOC, that 75% of the facilities needed to accomplish this goal will be completed by the end of 2013. He added that \$26 million has already been spent to set up blending facilities.

MPOC expects that exports of palm oil will increase this year, particularly because the government has already discontinued the duty-free export duty that was initiated in January 2013. According to MPOC chairman Lee Yeow Chor, "We are targeting emerging countries. We believe that is where the growth is" (<http://www.thesundaily.my/news/605429>). ■

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BRIEFS

Research at Oregon State University in Corvallis (USA) found that docosahexaenoic acid (DHA; 22:6n-3) can reduce the proteins involved in liver inflammation and fibrosis—common problems of the obese and overweight. The study, published in the *Journal of Nutrition* (doi:10.3945/jn.112.171322, 2013), was one of the first to directly compare the effects of two of the omega-3 fatty acids often cited for their nutritional value, DHA and EPA (eicosapentaenoic acid; 20:5n-3). In research with laboratory animals, the scientists found that EPA had comparatively little effect on preventing the fibrosis, or scarring that is associated with liver fibrosis. However, DHA supplementation reduced the proteins involved in liver fibrosis by more than 65%.

■ ■ ■

British researchers looked at data from about 165,000 people, and found that a 10% increase in body mass index (BMI) was linked to a 4% drop in serum 25-hydroxyvitamin D levels. The link between BMI and vitamin D levels was found in men and women, as well as in younger and older people, the investigators said. The findings suggest that a higher BMI leads to lower levels of vitamin D circulating in the body, while a lack of vitamin D has only a small effect on BMI, according to the authors of the study, published in *PLoS Medicine* (10: e1001383–e1001383, 2013). Elina Hypponen of University College London's Institute of Child Health led the study.

■ ■ ■

Consuming deep-fried foods such as French fries (chips), fried chicken, and donuts more than once per week is associated with an increased risk of prostate cancer. The increased risk ranges from 30 to 37%, and the effect appears to be slightly stronger with regard to more aggressive forms of the disease, according to a study by investigators at the Fred Hutchinson Cancer Research Center in Seattle, Washington, USA. Janet Stanford led the study, which appeared in *The Prostate* (doi:10.1002/pros.22643, 2013). ■

HEALTH & NUTRITION

A new look at old data

Reanalysis of clinical trial data resurrected from the 1960s by US researchers adds weight to arguments against simplistic dietary recommendations regarding fats and oils.

Christopher Ramsden of the US National Institutes of Health (NIH) and his team used modern statistical techniques to review data that were not included in the original 1978 publication of results from the Sydney Diet Heart Study (*Advances in Experimental Medicine and Biology* 109:317–330). That clinical trial, which was conducted from 1966–1973, followed 458 men, aged 30 to 59 years, with a history of heart disease. Roughly half of the subjects were told to replace the saturated fats in their diets (from dairy and animal sources) with linoleic acid (LA; 18:2n-6). The other subjects served as the control group and were told not to change anything.

The original researchers noted an increased risk of early death from any cause among the omega-6 group, but did not mine the data for further information. Ramsden

and his team, however, compared death rates from all causes, cardiovascular, and coronary heart disease.

The NIH researchers found that the omega-6 group had a higher risk of death from all causes and not just from CVD and coronary heart disease:

- The risk of all-cause death was 17.6% in the omega-6 group compared with 11.8% in the controls (which constitutes a hazard ratio, or HR, of 1.62)
- The risk of death from cardiovascular disease was 17.2% for the omega-6 group vs. 11% for the controls (for an HR of 1.70)
- The risk of death from coronary heart disease was 16.3% in the omega-6 group vs. 10.1 in the controls (for an HR of 1.74)

“Advice to substitute vegetable oils rich in polyunsaturated fatty acids (PUFA) for animal fats rich in saturated fatty acids has been a cornerstone of worldwide dietary guidelines for the past half century,” the scientists note in their article. “When this advice

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TABLE 1. Content of n-6 LA and n-3 α -LNA in commercially available edible oils^a

Cooking oil	LA (g per 100 g of cooking oil)	α -LNA (g per 100 g of cooking oil)
Vegetable oil*	Depends on specific oil	Depends on specific oil
Safflower†	74.6	0.0
Sunflower†	65.7	0.0
Cottonseed	51.5	0.0
Corn	53.5	0.2
Soybean	50.3	7.0
Canola	18.6	9.1
Olive	9.8	0.8
Butter oil	2.3	1.4
Coconut	1.8	0.0

^aAdapted from Use of dietary linoleic acid for secondary prevention of coronary heart disease and death: evaluation of recovered data from the Sydney Diet Heart Study and updated meta-analysis, *British Medical Journal*, <http://dx.doi.org/10.1136/bmj.e8707>, 2013. Data are from the US Department of Agriculture Nutrient Database. Note: Fatty acid contents of oils vary to some extent by season, latitude, and other conditions.

Abbreviations: n-6 LA=omega-6 linoleic acid; n-3 α -LNA=omega-3 α -linolenic acid.

*Food items labeled “vegetable oil” may contain one or more of the above oils.

†Varieties of safflower and sunflower oils with lower LA content are commercially available.

originated in the 1960s, PUFA were regarded as a uniform molecular category with one relevant biological mechanism—the reduction in blood cholesterol. Omega-6 [LA] was the best-known dietary PUFA at the time. Therefore, the terms “PUFA” and “LA” were often used interchangeably when interpreting clinical trial results and delivering dietary advice.”

The researchers further note that thinking about the general category of PUFA has changed, with an increased recognition that PUFA constitute “multiple species of omega-3 and omega-6 PUFA, each with unique biochemical properties and perhaps divergent clinical cardiovascular effects.”

Reaction to the new study, which appeared in the *British Medical Journal* (BMJ; <http://dx.doi.org/10.1136/bmj.e8707>, 2013), has been mixed. In an editorial accompanying the BMJ article, Philip Calder of the University of Southampton, UK, asserted that the new look at old data “provides important information about the impact of high intakes of omega-6 PUFA, in particular linoleic acid, on cardiovascular mortality at a time when there is considerable debate on this question.”

An article by FoodNavigator.com quotes a number of health professionals who urged caution in interpreting the findings.

“We now know that reducing artery inflammation—by boosting monounsaturated fat intake—helps stabilize artery walls and make them more resistant to damage,” said Catherine Collins, principal dietitian at St. George’s Hospital in London. “Should we

be concerned about our current intake of omega-6 polyunsaturates—LA in particular? As a dietitian, I think not.”

Inneke Herreman, secretary general of IMACE, the European Margarine Association, noted that the intake level of 15% of daily energy from PUFA used in the Sydney Diet Heart Study was greater than current dietary recommendations by many international health agencies. These recommendations suggest a total PUFA intake of up to 11% of daily energy, with a total omega-6 consumption of up to 9% of daily energy.

“Actually, the available clinical trial evidence demonstrates clear benefits of omega-6 consumption on blood lipids levels and large other well-designed and more recent prospective cohort studies demonstrate that higher intakes of omega-6 PUFA or total PUFA are associated with reduced risks of coronary heart disease events,” said Herreman.

The NIH authors suggested that benefits ascribed to PUFA in general might actually be due to n-3 PUFA. “Since n-6 LA is the most abundant dietary PUFA, and edible oil sources with markedly different contents of fatty acids are commercially available (Table 1), it is important to ascertain the benefits and risks specific to n-6 LA.”

Is a calorie a calorie by any other name?

Energy harvest from the human diet is consistently underestimated, a team of international scientists recently said, because key features of the digestive process are routinely ignored, including the activity of gut microbes and the metabolic cost of food digestion. The scientists spoke at a meeting of the American Association for the Advancement of Science on February 18, 2013, in Boston. (See <http://tinyurl.com/AAAS-Calorie>.)

“We’re misleading consumers,” Canada’s *Globe and Mail* newspaper quoted Geoffrey Livesey as saying. Livesey is an independent nutritional biochemist who advises the Food and Agricultural Organization of the United Nations on standards for food labeling. He spoke on improving the Atwater system—long a topic of debate among nutritionists.

Wilbur Atwater, a professor of chemistry at Wesleyan University in Middletown, Connecticut, USA, developed a system in the latter part of the 19th century and early 20th century for establishing the relative caloric content of the major food macronutrients. These include carbohydrates, proteins, and fats. What is missing from the system, the panelists said, is a consideration of the form of carbohydrates consumed, with more processed carbohydrates such as refined flour “offering easy access to food energy,” the newspaper report noted.

“The failure of the system is that it underestimates caloric differences,” Richard Wrangham, a biological anthropologist at Harvard University (Cambridge, Massachusetts, USA) reportedly said.

The panelists suggested that this lack of consideration of the type of macronutrient could lead to errors of up to 30%. Livesey said that the standard Atwater formula that pegs carbohydrate at 4 calories per gram and fat at 9 calories per gram works for easily digested foods but assumes that fiber has no energy value to the

body. He reportedly said that fiber used to be mostly cellulose, which was difficult to digest and would pass straight through the body; however, now pectin and soluble fiber are added, which are broken down in the large intestine into compounds that provide energy for the body. He said that this is equivalent to around two calories per gram of fiber.

Wrangham noted that “currently, the standard method for determining dietary energy value (the Atwater system) systematically over-estimates the energy gain that is derived from relatively unprocessed foods.” Consumers could reduce their calorie intake by consuming raw instead of cooked foods, because they are less digestible and take more energy to break down. Klaus Englyst from Southampton talks about “Bioavailability of carbohydrates.”

“We’re still at the beginning of a line of research that may provide people with more solid recommendations,” said Rachel Carmody, according to the *Globe and Mail* report. Carmody collaborates with Wrangham at Harvard University. “But it doesn’t take an enormous amount of science for someone—when faced with a highly processed form of food relative to a food with similar raw ingredients in a less processed form—to know what the right choice is.”

Vitamin D3, omega-3 fatty acids, and Alzheimer’s disease

Vitamin D3 and omega-3 fatty acids may enhance the immune system’s ability to clear the brain of amyloid plaques, one of the hallmarks of Alzheimer’s disease.

In a small pilot study in the *Journal of Alzheimer’s Disease* (doi:10.3233/JAD-121735, 2013) the researchers identified key genes and signaling networks regulated by vitamin D3 and the omega-3 fatty acid DHA (docosahexaenoic acid; 22:6n-3) that may help control inflammation and improve plaque clearance.

Previous *in vitro* work by the team helped clarify key mechanisms involved in helping vitamin D3 clear amyloid- β , the abnormal protein found in the plaque. The new study extends the previous findings with vitamin D3 and highlights the role of DHA.

“Our new study sheds further light on a possible role for nutritional substances such as vitamin D3 and omega-3 in boosting immunity to help fight Alzheimer’s,” said study author Milan Fiala, a researcher at the David Geffen School of Medicine at the University of California, Los Angeles (USA).

For the study, scientists drew blood samples from both Alzheimer’s patients and healthy controls, then isolated critical immune cells (macrophages) from the blood. Macrophages are responsible for destroying amyloid- β and other waste products in the brain and body.

The team incubated the immune cells overnight with amyloid- β . They added either an active form of vitamin D3 called 1 α ,25-dihydroxyvitamin D3 or an active form of the omega-3 fatty acid DHA called resolvin D1 to some of the cells to gauge the effect they had on inflammation and amyloid- β absorption.



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Both 1 α , 25-dihydroxyvitamin D3 and resolvin D1 improved the ability of the Alzheimer's disease patients' macrophages to destroy amyloid- β , and they also inhibited the cell death that is induced by amyloid- β . Researchers observed that each bioactive molecule utilized different receptors and common signaling pathways to do this.

Previous work by the team, based on the function of Alzheimer's patients' macrophages, showed that there are two groups of patients and macrophages. In the current study, researchers found that the macrophages of the Alzheimer's patients differentially expressed inflammatory genes, compared with the healthy controls, and that two distinct transcription patterns were found that further define the two groups: Group 1 had an increased transcription of inflammatory genes, while Group 2 had decreased transcription. Transcription is the first step leading to gene expression.

"Further study may help us identify if these two distinct transcription patterns of inflammatory genes could possibly distinguish either two stages or two types of Alzheimer's disease," said study author Mathew Mizwicki, an assistant researcher at the David Geffen School of Medicine.

While researchers found that 1 α , 25-dihydroxyvitamin D3 and resolvin D1 greatly improved the clearance of amyloid- β by macrophages in patients in both groups, they discovered subtleties in the effects the two substances had on the expression of inflammatory genes in the two groups. In Group 1, the

increased-inflammation group, macrophages showed a decrease of inflammatory activation; in Group 2, macrophages showed an increase of the inflammatory genes IL1 (interleukin-1) and TLR (toll-like receptors) when either 1 α , 25-Dihydroxyvitamin D3 or resolvin D1 were added.

More study is needed, Fiala said, but these differences could be associated with the severity of patients' nutritional and/or metabolic deficiencies of vitamin D3 and DHA, as well as the omega-3 fatty acid EPA (eicosapentaenoic acid; 20:5n-3).

"We may find that we need to carefully balance the supplementation with vitamin D3 and omega-3 fatty acids, depending on each patient in order to help promote efficient clearing of amyloid- β ," Fiala said. "This is a first step in understanding what form and in which patients these nutrition substances might work best."

According to Fiala, an active (not oxidized) form of DHA, which is the precursor of the resolvin D1 used in this study, may work better than more commercially available forms of DHA, which generally are not protected against the oxidation that can render a molecule inactive.

The next step is a larger study to help confirm the findings, as well as a clinical trial with DHA, the researchers said.

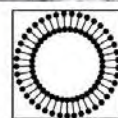
The US Alzheimer's Association contributed to the initial phase of the study.

Fiala is a consultant for the Smartfish Co., which is producing a drink with an active form of DHA. ■

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ENZYMATIC PRODUCTION OF ALKANES

An article in the *Proceedings of the National Academy of Sciences* (doi:10.1073/pnas.1218769, 2013) from the US Department of Energy's Brookhaven National Laboratory (BNL; Upton, New York) reports an explanation for why a reaction catalyzed by an enzyme that naturally produces alkanes—which are a major component of gasoline—typically stops after three to five cycles. And with that information, the researchers have found a way to keep the reaction going. The solution to this question could lead to renewed interest in incorporating the enzyme into bacteria, algae, or plants to produce biofuels requiring no further processing.

BNL biochemist John Shanklin, who led the research, said, "Alkanes are very similar to the carbon-chain molecules in gasoline. They represent a potential renewable alternative to replace the petrochemical component of gasoline." He added, "Unlike the process of breaking down plant biomass to sugars and fermenting them to ethanol, biologically produced alkanes could be extracted and used directly as fuel" (<http://tinyurl.com/BNL-enzyme>). Shanklin carried out this research with former Brookhaven postdoctoral

students Carl Andre, now working at BASF Plant Science in North Carolina, and Xiaohong Yu of BNL's Biosciences Department.

The recent discovery of an enzyme known as aldehyde-deformylating oxygenase (ADO), which naturally makes alkanes from precursors in certain bacteria, stimulated interest in harnessing this enzyme's action to make liquid biofuels. But early attempts to insert ADO into laboratory-based alkane "factories" produced disappointing results. Likewise, the BNL team's experiments in test tubes—using substrates synthesized with the help of Sunny Kim in BNL's Radiotracer and Biological Imaging group—yielded the same result others had observed: The enzyme stopped working after three to five turnovers and alkane production would cease.

Drawing on ADO's similarity to desaturases, with which the research team was already familiar, the scientists found that the alkane-producing system creates a by-product that is toxic to the ADO enzyme.

First, the scientists tested whether they could substitute hydrogen peroxide for the electron transfer proteins and oxygen normally required for the alkane-producing reaction—an approach that had worked for a related enzyme. But instead of stimulating alkane production, no alkane at all was produced; and in control experiments containing all the components plus hydrogen peroxide, alkane production was also blocked.

Shanklin commented, "It turns out one of the electron transport proteins was interacting with oxygen to produce hydrogen peroxide, and the buildup of hydrogen peroxide was 'poisoning' the ADO enzyme, completely inhibiting its activity."

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BRIEFS

The International Service for the Acquisition of Agri-Biotech Applications (ISAAA) has published a compilation its annual update on the adoption of biotechnology-based crops, countries where they are being planted, and traits that are being used. For example, ISAAA reports that biotech soybeans were grown in 11 nations in 2011; of the global hectareage of soybeans, about 75% were RoundupReady®. Data are also presented for corn, cotton, and canola. For further information see <http://tinyurl.com/ISAAA-crop-biotech>.

■ ■ ■

Tonio Borg, health commissioner for the European Union (EU), reportedly intends to engage member states of the EU, including the UK, Germany and France, to see whether an agreement can be reached on permissible grounds for banning cultivation of genetically modified crops in individual countries (<http://tinyurl.com/EU-GM-crops>). In 2010, the European Commission proposed that individual states could base their decision whether or not to allow GM cultivation within their borders on reasons beyond environment and health concerns.

If the current proposal can be agreed upon, all GM crops would need a safety assessment by the European Food Safety Authority, followed by EU approval. Only after these two steps could member states allow, restrict, or ban their cultivation at the national level.

■ ■ ■

The GENetic Engineering Risk Atlas (GENERA) is a long-term project to catalog, examine, and communicate the findings of all peer-reviewed scientific publications that can be used to analyze the relative risks of genetically engineered (GE) plants. At its web site (<http://www.biofortified.org/genera/studies-for-genera/>) GENERA presents a list that currently has over 600 citations to papers, presentations, and reports related to the topic. There is an accompanying list of independently funded studies.

Another source for listings of research regarding GE plants is the Bibliography Database of the Center for Environmental Risk Assessment (<http://tinyurl.com/CERA-database>). ■

To confirm that hydrogen peroxide buildup was the problem and to simultaneously test whether its depletion might enhance alkane production, Shanklin and his team tried adding catalase, which metabolizes hydrogen peroxide to oxygen and water.

"When we added both enzymes, instead of the reaction turning over three times before stopping, it ran for more than 225 cycles," Shanklin said.

So the scientists decided to make a "bi-functional" enzyme by linking the two together. Shanklin explained, "We reasoned that with the ADO and catalase enzymes linked, as the hydrogen peroxide concentration near the enzyme increases, the catalase could convert it to oxygen, mitigating the inhibition and thereby keeping the reaction going."

Living cells often contain levels of hydrogen peroxide sufficient to cause ADO inhibition. So there was a question about whether the dual enzyme would increase alkane production under these natural conditions.

Results to date have been encouraging: In experiments in test tubes and pilot studies in bacteria, the bi-functional enzyme resulted in at least a fivefold increase in alkane production compared with ADO alone. And, in addition to removing hydrogen peroxide as an inhibitor of ADO, the combo enzyme actually helps drive the alkane-producing reaction by producing oxygen, one of the key components required for activity.

"This bi-functional enzyme simultaneously decreases the concentration of the inhibitor and increases the concentration of a needed reaction component by converting an inhibitor into a substrate," Shanklin said.

Now the scientists are working to incorporate the combo enzyme in algae or green plants.

"While ADO-containing bacteria convert sugar that we feed to them into alkanes, it would be much more efficient to produce alkanes in photosynthetic organisms using carbon dioxide and sunlight," Shanklin said.

The scientists also suggest that the general approach of strategically designing fusion enzymes to break down small molecule inhibitors could be used to improve the efficiency of a wide range of reactions. Defeating natural inhibition, a process they describe as "protection via inhibitor metabolism," would allow such bifunctional enzymes to function more efficiently than their natural counterparts.

This article is based on material provided by Brookhaven National Laboratory (<http://tinyurl.com/BNL-enzyme>).

Using biotech to trace fish and fish products

At a meeting sponsored by the Food and Agriculture Organization (FAO) of the United Nations, fisheries experts considered ways to improve aquatic genetic resources for food and agriculture (<http://tinyurl.com/FAO-fish-tracing>).

Opening the meeting, held in Bangkok, Thailand, in late January, FAO Deputy Regional Representative for Asia and the Pacific Man Ho So, said, "Applying genetic principles to aquatic species used in aquaculture is a recent phenomenon and the sector has not yet used available technologies to increase production to the extent that has been done by the crop, poultry and livestock sectors."

So added, "Traceability is a key aspect of certification and eco-labeling. Genetic markers provide an extremely sensitive means to identify samples of fish, such as frozen material, filets and early life history stages. . . ." He also pointed out, "Molecular genetic diagnoses of fish and fish products have already identified cases of mislabeling and consumer fraud, and have helped convict offending parties."

In applying biotechnology to capture fisheries, genetic stock identification is becoming a powerful tool to identify species, to understand fishery dynamics, to differentiate farmed from wild stocks and to help identify fishery management units.

Proposed labeling of GM foods in New Mexico rejected

The legislature of the US state of New Mexico in January considered requiring the labeling of bioengineered (GM) foods sold in the state (see *Inform* 24:IPR, 2013). Through what the *Santa Fe New Mexican* newspaper cited as “a procedural mistake” on February 1, however, the report was rejected. The New Mexico Environment Department (NMED) had reviewed the proposal and said, “Every food manufacturer in the world who sells/distributes food in New Mexico would have to modify current labeling for food items shipped to New Mexico.” (<http://tinyurl.com/NewMex-GMfoods>) The NMED also pointed out there was an implication that food containing genetically modified material in its ingredients for sale through restaurants would have to be labeled a genetically modified food. “The fiscal impact on the restaurant industry would be significant.”

Furthermore, the costs associated with labeling GM foods could put New Mexico food processors at a disadvantage when selling their products outside New Mexico.

Benefits of *Bt* corn exceed rootworm resistance

Research recently reported from the University of Illinois at Urbana-Champaign (UIUC; USA) has examined possible explanations for the increase in yields of *Bt* corn that exceed

expectations. For part of the explanation, Frederick Below and Jason Haegel looked at how *Bt* corn uses nitrogen present in the soil.

Nitrogen is important nutrient for corn. The two researchers hypothesized that *Bt* corn uses nitrogen differently than strains that are not rendered resistant. This would lead to effects on corn production.

The researchers conducted experiments over two years, growing resistant and nonresistant crops and applying five different amounts of nitrogen. The resistant corn had higher yields than the nonresistant crops (nearly 21 bushels/acre, or 1,300 kg/hectare) and more easily tolerated low nitrogen levels.

More efficient use of nitrogen in the soil would be especially beneficial in areas where nitrogen is lost through heavy precipitation or erosion. Additionally, *Bt* corn would fare better at current levels of nitrogen use in the United States.

Healthy roots and efficient nutrient use of *Bt* corn could lead to changes in management practices that would further increase production. Banded or placed fertility, a method by which a farmer can place fertilizer where the roots are likely to be, would be more effective when used on the robust root system. Additionally increasing plant populations could further increase yield.

In a statement released by the Crop Science Society of America, Below said, “When you have a higher population of plants, each individual plant has a smaller root system, so that made it difficult to increase plant population when you had insects chewing on the roots. With the *Bt* corn, though you can protect the root system and grow more plants” (<http://tinyurl.com/CropSci-UIUC>).

The original article, entitled “Transgenic corn rootworm protection increases grain yield and nitrogen use of maize,” appeared in *Crop Science* 53:585–594 (2013); doi:10.2135/cropsci2012.06.0348. ■

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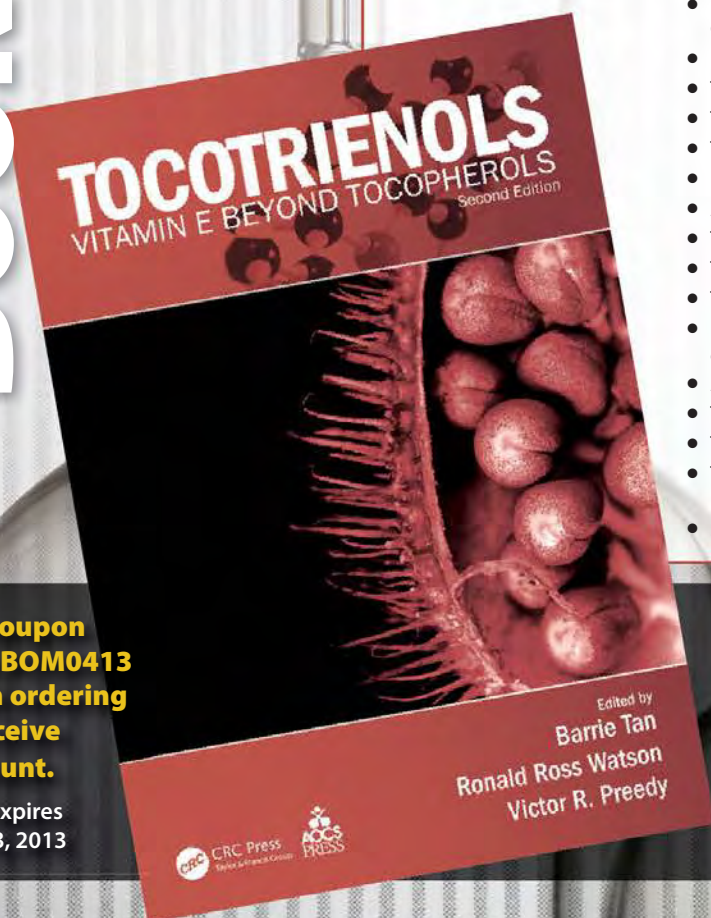


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Anglo-Dutch consumer products giant Unilever plans to have a recycle-and-recovery rate of 15% in its 14 biggest markets by the end of the decade, and conducted life-cycle analysis on 1,600 products as part of that effort. "Our goal is to follow the waste hierarchy set forth by the [US] Environmental Protection Agency," said Michael Hughes, a packaging executive at Unilever. "It is to reduce packaging, reuse packaging, and recycle packaging, and we have specific goals within each of those three targets." Hughes detailed Unilever's approach in an article in *Packaging World* online (<http://tinyurl.com/Unilever-Packaging>).

■ ■ ■

Procter & Gamble's single-dose laundry detergent—Tide Pods—was among the best product introductions in 2012, according to Deutsche Bank analyst Bill Schmitz, as reported by the *Cincinnati Business Courier* newspaper. The product, which was introduced in February 2012, achieved first-year sales of \$500 million. Schmitz was quoted as saying that 10.7% of US households tried Tide Pods, and 49% of those households became repeat customers.

■ ■ ■

Clariant AG (Muttens, Switzerland) sold three businesses to SK Capital Partners (New York, USA) for 502 million Swiss francs (\$550 million) at the end of 2012: textile chemicals, paper specialties, and emulsions. Also on the auction block during 2013 are Clariant's leather services and detergents and intermediates units, according to Clariant.

■ ■ ■

Evonik Goldschmidt Corp. (Hopewell, Virginia, USA) introduced a new trisiloxane surfactant at the annual meeting of the American Cleaning Institute in January 2013. Rewocare BDS 15 is a nonionic surfactant that was developed for rinse aids in automatic-dish and hard-surface cleaners. In further company news, Evonik said it is adding new capacity for nonsilicone surfactants in China, expected to be onstream by the end of 2013, and in Brazil in 2014. ■

SURFACTANTS, DETERGENTS, & PERSONAL CARE NEWS



Formulation tools and eco labels

The US Environmental Protection Agency (EPA) and several other organizations have introduced some useful tools for product formulators.

First, EPA developed an online list of more than 500 safer chelating agents, colorants, defoamers, enzymes, fragrances, oxidants, polymers, preservatives, solvents, surfactants, and other ingredients for cleaning products. Ingredients are grouped by their functional class and are rated in decreasing order of environmental safety, marked with either a green circle, a half-green circle, or a yellow triangle. See <http://www.epa.gov/dfe/saferingredients> for the Safer Chemical Ingredients List.

GreenBlue, a nonprofit organization working toward more sustainable products, provides an online list at <http://www.clean-ingredients.org> of about 430 preferred surfactants, solvents, chelating agents, and fragrances along with the companies that distribute the

chemicals. The group, which is based in Charlottesville, Virginia, USA, is expanding the categories to include all of those in the EPA list.

Finally, the American Cleaning Institute (ACI; a trade organization in Washington, DC) provides a list of more than 900 chemicals used by ACI member companies to formulate cleaning products.

Once a "green" product is formulated and ready for production, the issue of certification arises. A number of possibilities exist, including programs administered by the US government. The EPA runs the Design for the Environment (DfE) program. The DfE label is on more than 2,800 products—mostly cleaners—for institutional as well as some consumer applications. "Plans are to extend the DfE label to personal care products," according to *Chemical & Engineering News (C&EN)* magazine.

The US Department of Agriculture administered the BioPreferred program (www.biopreferred.gov), which certifies the percentage (by weight) of biobased content used in

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products and packaging. Roughly 900 products were certified before lack of funding caused the program to be suspended in 2013.

The EU Ecolabel, which was introduced in 1992, has been placed on more than 17,000 products, of which about 30% are household cleaning products, according to *C&EN*. "The label's administrators strive to harmonize assessment criteria with that used by national labeling programs such as the Nordic Swan and Germany's Blue Angel," the magazine report noted. More information is available at ec.europa.eu/environment/ecolabel.

Green Seal (www.greenseal.org), a nonprofit based in Washington, DC, calls itself the oldest life-cycle-based environmental sustainability label for "products, services, and companies." Founded in 1989, the organization certifies products in 11 categories such as paints and coatings, printing and writing papers, and institutional products. In January 2013, Green Seal announced the publication of two new standards to address the life cycle impacts of laundry care products.

GS-48, for household laundry care products, and GS-51, for products used in institutional and industrial settings, focus on product performance as well as overall environmental impact. To receive certification under either standard, laundry products cannot contain any components that are carcinogens, reproductive toxins, mutagens, neurotoxins/systemic toxins, endocrine disruptors, asthmagens, or respiratory or skin sensitizers.

GS-48 covers more than 17 categories of laundry care products including detergents, stain removers, bleaches, fabric care products such as fabric softeners and antistatic treatments, as well as antiwrinkle products and starch. "The standard is designed to make it easier for consumers to identify household laundry care products that meet the highest levels of sustainability available in the market today," said Green Seal in a statement.

GS-51 covers more than 20 categories of products for conventional laundry and dry cleaning, including detergents, prewash products, and spot removers; additives such as alkali boosters; and fabric care products such as antistatic treatment, starches, and fabric softeners.

Oleochemicals in 2012 and beyond

The use of oleochemicals in home and personal care products continued to grow in 2012 and is expected to grow in years to come, according to reports by several industry observers.

Frost and Sullivan, a market research firm based in London, estimated that the oleochemicals market in Europe will reach \$4.5 billion in revenue by 2018, growing at a rate of 2% per year. The firm expects North American revenues to reach \$3.91 billion by 2018, with growth coming mainly from edible applications and not soaps and detergents. Asia Pacific reportedly is the fastest growing market for oleochemicals with a growth rate of 8.2% (2013–2018), and the region accounted for over 60% of the global capacity in 2011. Europe was the second largest market in 2011 with an 18% share of production, according to the research firm. The global market for oleochemicals is expected to keep increasing as well, growing at 6% per year from 2013 to 2018.

Several companies are building plants in China and other Asian countries to take advantage of the growing market. Jiangsu Zhongdan, Noble Apex, Wuhan SFH Chemical, and Taiwan's Ho Tung

Chemical plan to start up a nonionic surfactant joint venture in 2013 to build an 80,000 metric ton (MT)/year fatty alcohol plant and a 120,000 MT/year ethoxylation plant, according to consultant Neil A. Burns. In similar news reported by Burns, US company Huntsman announced a 113,000 MT/year ethylene oxide (EO) plant expansion in Port Neches, Texas, bringing the plant's total capacity to 575,000 MT/year.

Last year also saw SABIC move into surfactants, beginning with construction of a 100,000 MT/year fatty alcohol plant in Al Jubail, Saudi Arabia. The plant will reportedly supply feedstock to SABIC's downstream ethoxylation plant, also in Al Jubail.

Methyl ester sulfonates (MES) from vegetable oil or animal fat feedstocks continue to gain market share, Burns noted. Jiangsu Haiqing Biotechnology announced the construction of a facility with 100,000 MT/year of MES capacity in the Jiangsu province of China, directed at the Chinese detergent market. When finished, the facility will be able to produce 200,000 MT/year of MES. This project comes on top of those already started or announced by Singapore's Wilmar, Malaysia's KLK, Japan's Lion, and US-based Sun Products Corp. (Sun's predecessor company, Huish, was one of the first companies outside of Japan to produce MES. See *inform* 12: 1152–1159, 2001.)

Burns also said that several new technologies will be released and promoted in 2013. Codexis (Redwood City, California, USA) and LS9 (South San Francisco, California) are developing fermentation technologies for sugar-based fatty alcohols. "According to Codexis, it will take about 3.7 MT of cellulosic sugar derived from 7.4 MT of biomass to produce one MT of detergent alcohol," said Burns on his blog at www.neilaburns.com.

All signs point to continued growth in the oleochemicals sector. Solazyme (also based in South San Francisco) announced in February 2013 that it has entered a \$20 million multi-year deal with Japan-based Mitsui & Co. Ltd. to develop a suite of triglyceride oils for use in the oleochemical industry. The agreement includes further development of Solazyme's high-myristic algal oil as well as other oils that the company said it is developing for the oleochemical and industrial sectors. End use applications may include high-performance polymer additives, aviation lubricants, and toiletry and household products.

For more on green chemicals in general and oleochemicals in particular, see the Green Blog by Doris de Guzman, formerly of *ICIS Chemicals Business* magazine (<http://tinyurl.com/Oleo-Update>).

Are hand sanitizers without alcohol effective?

Hand sanitizers are a go-to product in many developed countries as consumers scramble to avoid germs. But are new products produced without alcohol as effective at killing microbes as traditional formulations with alcohol?

A recent article in *The Wall Street Journal* (*WSJ*; <http://tinyurl.com/WSJ-Hands>) looks at three US companies that are using non-alcohol antimicrobial ingredients in their hand sanitizers. By adding quaternary ammonium compounds (quats) in place of alcohol, the companies say their products kill bacteria for up to six hours after application. (Quats, of course, have long been added to hard-surface household cleaners used to sanitize surfaces, as well as fabric softeners toilet cleaners, and other household products.)

Aside from in-house testing by manufacturers, few studies have been undertaken on the effectiveness of quats in hand sanitizers. The *WSJ* article quotes Jason Tetro, a microbiologist at the University of Ottawa in Ontario, Canada, as saying that it is true quats linger on the hands while alcohol evaporates in 10 or 20 seconds. "But in real-life use, quats in their dry state may not effectively kill bacteria as moisture is needed for their action," Tetro said, "or they could rub off or get covered by dust."

The issue of product safety was not addressed in the *WSJ* report. However, given that most hard-surface cleaners with quats used on food preparation surfaces call for the product to be rinsed off after disinfection and before food preparation, efficacy is not the only question facing the makers of alcohol-free hand sanitizers.

CEOs focus on sustainability, innovation

Sustainability and innovation topped the list of approaches that can help compensate for consistently weak consumer demand, according to three CEOs of consumer products companies. The three, speaking at a panel session during the American Cleaning Institute (ACI) annual conference in Orlando, Florida, USA, were Doug Baker, CEO of Ecolab; Don Knauss, CEO of Clorox Co.; and Steve Van Andel, chairman of Amway. They spoke on February 1, 2013.

Baker pointed to the strain that population increase will put on supplies of water and other natural resources, according to a report in

HAPPI magazine. Knauss suggested that four key trends will impact the global cleaning industry: health and wellness, sustainability; multicultural shift, and affordable convenience.

Knauss focused his remarks on sustainability, noting that, in the past five years, Clorox had introduced Green Works cleaners, acquired Burt's Bees (a line of "natural" personal care products), and revamped its Brita water filter business.

Amway Chairman Steve Van Andel noted that 90% of Amway's \$11.3 billion in sales in fiscal 2012 took place outside the United States.

OTHER ISSUES

The HAPPI coverage of the meeting also highlighted regulatory actions of note. According to the report, Jason Grev of Ecolab reviewed regulatory activities in 2012, noting that the US states of Maine, Washington, and Minnesota enacted chemical management programs. "This year [2013], Connecticut, Florida, Illinois, Maryland, Massachusetts, Michigan, Oregon, New York, and Vermont are all considering similar legislation," HAPPI said.

Sun Products' Brian Del Buono discussed the "widespread effort by federal and state governments and nongovernmental organizations to force companies to reveal confidential business information (CBI)." He added that industry has been proactive regarding CBI via the Consumer Voluntary Ingredient Communication Initiative, according to the *HAPPI* coverage.

ACI—formerly The Soap & Detergent Association—is a trade association based in Washington, DC. ■

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BOOK REVIEW

Lipids in Nanotechnology

Moghis U. Ahmad (ed.), AOCS Press,
2012, 294 pages
\$195 (members) or \$136 (nonmembers),
ISBN 978-0-9818936-7-9

Chris Dayton

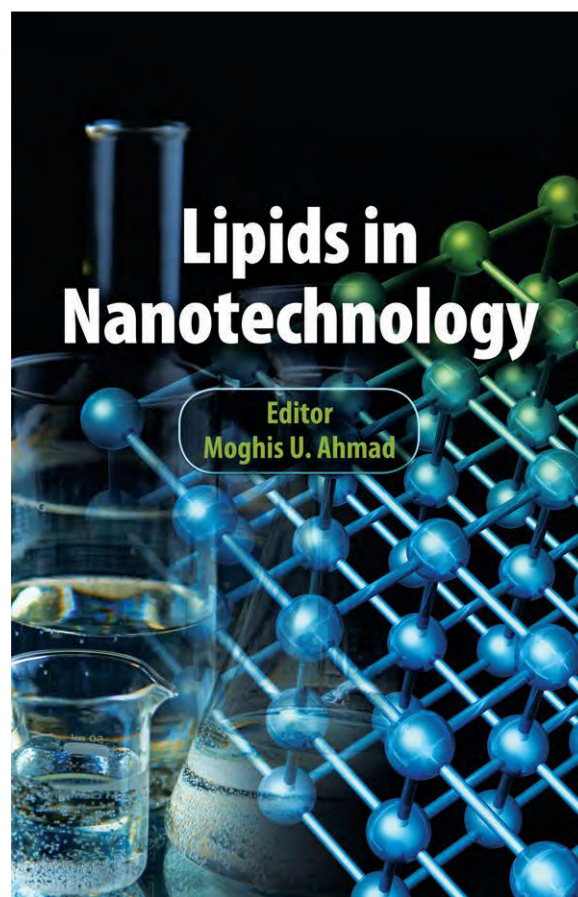
Lipids in Nanotechnology reviews lipid chemistry, emulsions, delivery systems, and the technologies to produce nanoemulsions and encapsulations. The introductory chapter discusses two main applications for nanotechnology in food applications: food additives and food packaging. No detailed information is provided for the food packaging application or other industrial applications outside of the food and drug arenas.

The first few chapters of the book focus on basic lipid chemistries and the utilization of phospholipids from milk and marine sources compared with traditional phospholipids obtained from soybeans. Unfortunately, a great deal of overlap in lipid chemistry discussions in the subsequent chapters of the book dilutes the transfer of new information to the reader.

Three excellent chapters are included on the formulation, engineering, and delivery of substrates via lipid-emulsified systems including lyotropic liquid crystals. The authors review traditional methods of producing emulsions utilizing colloid mills, high-pressure homogenization, microfluidizer, sonication, and extrusion as well as newer techniques such as microchannel arrays, solvent displacement, and solvent evaporation. The remaining chapters focus on pharmaceuticals and drug delivery systems via the various types of emulsions presented earlier.

The book is missing chapters or substantive discussions for applications in the cosmetic or skin care fields. Additionally, I would have expected a chapter on concerns involving: toxicity and safety of molecules and delivery systems utilizing the technology.

Lipids in Nanotechnology provides a good review of emulsion chemistries and technology with a focus on liposomes, vesicles, micelles, and mesophases and how they may be applied in the food and drug industries. The chapters are well illustrated and referenced. The book would benefit from uniform definitions and abbreviations of terms used throughout all of the chapters.



I do not see a second edition in the future, but would like to see a new book covering the larger fields of emulsions, surfactants, and their applications.

Chris Dayton has a degree in chemistry with 27+ years of industrial fats and oils research and development experience. He can be contacted at chris.dayton@bunge.com.

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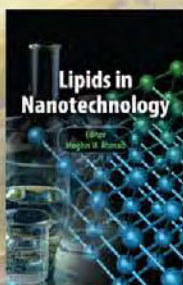
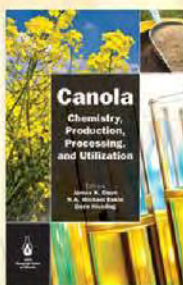
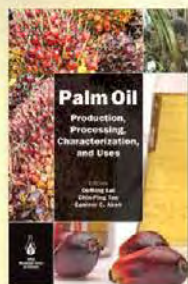
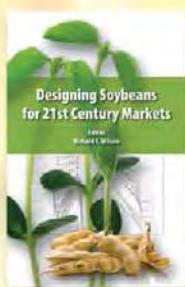
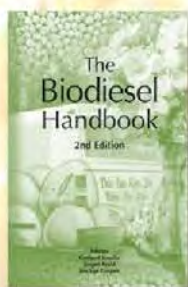


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PEOPLE NEWS

Kemper, Hill elected to lead AOCS

Timothy G. Kemper, Global Technology Director, Solvent Extraction, Desmet Ballestra Group, Marietta, Georgia, USA, was elected AOCS president in the 2013–2014 officer election.



Kemper

Steven Hill, Senior Director, Research and Nutrition, Kraft Foods, Northfield, Illinois, USA, was elected vice president. Under AOCS by-laws, the vice president is also president-elect and runs unopposed for president the following year.

W. Blake Hendrix, president and CEO, Desmet Ballestra North America, Marietta, Georgia, was elected to a two-year term as treasurer.

The new officers will be installed April 29, 2013, during the 104th AOCS Annual Meeting & Expo in Montréal, Québec, Canada.



Hill

Elected as AOCS Governing Board members-at-large were: **Douglas M. Bibus**, community faculty, Center for Spirituality and Healing, University of Minnesota, president, Lipid Technologies, LLC and director, Holman Center for Lipid Research, Austin, Minnesota, USA; **Carol J. Lammi-Keefe**, Alma Beth Clark professor and head, Human Nutrition and Food, School of Human Ecology and adjunct professor, Pennington Biomedical Research Center, Louisiana State

University, Baton Rouge, Louisiana, USA; **Michael A. Snow**, industrial director, Bunge North America, St. Louis, Missouri, USA; and **Manfred Trautmann**, vice president and general manager BU Emulsions, Detergents & Intermediates, Clariant International, Muttentz, Switzerland.

Continuing in their current member-at-large terms are **Richard H. Barton**, owner and president, N. Hunt Moore & Associates, Inc., Collierville, Tennessee, USA; **Rick Della Porta**, research fellow, Frito-Lay, Inc., Plano, Texas, USA; **Robert Moreau**, research chemist, US Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, Wyndmoor, Pennsylvania, USA; **Len Sidisky**, manager, Gas Separations Business Unit, Supelco (Division of Sigma Aldrich), Bellefonte, Pennsylvania, USA; and **Masaki Tsumadori**, research fellow, Global R&D, Kao Corp., Wakayama-shi, Japan.

Neil R. Widlak, director, Product Services and Development, ADM Cocoa, Milwaukee, Wisconsin, USA, continues as secretary.

Ballots were emailed or mailed to eligible members in December 2012. Ballots received prior to the deadline were counted at AOCS Headquarters on February 19, 2013.

Messing to receive 2013 Wolf Prize

Joachim Messing, director of the Waksman Institute of Microbiology at Rutgers University (New Brunswick, New Jersey, USA), will receive the 2013 Wolf Prize in Agriculture from the Wolf Foundation of Israel in May 2013. The Wolf Prize honors scientists whose “achievements are in the interest of mankind.” He will share the \$100,000 prize with **Jared Diamond** of the University of California, who is well known for his book *Guns, Germs and Steel* (1999).

A professor of molecular biology, Messing is being recognized for innovations in recombinant DNA cloning (i.e., genetic engineering, or GE) and for deciphering the genetic code of crop plants. According to Rutgers (<http://tinyurl.com/Messing-Wolf>), Messing became famous for developing a GE technique now widely used in laboratories to create plants that have produced disease-resistant crops considered vital to feeding the world’s population.

And instead of profiting from this discovery, Messing gave away this scientific blueprint, which has been used to decipher the genetic code of plants such as rice and corn. In the announcement of his award, he was quoted as saying, “I thought it was important to be generous and make this freely available without restrictions so biotechnological innovations could move forward.”

In his present work Messing is focusing on providing more sustainable, healthful, and productive sources of food for the world’s population and extracting biofuels for energy from plants like duckweed and drought-tolerant sorghum that grow either on water or on marginal land and do not compete with land used in food production.

Schroder to head Bunge Ltd.

Bunge Ltd. announced on February 7, 2013, that **Alberto Weisser** will retire as chief executive officer (CEO) effective June 1, 2013. The board of directors has appointed **Soren Schroder**, currently CEO of Bunge North America, to succeed Weisser as CEO of the company and expects Schroder to become a director before June 1. The board also appointed Weisser as executive chairman, serving until December 31, 2013.

According to **L. Patrick Lupo**, deputy chairman and lead independent director of Bunge Limited, “Under [Weisser’s] leadership, Bunge became a public company and grew from a regional operation to a global player, active in over 40 countries.” Weisser joined Bunge in 1993 as chief financial officer. He was appointed CEO in January 1999 and chairman in July 1999.

Investors.com (<http://tinyurl.com/Bunge-sugar>) reported that fourth-quarter earnings for Bunge fell 66%, whereas analysts had been expecting growth. Weisser associated the drop with negative effects in Bunge’s Brazilian ethanol operations and adverse effects in Brazil of weather on sugar cane yields. ■

IN MEMORIAM

RICHARD AUGUST RECK

On January 25, 2013, Richard August Reck died in Hinsdale, Illinois, USA at the age of 92. He joined AOCS in 1950, and was an emeritus member at the time of his death.

Reck was born in Chicago, Illinois, in 1920. He earned his bachelor's degree at the University of Illinois at Urbana-Champaign (USA), completed his master's degree at Indiana University (IU; Bloomington, USA), and also carried out doctoral work at IU.



During World War II, Reck carried out civilian scientific research on blood preservatives and malaria. His work was awarded a citation from General Lewis Hershey (director of the Selective Service System 1936–1970) for his contribution to the war effort.

Reck was hired in 1945 as a research chemist for Armour & Co., in Chicago, Illinois. He stayed with the company, subsequently known as Armak Co. and then Akzo Nobel, for 43 years. He served variously as assistant research director, plant manager, director of marketing, and director of strategic projects. He was awarded 139 patents. After he retired from Akzo Nobel, he worked as a private chemical consultant for eight years.

As an outgrowth of his work with Armour, Reck was an active participant in AOCS. Through the years he served on the Technical Committee, presented at the World Conference on Oleo Chemicals (now known as the Montreux meeting), traveled outside the United States to present papers internationally, presented at AOCS meetings, and led AOCS short courses.

He also published in the *Journal of the American Oil Chemists' Society* on topics such as the industrial uses of palm, palm kernel and coconut oils; nitrogen derivatives of long-chain fatty acids; and marketing of oleochemicals. He contributed a chapter on cationic surfactants to Volume 2 of *Kirk-Othmer's Encyclopedia of Chemical Technology* in 1978, and also published in the journal *Industrial and Engineering Chemistry*.

Besides AOCS, Reck was a member of the American Chemical Society and the chemistry honorary society Phil Lambda Upsilon.

Reck is survived by his wife of 67 years, Mary Ellen; his children Pamela and Richard Alan; and two grandsons.

GLENN FULLER

AOCS Emeritus Member Glenn Fuller died in California on September 15, 2012, at the age of 83. He lived much of his life in California, graduating with a bachelor's degree

in chemistry from Stanford University in 1950. He then earned an M.S. and a Ph.D. from the University of Illinois-Urbana Champaign (USA), working in the laboratory of Nelson Leonard, in 1951 and 1953, respectively.

He returned to California and went to work at Shell Development in Emeryville. When Shell dismantled its Emeryville location in 1964, Fuller decided to remain in the San Francisco Bay area, where he taught chemistry for a year at Mills College before moving to the US Department of Agriculture Western Regional Research Laboratory, where he served until he retired in 1993.

His initial contributions to the field of fats and oils included elucidating the chemistry underlying oxidation of polyunsaturated fats. He was an early advocate of high oleic acid-content oils as healthful alternatives to solid fats and of high-linoleate content oils for the nutritional benefits.

Fuller was instrumental in introducing high-oleic safflower oil as a beneficial oil and a successful crop for California.

His research on lipid oxidation led him into studies of castor oil, which contains 90% ricinoleate, a hydroxyl fatty acid. He led research identifying useful chemical products based on the hydroxyl group chemistry and was involved in research on detoxification and deallergenization of castor oilseed presscake.

He subsequently moved into research on the post-harvest chemistry of fruits and nuts. For example he introduced the idea of using fatty acid ethyl esters as coatings for grapes to accelerate drying of raisins, and he also conducted research on aflatoxin in nut crops. Later research included mechanisms of post-harvest physiology, especially cytokinins and gibberellins as well as an investigation of nitrogen fixation as it related to the chemistry, biochemistry, and physiology of mycorrhizal fungi.

Fuller served the American Chemical Society at the local and national level. He received the Distinguished Service Award of the ACS Agricultural and Food Chemistry Division in 1999 and was recognized as an ACS Fellow in March 2010.

During his membership in AOCS, Fuller was an active member. He presented a number of papers at AOCS meetings, and published in the *Journal of the American Oil Chemists' Society*. He was an active participant in the California section, and served as Technical Program Chairman of the 1986 annual meeting, held in Hawaii.

Fuller was awarded four patents and had over 70 publications, including *Agricultural Materials as Renewable Resources: Nonfood and Industrial Applications*; *Chemicals via Higher Plant Bioengineering*; *Ecology and Metabolism of Plant Lipids*; and *Functional Properties of Proteins and Lipid*, all published by the American Chemical Society.

Fuller's wife of 50 years, Verna, preceded him in death in 2005. He is survived by his daughter Nancy, son Eric, and two grandsons. ■



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PATENTS

Agent for skin external use containing salt of ascorbic acid derivative, method for stabilizing the agent for skin external use, and stabilizer

Kato, E., *et al.*, Showa Denko K.K., US8278350, October 2, 2012

An agent for skin external use of the invention contains a salt of higher fatty acid ester of ascorbic acid-2-phosphoric acid ester and a polyhydric alcohol. According to the present invention, occurrence of turbidity or precipitation with time can be prevented to enhance stability even when the agent for skin external use is prepared using a specific salt of higher fatty acid ester of ascorbic acid-2-phosphoric acid ester. Therefore, the present invention is useful for all agents for skin external use, particularly cosmetics.

Lipidated glycosaminoglycan particles and their use in drug and gene delivery for diagnosis and therapy

Margalit, R., and D. Peer, Tel Aviv University Future Technology Development L.P., US8277847, October 2, 2012

Lipidated glycosaminoglycan particles, prepared by reacting a glycosaminoglycan with at least one lipid to cross-link the carboxylic acid groups in the glycosaminoglycan with a primary amine in the lipid, are used to encapsulate drugs for use in the treatment of pathological conditions in an animal.

Wiping product having enhanced oil absorbency

Smith, M.C.H., *et al.*, Kimberly-Clark Worldwide, Inc., US8282776, October 9, 2012

Wiping products are disclosed containing an additive composition that enhances the cleaning properties of the product. The additive composition, for instance, comprises an aqueous dispersion containing an α -olefin polymer, an ethylene-carboxylic acid copolymer, or mixtures thereof. The α -olefin polymer may comprise an interpolymer of ethylene and octene, while the ethylene-carboxylic acid copolymer may comprise ethylene-acrylic acid copolymer. The additive composition may also contain a dispersing agent, such as a fatty acid. The additive composition increases various properties of the product including the ability of the product to quickly absorb oil. For instance, the additive composition can decrease the Oil Absorbency Rate by from about

20% to about 80% and can decrease the Reverse Osmosis Oil Wet Out time by from about 10% to about 80%.

Natural marine source phospholipids comprising polyunsaturated fatty acids and their applications

Sampalis, F., Neptune Technologies & Bioresources, Inc., US8278351, October 2, 2012

A phospholipid extract from a marine or aquatic biomass possesses therapeutic properties. The phospholipid extract comprises a variety of phospholipids, fatty acid, metals, and a novel flavonoid.

Process for the manufacture of diesel range hydrocarbons

Myllyoja, J., *et al.*, Neste Oil Oyj, US8278492, October 2, 2012

The invention relates to a process for the manufacture of diesel range hydrocarbons wherein a feed comprising fresh feed is hydrotreated in a hydrotreating step and isomerized in an isomerization step and the fresh feed contains at least 20% by weight triglyceride C_{12} - C_{16} fatty acids or C_{12} - C_{16} fatty acid esters or C_{12} - C_{16} fatty acids or combinations of thereof and feed contains 50–20,000 w-ppm sulfur calculated as elemental sulfur.

Electrolytic solution for electrolytic capacitor and electrolytic capacitor using the same

Takaoka, R., Panasonic Corp., US8279581, October 2, 2012

An electrolytic solution for an electrolytic capacitor includes a solvent and an electrolyte dissolved in the solvent. This electrolyte includes at least one of a carboxylic acid and a salt of the carboxylic acid. The carboxylic acid has a carboxyl group and at least one or more of substituents bonded to each terminal carbon of a straight main chain. The substituent bonded to the each terminal carbon of the main chain is hydrophilic, and/or a hydrophilic substituent is bonded to at least one of carbons other than the both terminal carbons of the main chain.

Microemulsions and their use for improving the biological efficacy of pesticides

Bohus, P., *et al.*, Lamberti S.p.A., US8282950, October 9, 2012

Homogenous and stable adjuvants in the form of microemulsions for use in agriculture containing: (a) a mixture of surfactants comprising (i) one or more anionic derivatives of an alkylpolyglycoside; (ii) one or more alkylpolyglycosides; (iii) one or more

AOCS MEETING WATCH

April 3–4, 2013. AOCS Oils and Fats World Market Update 2013, Ukrainian House, Kiev, Ukraine. <http://worldmarket.aocs.org>

April 28–May 1, 2013. 104th AOCS Annual Meeting & Expo, Palais des congrès de Montréal, Montréal, Québec, Canada. <http://AnnualMeeting.aocs.org>

July 16–17, 2013. AOCS Technical Services Workshop: Laboratory Methods, Des Moines, Iowa, USA. <http://www.aocs.org/labworkshop>

August 20–23, 2013. XV Latin American Congress and Exhibition on Fats and Oils, Sheraton Santiago Hotel and Convention Center, Santiago, Chile. <http://lacongress.aocs.org>

November 6–8, 2013. Australasian Section AOCS Biennial Meeting and Workshops, NOAH's on the Beach, Newcastle, New South Wales, Australia. <http://www.aocs.org/australasian>

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

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

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

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

anionic derivatives of a fatty alcohol; (b) one or more methyl esters of fatty acids deriving from the transesterification of vegetable oils, one or more vegetable oils, or mixture thereof; (c) one or more nonionic surfactants; (d) water.

Methods and systems for biomass conversion to carboxylic acids and alcohols

Holtzapfel, M.T., and R. Davison, Texas A&M University System, US8283141, October 9, 2012

The disclosure includes a method, process, and apparatus for the conversion of biomass to carboxylic acids and/or primary alcohols. The system may include a pretreatment/fermentation subsystem operable to produce a fermentation broth containing carboxylic acid salts from biomass, such as lignocellulosic biomass. The system may also include a dewatering subsystem operable to remove excess water from the fermentation broth to produce a concentrated product. The system may also include an acid springing subsystem operable to produce a mixed carboxylic acid product. The system may also include a hydrogenation subsystem operable to produce an alcohol mixture, such as a mixture containing primary alcohols.

Methods of operating this system or other systems to obtain a carboxylic acid or alcohol mixture are also provided.

Monitoring and manipulating cellular transmembrane potentials using nanostructures

Ignatius, M., *et al.*, Life Technologies Corp., US8290714, October 16, 2012

The use of nanostructures to monitor or modulate changes in cellular membrane potentials is disclosed. Nanoparticles having phospholipid coatings were found to display improved responses relative to nanoparticles having other coatings that do not promote localization or attraction to membranes.

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.



EXTRACTS & DISTILLATES

Development of rapid determination of 18 phthalate esters in edible vegetable oils by gas chromatography tandem mass spectrometry

Liu, Y., *et al.*, *J. Agric. Food Chem.* 61:1160–1164, 2013.

A simultaneous and fast determination of 18 phthalic acid esters (PAE) in edible vegetable oils was developed. After solvent extraction, the PAE in the oil sample were further cleaned up by solid-phase extraction. After concentration, the extract was directly injected into gas chromatography tandem mass spectrometry (GC–MS/MS) in positive-ion electron impact (EI) mode. Method quantification limits of 18 PAE were between 0.01 and 0.1 mg/kg. Quantitative recoveries ranging from 63.9 to 115.3% were obtained by analysis of spiked oil. The relative standard deviations were less than 15% ($n = 6$). The method could potentially overcome the interference from large amounts of lipids and pigment. It was applied to real sample and shown to be a rapid and reliable alternative for determination and confirmation of PAE in routine analysis.

Effect of the growth stage and cultivar on policosanols profiles of barley sprouts and their adenosine 5'-monophosphate-activated protein kinase activation

Seo, W.D., *et al.*, *J. Agric. Food Chem.* 61:1117–1123, 2013.

Adenosine 5'-monophosphate-activated protein kinase (AMPK) is an intracellular sensor that can regulate glucose levels within the cell. For this reason, it is well known to be a target for drugs against diabetes and obesity. AMPK was activated significantly by the hexane extract of barley sprouts. This AMPK activation emerges across the growth stages of the sprout, becoming most significant (3 times above the initial stages) 10 days after sprouting. After this time, the activation decreased between 13 and 20 days post-sprouting. Analysis of the hexane extracts by gas chromatography–mass spectrometry showed that the amounts of policosanols (PC, which are linear, primary aliphatic alcohols with 20–30 carbons) in the plant dramatically increased between 5 days

CONTINUED ON PAGE 246

JAOCS

JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY

Journal of the American Oil Chemists' Society (March)

- Effects of added phosphates on lipid stability during salt curing and rehydration of cod (*Gadus morhua*), Nguyen, M.V., S. Arason, G. Thorkelsson, A. Gudmundsdottir, K.A. Thorarinsdottir, B.N.Vu
- Analysis of CLA isomer distribution in nutritional supplements by single column silver-ion HPLC, Cossignani, L., L. Giua, G. Lombardi, M.S. Simonetti, P. Damiani, and F. Blasi
- Discrimination of origin of sesame oils using fatty acid and lignan profiles in combination with canonical discriminant analysis, Jeon, H., I.-H. Kim, C. Lee, H.-D. Choi, B.H. Kim, and C.C. Akoh
- Simplex-centroid mixture design applied to the aqueous enzymatic extraction of fatty acid-balanced oil from mixed seeds, Li, Y., Y. Zhang, M. Wang, L. Jiang, and X. Sui
- Synthesis of wax esters from crude fish fat by lipase of *Burkholderia sp.* EQ3 and commercial lipases, Ungcharoenwivat, P. and A. H-Kittikun
- A simple enzymatic approach for selective acetylation of phosphatidylethanolamine, Karuna, .S.L., V. Vandana, P. Vijaya Lakshmi, and R.B.N. Prasad
- Lipase-catalyzed synthesis of medium-long-medium type structured lipids using tricaprylin and trilinolenin as substrate models, Bai, S., S. Aziz, M. Khodadadi, C. Bou Mitri, R. St-Louis, and S. Kermasha
- Optimization of reaction conditions in the enzymatic interesterification of soybean oil and fully hydrogenated soybean oil to produce plastic fats, Pacheco, C., C. Palla, G.H. Crapeste, and M.E. Carrín
- Acidification of alperujo paste prevents off-odors during their storage in open air, Ruiz-Méndez, M.V., C. Romero, E. Medina, A. García, A. de Castro, and M. Brenes
- The effect of germination on phenolic compounds and antioxidant activity of pulses, Gharachorloo, M., B. Ghiassi Tarzi, and M. Baharinia
- Accumulation of 5-hydroxymethylfurfural in oil during frying of model dough, Göncüoğlu, N., and V. Gökmen
- Flaxseed cyclolinopeptides: analysis and storage stability, Aladedunye, F., E. Sosinska, and R. Przybylski
- Contents of carotenoids, tocopherols and sterols in *Acacia cyanophylla* seed oils, Nasri, N., W. Elfalleh, N. Tlili, L. Martine, O. Berdeaux, C. Salles, S. Triki, and A. Khaldi
- Chemo-enzymatic synthesis and antimicrobial evaluation of alkyloxy propanol amine-based cationic ether lipids, Reddy, J.R.C., B.V.S.K. Rao, M.S.L. Karuna, K.P. Kumar, U.S.N. Murthy, and R.B.N. Prasad
- Study of the properties of thermoset materials derived from epoxidized soybean oil and protein fillers, Fombuena, V., L. Sánchez-Nácher, M.D. Samper, D. Juárez, and R. Balart

- Extraction and characterization of seed oil from naturally grown Chinese tallow trees, Yang, X.-Q., H. Pan, T. Zeng, T.F. Shupe, and C.-Y Hse



Journal of Surfactants and Detergents (March)

- Use of furandicarboxylic acid and its decyl ester as additives in the Fischer's glycosylation of decanol by D-glucose: physicochemical properties of the surfactant compositions obtained, van Es, D.S., S. Marinkovic, X. Odube, and B. Estrine
- Synthesis and characterization of glucosamide surfactant, Han F., Y. Deng, P. Wang, J. Song, Y. Zhou, and B. Xu
- Synthesis and evaluation of nonionic polymeric surfactants based on acrylated polyethylene glycol, Monem Eissa, A.-E., M. El Hefnawy, and M. Deef-Allah
- Microbial oxidation of medium chain fatty alcohol in the synthesis of sophorolipids by *Candida bombicola* and its physicochemical characterization, Pulate, V.D., S. Bhagwat, and A. Prabhune
- Synthesis and surface activities of novel succinic acid monofluoroalkyl sulfonate surfactants, Zhang, L., J. Shi, A. Xu, B. Geng, and S. Zhang
- Synthesis and surface-active properties of *F*-alkylated polar loops, Khalfallah, A., B. Boughariou, and A. Hedhli
- Application of green commercial surfactant in preparing purely acrylic latex via semi-continuous seeded emulsion polymerization, Chen, L.
- Behavior of cetyltrimethylammonium bromide, *tert*-octylphenol (9.5 EO) ethoxylate and ethanol mixtures at the water-air interface, Bielawska, M., B. Jańczuk, and A. Zdziennicka
- Real time study of detergent concentration influence on solid fatty acid film removal processes, Favrat, O., J. Gavoille, L. Aleya, and G. Monteil
- Synthesis, surface properties, synergism parameter and inhibitive performance of novel cationic Gemini surfactant on carbon steel corrosion in 1 M HCl solution, Hegazy, M.A., and A.S. El-Tabei
- Preparation of some eco-friendly corrosion inhibitors having antibacterial activity from sea food waste, Hussein, M.H.M., M.F. El-Hady, H.A.H. Shehata, M.A. Hegazy, and H.H.H. Hefni
- Surface and biological activity of some prepared iminium surfactants based on Schiff bases, Aiad, I., M.M. EL-Sukkary, A. El-Deeb, M.Y. El-Awady, and S.M. Shaban

- Spectroscopic investigations of physicochemical interactions on mild steel in an acidic medium by environmentally friendly green inhibitors, Sakunthala, P., S.S. Vivekananthan, M. Gopiraman, N. Sulochana, and A.R. Vincent
- Spectrophotometric determination of benzalkonium bromide in pharmaceutical samples with alizarin green, Liu, Y., H. Wu, and W. Ma
- Estimation of micellization parameters of SDS in the presence of some electrolytes for emulsion polymerization systems, Naderi Miqan, S., F.F. Tabrizi, H. Abedini, and H.A. Kashi
- Synthesis and aqueous solution properties of α -dimethyl oxamino dodecyl acid, Qi, L.Y., H. Bao, Y. Fang, and Y. Hu

Lipids

Lipids (March)

- Porcine G_{α}/G_{β} switch gene 2 (*GOS2*) expression is regulated during adipogenesis and short-term *in-vivo* nutritional interventions, Ahn, J., S.-A. Oh, Y. Suh, S.J. Moeller, and K. Lee
- Hepatic isoprenoid metabolism in a rat model of Smith-Lemli-Opitz syndrome, Keller, R.K., D.A. Mitchell, C.C. Goulah, and S.J. Fliesler
- Membrane cholesterol affects stimulus-activity coupling in type 1, but not type 2, CCK receptors: use of cell lines with elevated cholesterol, Harikumar, K.G., R.M. Potter, A. Patil, V. Echeveste, and L.J. Miller
- Sphingolipid content in the human uterus and pair-matched uterine leiomyomas remains constant, Paweł, K., A. Chabowski, and J. Górski
- Lysophosphatidic acid produced by hen egg white lysophospholipase D induces vascular development on extra-embryonic membranes, Morishige, J., Y. Uto, H. Hori, K. Satouchi, T. Yoshiomoto, and A. Tokumura
- Biosynthesis of long-chain polyunsaturated fatty acids in the marine ichthyosporean *Sphaeroforma arctica*, Vrinten, P., I. Mavraganis, X Qiu, and T. Senger
- The use of lipids and fatty acids to measure the trophic plasticity of the coral *Stylophora subseriata*, Seemann, J., Y. Sawall, H. Auel, and C. Richter
- Measurements of diacylglycerols in skeletal muscle by atmospheric pressure chemical ionization mass spectrometry, Lee, S.-Y., J.R. Kim, M.-Y. Ha, S.-M. Shim, and T.-S. Park
- High-throughput analysis of algal crude oils using high-resolution mass spectrometry, Lee, Y.J., R.C. Leverence, E.A. Smith, J.S. Valenstein, K. Kandel, and B.G. Trewyn
- An improved high-throughput lipid extraction method for the analysis of human brain lipids, Abbott, S.K., A.M. Jenner, T.W. Mitchell, S.H.J. Brown, G.M. Halliday, and B. Garner ■

(109.7 mg/100 g) and 10 days (343.7 mg/100 g) post-sprouting and then levels fell, reaching 76.4 mg/100 g at 20 days post-sprouting. This trend is consistent with PC being the active ingredient in the barley plants. We validate this by showing that hexacosanol is an activator of AMPK. The richest cultivar for PC was found to be the Daejin cultivar. Cultivars had a significant effect on the total PC content (113.2–183.5 mg/100 g) within the plant up to 5 days post-sprouting. However, this dependence upon the cultivar was not so apparent at peak stages of PC production (10 days post-sprouting). The most abundant PC in barley sprout, hexacosanol, contributed 62–80% of the total PC content at every stage. These results are valuable to determine the optimal times of harvest to obtain the highest yield of PC.

Stability and bioaccessibility of β -carotene in nanoemulsions stabilized by modified starches

Liang, R., *et al.*, *J. Agric. Food Chem.* 61:1249–1257, 2013.

Oil-in-water nanoemulsions stabilized by food-grade biopolymer emulsifiers (modified starches) were fabricated using high-pressure homogenization in an effort to improve the stability and bioaccessibility of β -carotene. Physicochemical and biological properties of β -carotene nanoemulsions were investigated considering the particle size, β -carotene retention, and *in vitro* digestion. During 30 days of storage at different conditions, the mean diameters of the emulsion systems were increased by 30–85%. The retention of β -carotene in nanoemulsions was significantly higher compared to that of the β -carotene dispersed in bulk oil. After *in vitro* digestion, the bioaccessibility of β -carotene was increased from 3.1% to 35.6% through nanoencapsulation. The results also indicated that modified starch with high dispersed molecular density led to a higher retention but lower bioaccessibility of β -carotene in nanoemulsions. This could be due to the thick and dense interfacial layer around the oil droplets. This result provides useful information for developing protection and delivery systems for carotenoids.

Vitamin K and the nervous system: an overview of its actions

Ferland, G., *Adv. Nutr.* 3:204–212, 2012

The role of vitamin K in the nervous system has been somewhat neglected compared with other physiological systems despite the fact that this nutrient was identified some 40 years ago as essential for the synthesis of sphingolipids. Present in high concentrations in brain cell membranes, sphingolipids are now known to possess important cell signaling functions in addition to their structural role. In the past 20 years, additional support for vitamin K functions in the nervous system has come from the discovery and characterization of vitamin K-dependent proteins that are now known to play key roles in the central and peripheral nervous systems. Notably, protein Gas6 has been shown to be actively involved in cell survival, chemotaxis, mitogenesis, and cell growth of neurons and glial cells. Although limited in number, studies focusing on the relationship between vitamin K nutritional status and behavior and cognition

have also become available, pointing to diet and certain drug treatments (i.e., warfarin derivatives) as potential modulators of the action of vitamin K in the nervous system. This review presents an overview of the research that first identified vitamin K as an important nutrient for the nervous system and summarizes recent findings that support this notion.

Enzymatic modification of lipids for *trans*-free margarine

Pande, G., and C.C. Akoh, *Lipid Technol.* 25:31–33, 2013.

Several studies have shown that high intake of *trans* fat is associated with increased risk of chronic diseases especially cardiovascular disease. The levels of *trans* fat in the American diet is of concern. Structured lipid is a lipid that has been modified from its native form either by biocatalysts or chemical catalysts. These modifications result in change in the triacylglycerol molecular species, which further alters the physicochemical properties such as melting properties, solid fat content, and oxidative stability of lipids. The process allows the production of a wide range of functional and nutritional lipids that may meet consumer needs. Enzymatically synthesized structured lipids can be used as a substitute for conventional lipids in *trans*-free margarine formulations. This article gives an overview of *trans* fatty acids and enzymatic modification of lipids for producing *trans*-free margarine.

Antitumor effect of oleic acid, mechanisms of action, a review

Carrillo, C., *et al.*, *Nutr. Hosp.* 27:1860–1865, 2012

The beneficial effects of oleic acid in cancer processes can no longer be doubted, but little is known about the mechanisms of action behind this phenomenon. The aim of the present review is to clarify whether oleic acid has an effect on important mechanisms related to the carcinogenic processes. We searched electronic databases, and bibliographies of selected articles were inspected for further reference. We focused our research on two cellular transformations characterizing cancer development: proliferation and cell death or apoptosis. Numerous studies have reported an inhibition in cell proliferation induced by oleic acid in different tumor cell lines. Herein, oleic acid could suppress the over-expression of HER2 (erbB-2), a well-characterized oncogene that plays a key role in the etiology, invasive progression, and metastasis in several human cancers. In addition, oleic acid could play a role in intracellular calcium signaling pathways linked to the proliferation event. Regarding cell death, oleic acid has been shown to induce apoptosis in carcinoma cells. The mechanisms behind the apoptotic event induced by oleic acid could be related to an increase in intracellular ROS [reactive oxygen species] production or caspase 3 activity. Several unsaturated fatty acids have been reported to induce apoptosis through a release of calcium from intracellular stores. However, evidence regarding such a role in oleic acid is lacking. Oleic acid plays a role in the activation of different intracellular pathways involved in carcinoma cell development. Such a role could be the root of its anti-tumoral effects reported in clinical studies.

Lipid oxidation products of heated soybeans as a possible cause of protection from ruminal biohydrogenation

Kaleem, M., et al., *Eur. J. Lipid Sci. Technol.* 115:161–169, 2013

Heating oilseeds has been shown to improve the milk fatty acid profile when given to dairy cows, compared to raw oilseeds. However, results from published studies are conflicting. The conditions of heating and storage of the oilseeds could be responsible for these differences, probably partly through their effects on lipid oxidation, the products of which could act on ruminal biohydrogenation (BH). Thus, 15 different treatments were applied to ground soybeans: three levels of heating (no heating, 30 min at 110°C or 150°C) × 5 ambient storage durations (0, 1, 2, 4, or 6 months). Soybeans were incubated *in vitro* with ruminal fluid for 6 h. Triacylglycerol (TAG) polymers, hydroperoxides and hydroxyacids (HOA), aldehydes, and fatty acids were assayed in soybeans and ruminal culture. No TAG polymer was detected in any treatment. Soybeans stored for a long time had a high content of HOA, whereas those heated at 150°C, whatever the storage duration, had high aldehyde contents. The percentage disappearance of *cis*-9,*cis*-12 18:2 and *cis*-9,*cis*-12,*cis*-15 18:3 in incubates decreased significantly in cultures with heated soybeans, especially at 150°C, suggesting that this partial protection of polyunsaturated fatty acids from BH was at least in part linked to the aldehyde content of the heated soybeans.

A review of analytical methods measuring lipid oxidation status in foods: a challenging task

Barriuso, B., et al., *Eur. Food Res. Technol.* 236:1–15, 2013

Lipid oxidation analysis in food samples is a relevant topic since the compounds generated in the process are related to undesirable sensory and biological effects. Proper measurement of lipid oxidation remains a challenging task since the process is complex and depends on the type of lipid substrate, the oxidation agents, and the environmental factors. A great variety of methodologies have been developed and implemented so far, for determining both primary and secondary oxidation products. Most common methods and classical procedures are described, including peroxide value, thiobarbituric acid-reactive substance analysis, and chromatography. Some other methodologies such as chemiluminescence, fluorescence emission, Raman spectroscopy, infrared spectroscopy, or magnetic resonance provide interesting and promising results. Therefore, attention should be paid to these alternative techniques in the area of food lipid oxidation analysis. ■

More Extracts & Distillates can be found in the supplement to the digital edition of Inform. Log in to read the April 2013 issue at aocs.org/login.



STATISTICAL ANALYSIS FROM MINTEC

Peanut oil prices have fallen since mid-2012 owing to a very good US peanut crop of 2.3 million metric tons (MMT) [shelled] estimated for 2012/13. This is an increase of 85% compare to the country's drought-stricken 2011/12 crop (Fig. 1). World peanut production is expected to rise 3% to 27.4 MMT in 2012/13 while peanut oil production is forecast to rise to 5 MMT, up 4% year-on-year.

The soybean oil premium over palm oil has increased over the past year as palm oil prices have fallen while soybean oil prices have remained relatively flat (Fig. 2). World palm oil production for 2012/13 is forecast to reach 53.3 MMT, up 5% year-on-year. This, combined with already high stock levels, has led to significant price reductions. World soybean ending stocks are estimated to have declined by more than 20% year-on-year in 2011/12 as drought affected crops in the United States and South America. However, production is expected to recover in 2012/13, with the most recent forecasts suggesting production will rise 13% to 269 MMT.

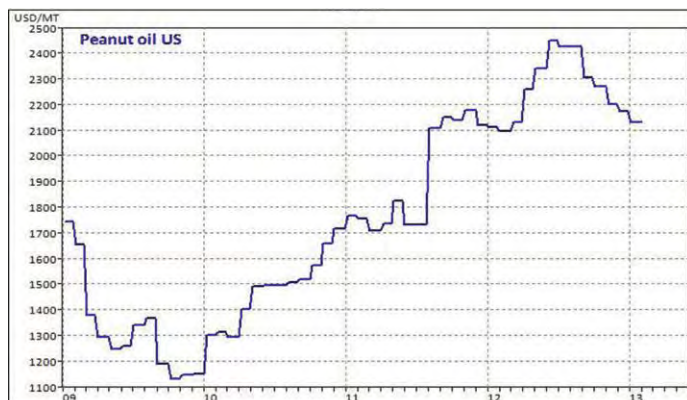


FIG. 1. US peanut oil prices, 2009–2013. USD/MT, US dollars/metric ton.

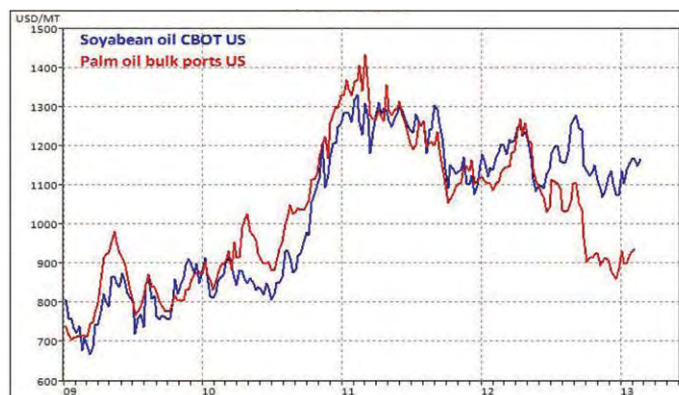


FIG. 2. Prices for soybean oil [Chicago Board of Trade (United States)] and palm oil bulk (at US ports) for 2009–2013. USD/MT, US dollars/metric ton.

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AOCS 2013 award recipients announced

AOCS awards have a rich history of 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 104th AOCS Annual Meeting & Expo to be held April 28–May 1, 2013, in Montréal, Québec, Canada. The following list includes awards for whom recipients had been named by the deadline for this issue of *Inform*.



Ohlson

SOCIETY AWARDS Award of Merit

RAGNAR OHLSON, retired, Sweden
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.



Dumelin



Howell



Mossoba



Orthoefer



Szuhaj

AOCS Fellows

ERICH E. DUMELIN, retired, Switzerland

STEVEN (STEVE) A. HOWELL, Marc-IV Consulting Inc. and National Biodiesel Board (NBB), USA

MAGDI M. MOSSOBA, US Food and Drug Administration, USA

FRANK T. ORTHOEFER, Consultant, USA

BERNARD (BERNIE) F. SZUHAI, Consultant, USA

A plaque and Fellow membership status

Fellows are selected for exceptional recognition for achievements in science as well as for unusually important service to AOCS or to their profession.

Corporate Achievement Award

Ladang Tai Tak (Malaysia) and partners: **CSIRO** (Australia) and **IHMS Sdn Bnd** (Malaysia)

A plaque and certificates to the partners

The Award recognizes industry achievement for an outstanding process, product, or contribution that has made the greatest impact on its industry segment. The joint nomination of Ladang Tai Tak, Malaysia and partners CSIRO, Australia and IHMS, Malaysia is in recognition of the application of ultrasound technology to significantly reduce oil loss and waste streams in the milling of palm oil leading to improved commercial returns for industry and environmental benefits.



Garti

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.

SCIENTIFIC AWARDS Supelco/Nicholas Pelick– AOCS Research Award

NISSIM GARTI, Hebrew University of Jerusalem, Israel

\$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

ALEJANDRO G. MARANGONI, University of Guelph, Canada

\$4,000 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.



Meier

AOCS Young Scientist Research Award

MICHAEL (MIKE) A.R. MEIER, Karlsruhe Institute of Technology (KIT), Germany

\$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 dis-

ciplines represented by AOCS Divisions. Vijay K.S. Shukla and the International Food Science Centre A/S of Denmark sponsor the award.



Eller

DIVISION/SECTION AWARDS Analytical Division

Herbert J. Dutton Award

FRED J. ELLER, US Department of Agriculture, USA

\$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.



Ermacora



Sun

Student Awards

ALESSIA ERMACORA, Technische Universität Berlin, Germany

CHENXING SUN, University of Alberta, Canada

\$250 honorarium, \$500 travel stipend, and a certificate

Biotechnology Division Student Awards

1st place—**YUNING GAO**, University of Alberta, Canada

\$300 honorarium and a certificate

2nd place—**WORAWAN PANPIPAT**, Aarhus University, Denmark

\$200 honorarium and a certificate

3rd place—**EBENEZER A. IFEDUBA**, University of Georgia, USA

\$100 honorarium and a certificate



Forster

Edible Applications and Technology Division Achievement Award

DAVID G. FORSTER, retired, Canada

\$500 honorarium and a plaque

The award recognizes and honors those individuals who have significant lifetime and meritorious achievements in edible oils. Through their involvement they have made significant contributions to the knowledge, technology, and history of the industry.

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Wang

Timothy L. Mounts Award

TONG (TONI) WANG, Iowa State University, USA

\$500 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.



Ryckebosch

Student Award

ELINE RYCKEBOSCH, KU Leuven, Belgium

\$500 travel stipend and a certificate

The award is sponsored by Archer Daniels Midland Company.



Emken

Health and Nutrition Division Ralph Holman Lifetime Achievement Award

EDWARD EMKEN, Consultant, USA

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

The award recognizes outstanding performance and meritorious contributions to the health and nutrition interest area. The award is named after Ralph Holman in recognition of his lifetime service to the study of essential fatty acids.



Kitson

Student Award

ALEX P. KITSON, University of Waterloo, Canada

\$500 honorarium and a certificate

Industrial Oil Products Division ACI/NBB Glycerine Innovation Award

B. L. A. PRABHAVATHI DEVI, Indian Institute of Chemical Technology, India

\$5,000 honorarium and a plaque

The ACI/NBB Glycerine Innovation Award, sponsored by the American Cleaning Institute and the National Biodiesel Board, recognizes achieve-



Devi



Tabtabaei

ments in research relating to new applications for glycerine, particularly those with commercial viability.

Student Award

SOLMAZ TABTABAEI, University of Toronto, Canada

\$500 travel stipend and a certificate

Lipid Oxidation and Quality Division Edwin Frankel Best Paper Award

A Kinetic Model Describing Antioxidation and Prooxidation of β -Carotene in the Presence of α -Tocopherol and Ascorbic Acid (*Journal of the American Oil Chemists' Society* 89:815–824, 2012)

NAOMI SHIBASAKI-KITAKAWA, MASAHICO MURAKAMI, MASAKI KUBO, and TOSHIKUNI YONEMOTO

Tohoku University, Japan

Plaque and certificates for all authors

The award recognizes the best paper relating to lipid oxidation or lipid quality published during the previous year by AOCS Press. Kalsec Inc. sponsors the award.

Phospholipid Division Best Paper Award

Ultrafiltration of Whey Buttermilk to Obtain a Phospholipid Concentrate (*International Dairy Journal* 30:39–44, 2012)

GERD KONRAD, THOMAS KLEINSCHMIDT, and CLAUDIA LORENZ

Anhalt University, Germany

Plaque and certificates for all authors

The award recognizes an outstanding paper related to phospholipids published during the previous year. International Lecithin & Phospholipid Society (ILPS) sponsors the award.



Mag

Processing Division Distinguished Service Award

THEODORE (TED) K. MAG, retired, Canada

\$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.

Student Awards

MEIZHEN XIE, Oklahoma State University, USA

\$1,000 honorarium and a certificate



Xie

Protein and Co-Products Division ADM Best Paper Award

Chemistry/Nutrition

A Dynamic Light Scattering Study on the Complex Assembly of Glycinin Soy Globulin in Aqueous Solutions (*Journal of the American Oil Chemists' Society* 89:1183–1191, 2012)

VÍCTOR M. PIZONES RUIZ-HERNESTROSA^{1,2}, MARÍA J. MARTINEZ¹, JUAN M.R. PATINO², and ANA M.R. PILOSO¹

¹Universidad de Buenos Aires, Argentina, and ²Universidad de Sevilla, Spain

Engineering/Technology

Ethanol Production from Soybean Fiber, a Co-product of Aqueous Oil Extraction, Using a Soaking in Aqueous Ammonia Pretreatment (*Journal of the American Oil Chemists' Society* 89:1345–1353, 2012)

BISHNU KARKI, DEVIN MAURER, SHANNON BOX, TAE HYUN KIM, and STEPHANIE JUNG

Iowa State University, 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.



Raney

Surfactants and Detergents Division Samuel Rosen Memorial Award

KIRK H. RANEY, Shell, 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.

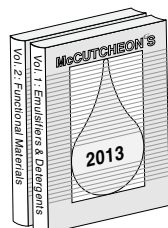
American Cleaning Institute (ACI) Distinguished Paper

On the Characteristic Curvature of Alkyl-Polypropylene Oxide Sulfate Extended Surfactants (*Journal of Surfactants and Detergents* 15:157–165, 2012)

CHARLES E. HAMMOND¹ and EDGAR J. ACOSTA²

¹Sasol North America Inc, USA, and ²University of Toronto, Canada

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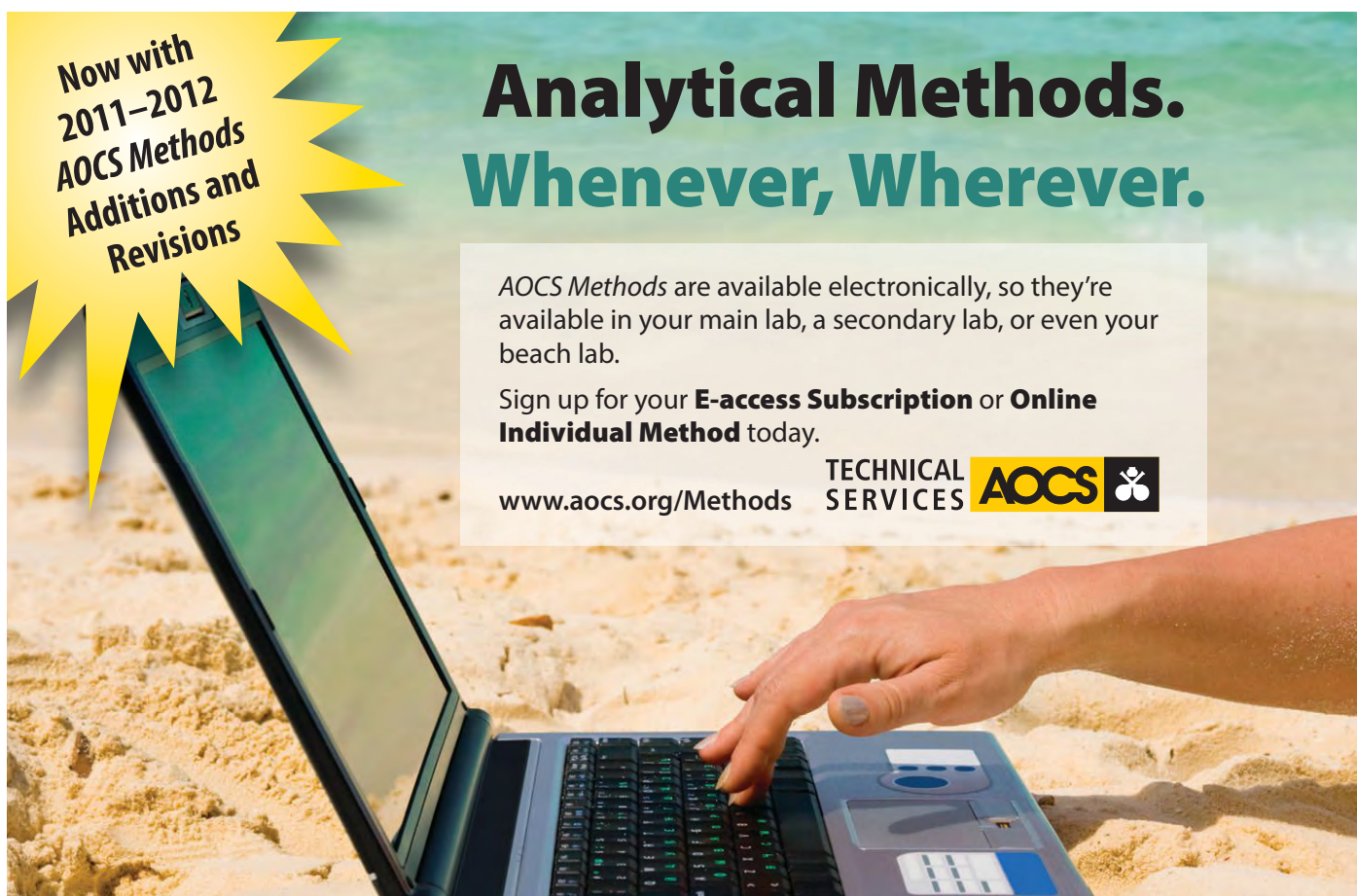
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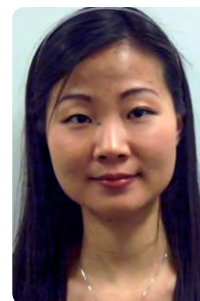
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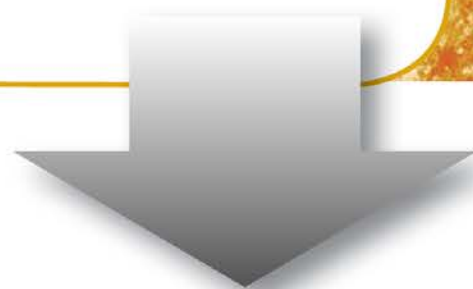
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This hillside in the Central Plateau reveals the typical deforestation experts say has felled 98 percent of Haiti's tree cover.



What does it take to start a biodiesel industry?

- Establishing a new industry in a developing country requires the entrepreneur to accept conditions as they are, and to innovate with whatever is available.
- In a developing nation, job creation can be more important than profits.
- In describing efforts to establish a basis for a biodiesel industry in Haiti, consultant Kathleen Robbins asks the provocative question, “How do you create a vibrant economy where there isn’t one?”

Marguerite Torrey

If you wanted to start a business making biodiesel in a developing nation like Haiti, how would you go about it? What would you need to get it off the ground?

Kathleen Robbins found that—no matter how improbable the connection may seem at first—she needed to add “develop biodiesel” to the list of things to do for a project bringing modern communications technology in the form of cell (mobile) phones to Haiti.

CELL PHONES IN HAITI

Two US-owned companies introduced cell phones in Haiti in the mid-1990s, but their uptake was fairly slow, until the Irish cell phone

company Digicel entered the market in 2006. Since then, cellular telephone services have expanded rapidly owing, in part, to the introduction of low-cost phones complying with GSM (Groupe Spécial Mobile) digital systems (<http://tinyurl.com/cell-phones-Haiti>).

However, conditions within Haiti—for example, the lack of a reliable electric power grid to charge these phones—initially hampered their adoption. Chinese-made solar-powered chargers for cell phones became available in Haiti in 2007 at a cost of \$10 each compared with Haitian-made chargers at \$17.50. In light of the poverty in the country (see Sidebar, Facts about Haiti) most people purchased the cheaper models. By the time they discovered how poorly made they were, the Haitian manufacturer had gone out of business.

OPPORTUNITIES FOR JATROPHA

The solution to the problem of how to charge these cell phones in a way that Haitians can afford lay in using what is available in Haiti as opposed to what works somewhere else.

One possible solution happened to be growing right on the island. *Jatropha curcas* (gwo medisyen, or “big medicine,” in Haitian Creole) is a shrubby tree that is native to Haiti. Its seeds are known for their high oil content, and efforts are already under way outside of Haiti to use jatropha oil to make biodiesel and aviation fuel. So, why couldn’t Haitians use this native plant to make biodiesel that could then be used to fuel generators to charge the cell phones—and by extension to stimulate the Haitian economy? Furthermore, doing so would encourage the planting of more perennial jatropha trees, which could alleviate two other problems that plague the country: deforestation and erosion (see Sidebar, Facts about Haiti).

Robbins points out that since jatropha is a native plant, it is already adapted to the boom-or-bust rainfall regime of Haiti. It likes a warm climate, and cannot grow where frost occurs.

During the dry season in Haiti, jatropha plants shed their leaves and remain dormant until rain comes. Then, within three months, the plants produce leaves, flowers, and finally seeds. Under these conditions jatropha can produce at least two crops a year. If irrigation is available, it may even be possible to obtain three crops a year, as research in the Dominican Republic, Haiti’s neighbor on the island of Hispaniola, has already demonstrated.

Jatropha seeds can contain as much as 35% oil (the University of Illinois Sustainable Technology Center tested one sample having a 49.9% oil content), which in rural Haiti can be used to fuel lamps and stoves. If the oil is transesterified, the resultant biodiesel can also be used to fuel diesel generators and vehicles, and the by-product glycerine can be used to make soap.

It may even be possible to use the jatropha seed cake as animal food if varieties without toxic phorbol esters are

CONTINUED ON NEXT PAGE

Facts about Haiti

COUNTRY

- The country of Haiti is more mountainous as a percentage of land than Switzerland.
- There are numerous microclimates in the country including lush green cloud forests (in some of the mountain ranges and the protected areas), high mountain peaks, arid desert, mangrove forest, and palm tree-lined beaches.
- The rainy seasons can bring as little as 700 mm of precipitation per year, or more than 1,200 mm.
- Charcoal production is a major factor in the deforestation that experts say has felled 98% of Haiti’s tree cover, with the remaining 2% “disappearing fast” (<http://tinyurl.com/NYT-Haiti-2009>).

PEOPLE

- Eighty percent of Haitians are “informally employed.” That is, they work intermittently as short-term jobs become available.
- The average annual income is about \$500.
- Sixty percent of the food consumed in the country is imported.
- Eighty percent of Haiti’s college graduates presently live in the United States and Canada. About 1.5% of African Americans are Haitian, but 11% of African-American physicians are Haitian.
- The literacy rate (those age 15 and over who can read and write) is 62% (2010). For comparison, the literacy rate through South American and Caribbean nations is ~90%.

ECONOMY

- In 1804 Haiti was the richest colony in the French Empire. It accounted for 40% of Emperor Napoleon Bonaparte’s income. At that time, it had a higher gross domestic product than the fledgling United States.
- In 1950 Haiti was more prosperous than the Dominican Republic (the country with which Haiti shares the island of Hispaniola).
- At present Haiti is the poorest country in Western Hemisphere.
- In 2009 Haiti spent \$400,000,000 to import petrodiesel. Much of this was used to fuel generators that provide electricity to individual villages.
- There is no national electrical power grid.
- The country is heavily dependent on the estimated US\$3 billion in annual remittances from the United States, France, and other countries where Haitians live.
- According to the US Central Intelligence Agency, there were 4.2 million cell phones in Haiti in 2011 for the country’s 9.8 million inhabitants (<http://tinyurl.com/cell-phones-Haiti>). The nation’s telecommunications infrastructure is among the least developed in Latin America and the Caribbean.

commercially developed. The seed cake from which the oil has been removed contains more nitrogen than chicken manure, and its protein content is higher than soybeans. Without phorbol esters, the seeds could be fed to swine, poultry, and fish such as tilapia.

Bees pollinate jatropha flowers, so honey might also be a product that results from jatropha cultivation.

STARTING A BIODIESEL INDUSTRY IN HAITI

Digicel, the main cell phone provider in Haiti, is presently powering each of its 500+ cell towers in the country with petrodiesel generators. The company has committed to buying all the biodiesel that Jatropha Pepinyè (Haitian Creole for “jatropha nursery”) can produce (see below), so long as it meets standards.

Robbins emphasizes that establishing a jatropha industry in Haiti requires one to accept conditions in the country just as they are. The infrastructure on which developed nations depend is not there—no electricity, few wells for water and no electricity to drive pumps, poor roads, no mechanical harvesters . . . the list goes on and on.

Robbins and Rob Fisher (former University of Georgia-Athens professor and landscape architect), who are team members of the US non-profit organization Partner for People and Place (www.peopleandplace.org), have been working with Haitians in the northeastern mountains of the country near Terrier Rouge to

develop a jatropha industry since 2007. Partner for People and Place brings together sponsors and specialists, looks for solutions that respect the culture and ecology of Haiti, and uses local people to administer and implement development.

Taking account of the limitations in Haiti requires a change in attitude. Whereas in a developed nation the primary goal of a company is profits, in Haiti job creation is more important, at least in the short term. No Western nation would consider harvesting jatropha by hand, but that is the method of choice for Haiti because (i) there are no mechanical harvesters and (ii) there is a desperate need for jobs. As a start, Partner for People and Place envisions 1,000 growers, each farming 1–2 hectares of jatropha. Seeds are harvested by individuals, passing through the groves every 5–7 days, because the native jatropha varieties ripen unevenly over a period of 6–8 weeks. Calculations indicate that the total production from these 1,000 growers could be 1,000,000 gallons (3,800,000 liters) of biodiesel annually.

Jatropha Pepinyè, a farmers’ co-op jointly sponsored by Partner for People and Place and Esperance et Vie (www.esperanceetvie.org), has been growing jatropha seedlings for five years to provide planting stock for co-op members. So far, approximately 50 hectares have been planted. The decision was made early-on to start the business with seeds from local plants, since they are already adapted to a climate having wide swings in annual rainfall. In its initial efforts to collect native seeds, Jatropha Pepinyè offered to give the first 100 people to bring in two

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TECHNICAL
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coffee cans full of jatropha seeds a hand-cranked charger for a Digicel cell phone. From the enthusiastic response, Jatropha Pepinyè started its work.

Two members of the University of Illinois Urbana-Champaign (UIUC; USA) Sustainable Technology Center, Tim Lindsay and Joseph Pickowitz, identified a diesel-powered Desmet Rosedowns Mini 40 expeller that had been used by UIUC; according to company specifications, it has a nominal capacity of 40 kilograms/hour depending on what kind of seed is being processed. Lindsay and Pickowitz helped set up the expeller at Jatropha Pepinyè in 2009, and got it up and running. In the initial work to develop procedures, seeds and any accompanying dirt have been fed straight into the expeller, meaning that the resultant oil is not especially clean.

Thus, there are no immediate plans to sell the oil as such for fuel without further processing. To use the triglyceride oil without treatment could void the warranty of, for example the Caterpillar diesel engines Digicel presently uses to power its cell towers.

PROGRESS

Plants. Jatropha Pepinyè already has 50 hectares of jatropha planted in seven plots at Terrier Rouge. About 6 hectares are planted with a nontoxic variety of jatropha, developed by CHIBAS Bioenergy founder Gael Pressoir, a Haitian Ph.D. who initially worked in Mexico on breeding this cultivar.

Seedlings are planted at a rate of 1,650 plants per hectare at a spacing of 2 meters \times 3 meters. Planting has been carried out by hand (again, the need to provide jobs), and the work has been arduous. The land on which the trees are being planted has not been cultivated for 30 years, and the predominant plant growing on the land is mesquite trees, which are well known for the reach of their lateral roots and the depth to which their taproots will grow in search of water.

Yields of jatropha seeds from the plantings in Haiti have not yet met expectations. Less than 50 kilometers away, in research plots located in the Dominican Republic, yields have been about 4–5 metric tons (MT) of seed per hectare, whereas with the same fertilizer and a basically similar soil at Terrier Rouge the number is 0.5 MT/ha. One contributing factor to the difference may be that the Dominican Republic trees are flood-irrigated during the dry season, allowing a third harvest each year. Another is that the Haitian plants are less than two years old, whereas the Dominican plants have reached full production maturity.

Products. By-product glycerine from the production of biodiesel is being used to manufacture soap. This is being sold in the cities of Port au Prince and Cap-Haïtien and to the Royal Caribbean Cruise Ship Line, which docks at the port of Labadee.

Pickowitz and Lindsay have found that more oil can be expelled from jatropha seeds if they are first heated to 100°C. They are presently using a rocket heater (a 95+% efficient stove that uses biomass) to warm the heat transfer fluid for the expeller, but they are developing plans to use a solar heater that would be augmented by a rocket heater. To date, the biodiesel being produced by Jatropha Pepinyè is being used on-site to fuel generators.

As anticipated, the efforts to produce jatropha oil are leading to other saleable products that benefit the Haitian people. For

INFORMATION

For further information contact Kathleen Robbins at: krobbins513@hotmail.com; or Rob Fisher at: rob@peopleandplace.org.

ORGANIZATIONS WORKING WITH JATROPHA PEPINYÈ

- www.peopleandplace.org/files/download/18
- www.esperanceetvie.org
- <http://tinyurl.com/FAO-bioenergy-Haiti>
- <http://tinyurl.com/Pepinye-Dec2010>

OTHER ORGANIZATIONS WORKING TO HELP IN HAITI

- www.mohhaiti.org/about_haiti#.UOr5TazNI8E
- http://transformhaiti.com/?page_id=789

GENERAL

- Elbehri, A., A. Segerstedt, and P. Liu, *Biofuels and the Sustainability Challenge: A global assessment of sustainability issues, trends and policies for biofuels and related feedstocks*, UN Food and Agricultural Organization, Rome, Italy, 2013, 188 pp. Available at www.fao.org/docrep/017/i3126e/i3126e.pdf.
- US Central Intelligence Agency, *The World Factbook: Haiti*. Available at <https://www.cia.gov/library/publications/the-world-factbook/geos/ha.html>.

example, the Jatropha Pepinyè plots are fenced in for purposes of the study. These trees provide shade to the soil, making it cooler and more productive of grass. Sheep have been grazed in some of these plots—sheep will not eat jatropha leaves—and their meat has been sold to the Jordanian troops stationed in Haiti by the United Nations. The Haitians working on the project would have preferred to raise goats in the enclosures, since the national diet favors goat meat, but goats are notorious for their ability to climb over fences and escape. When that problem is solved, plans are to raise goats between the trees, for they too will not eat jatropha.

Obviously, much needs to be done to make Jatropha Pepinyè a profitable, sustainable business, but those who are involved in the project are making every effort to do the things necessary to make it succeed—taking account of conditions as they are, working with people “where they are,” and looking to innovate wherever they can and with whatever they can.

Marguerite Torrey is Technical Projects Editor for Inform. She may be contacted at mtorrey@aocs.org.

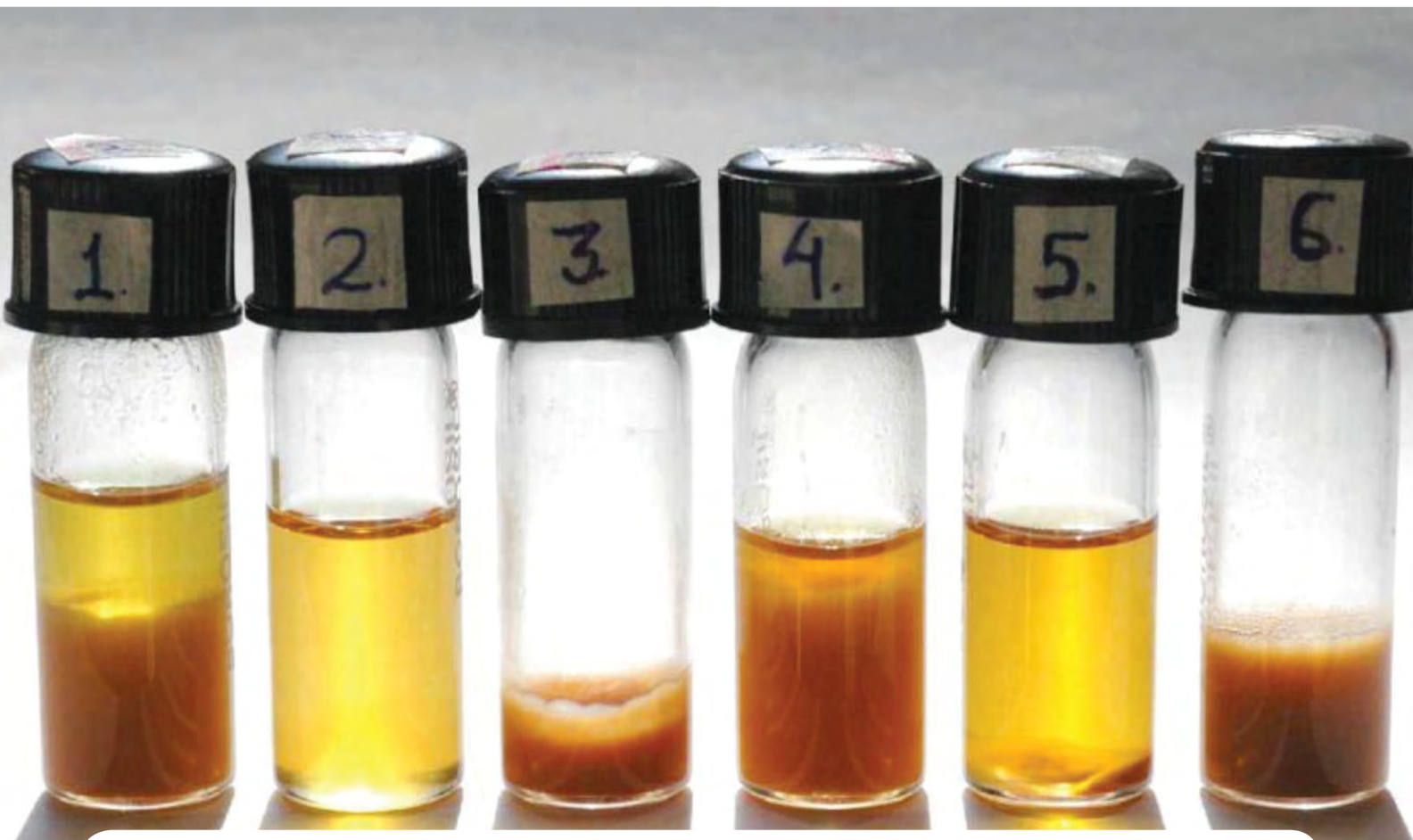


FIG. 1. Photograph illustrating neat crude oil extraction from rice bran at 5°C. (1) Hexane extract (normal extraction); (2) hexane extract at 5°C; (3) hexane extract (normal extraction of residual bran) (from 5°C extracted spent rice bran); (4) acetone extract (normal extraction); (5) acetone extract at 5°C; (6) acetone extract (normal extraction of residual bran) (from 5°C extracted spent rice bran). Source: Gopala Krishna *et al.*, 2011.

Rice bran oil: nature's healthful oil

- Rice bran oil has an ideally balanced fatty acid profile, is rich in natural antioxidants and nutraceuticals, and can reduce low density lipoprotein (LDL) and serum cholesterol.
- Global production currently realizes only 19% of rice bran oil's potential.
- Better extraction and by-product recovery are needed to achieve its potential.

A.G. Gopala Krishna

Rice is grown in as many as 60 countries, but only 12 produce major amounts. In 2009, total world production of rice was 455.7 million metric tons (MMT).

Rice bran is a by-product of rice milling, and is produced during the polishing of brown rice to prepare white rice. The bran contains 15–25% oil depending on the cultivar, agricultural practices, and the extent of polishing. The potential for production of rice bran and rice bran oil (RBO) in major rice-growing countries is presented in Table 1. Although rice bran has reached its full potential, only 19% of RBO's potential is realized—even though paddy (rough rice) is produced in as many as 15 major rice-growing countries in the world.

While China realizes only 4.9% of its potential for RBO (90,000 metric tons, or MT), India produces 65.7% of its potential (820,000 MT). Indonesia does not produce any RBO at all. Tables 1 and 2 (next page) show the production of the oil and its uses in food and for other purposes in various countries.

RBO is produced by solvent extraction. Among other properties, RBO:

- has an ideally balanced fatty acid profile and is rich in natural antioxidants and nutraceuticals.
- can reduce low density lipoprotein (LDL) and serum cholesterol.
- contains antioxidants such as oryzanol, tocopherols and tocotrienols, phytosterols, and squalene.

In India, RBO is considered a nutraceutical (food as medicine) oil that is suitable for all cooking needs.

CHEMICAL COMPOSITION OF RBO

According to the literature, crude RBO comprises 95% saponifiable and 4.2% nonsaponifiable lipids. The saponifiable components include triacylglycerols (71%), diacylglycerols (3%), monoacylglycerols (5%), phospholipids (4%), and glycolipids (6%); on saponification these yield alkali salts of fatty acids (FA) and glycerol. Waxes (3%) and oryzanol (1.8%) are also present in the oil. These saponify with difficulty and may be found in the unsaponifiable matter (as such or in the saponified forms, viz, long-chain alcohols from waxes, phytosterols from oryzanol). If proper care is not exercised, this may eventually increase the level of unsaponifiable matter in the oil.

Like groundnut oil, sesame oil, and corn oil (Table 3, page 263), RBO contains a high proportion of monounsaturated (40–50%) and diunsaturated FA (29–42%). It has comparatively higher amounts of different classes of unsaponifiable matter than other edible oils.

The triacylglycerol composition of RBO is similar to other edible oils, although some differences in the content of triolein (OOO) and palmitodilinolein (PLL/LPL) have been observed (a detailed table can be found in the digital edition of *inform*. Log in to read the April 2013 issue at aocs.org/login).

SPECIFICATION FOR RBO

Japan and India have formulated specifications for RBO, and a Codex Alimentarius Commission standard for the oil also exists (detailed tables can be found in the digital edition of *inform*. Log in to read the January 2013 issue at aocs.org/login). The limit for unsaponifiable matter for different vegetable oils under Indian and Codex standards indicates a higher unsaponifiable matter content for RBO under both the Indian (3.5%, 4.5%), and the Codex

More information on rice bran oil

Looking to pad your rice bran oil knowledge? Mill through the AOCS Press Monograph Series on Oilseeds! The third volume in the series, *Gourmet and Health-Promoting Specialty Oils* (ISBN: 978-1-893997-97-4) contains a chapter dedicated to recent work in rice bran oil. Written by J. Samuel Godber, Department of Food Science at Baton Rouge University (Louisiana, USA), the chapter provides additional detail into the cultivation, production, health benefits, and challenges of the industry. It also provides information about new production techniques and additional information about rice bran oil not covered in this article.

The chapter can be individually downloaded and purchased at the AOCS store online (<http://www.aocs.org/Store/ProductDetail.cfm?ItemNumber=3373>) for \$25 for AOCS members. The full volume, which also discusses olive oil, avocado oil, flax seed oil, and many others, can be purchased for \$132 by AOCS members (<http://www.aocs.org/Store/ProductDetail.cfm?ItemNumber=1986>).

(6.5%) standards specification. Processing of the oil (chemical or physical refining) contributes to oryzanol retention, acidity variation, unsaponifiable matter content changes, color variation, and haziness in the refined oil.

Realizing these problems, the Prevention of Food Adulteration Act, 1954 (PFA), India, [currently known as the Food Safety and Standards Authority of India (FSSAI)] rules have

CONTINUED ON NEXT PAGE

TABLE 1. Production of rice, the potential for rice bran production, and the potential for and actual production of rice bran oil in different major rice-growing countries during 2009^a

Country	Production of:			
	Rice (MMT), actual	Rice bran (MMT), potential ^b	Rice bran oil	
			Potential ^c (MMT)	Actual (MMT)
China	131.186	9.18	1.84	0.090
India	89.178	6.24	1.25	0.820
Indonesia	42.954	3.01	0.60	—
Bangladesh	31.832	2.23	0.45	0.002
Vietnam	25.943	1.82	0.36	0.011
Myanmar	21.799	1.53	0.31	0.101
Thailand	21.421	1.50	0.30	0.045
Philippines	10.850	0.76	0.15	—
World	455.707	31.90	6.38	1.20

^aSource: www.fao.org/crop/statistics/en. Accessed 10 September 2012.

^bCalculated as 10% of brown rice; brown rice is equivalent to 70% of rough rice or paddy.

^cCalculated as 20% of rice bran. Abbreviation: MMT, million metric tons.

TABLE 2. Rice bran oil production and use (in 1000 metric tons) in 2009^a

Country	Production	Domestic supply quantity	Uses	
			Food	Other
India	820	783	563	220
Myanmar	101	101	—	101
China	90	90	90	—
Japan	61	85	75	10
Thailand	45	33	33	—
Brazil	15	15	15	—
Viet Nam	11	11	11	—
Democratic People's Republic of Korea	11	11	—	11
Cambodia	10	10	—	10
Republic of Korea	10	10	10	—
Nepal	9	9	9	—
Sri Lanka	7	7	7	—
Pakistan	5	5	5	—
Lao People's Democratic Republic	4	4	4	—
Bangladesh	2	2	2	—
World	1,203	1,178	826	352
Asia	1,188	1,163	811	352

^aSource: www.fao.org/crop/statistics/en. Accessed 10 September 2012.

been amended from time to time for the specification of RBO by raising the limit of unsaponifiable matter of 3.5% to 4.5% with 1% oryzanol in the oil. For chemically refined oils, the earlier limit of 3.5% unsaponifiable matter level still holds, and for physically refined RBO this level is increased to a maximum of 4.5% with 1% oryzanol in the oil (detailed table in the digital edition of the April 2013 issue of *inform* at aocs.org/login). Dark color in physically refined oil is still a problem in marketing the oil.

EXTRACTION, PROCESSING, AND REFINING

RBO was first extracted with food-grade hexane in India starting in the 1960s. There is considerable lipase activity in rice bran, though, and with storage the free fatty acid (FFA) levels in the extracted oil increase. Therefore, oil extraction should be done on fresh bran or on the bran obtained soon after milling, to prevent the lipase action

on bran oil and to ensure the quality of the extracted oil.

Refining of RBO is accomplished by two methods, one by chemical reaction with alkali, known as alkali refining/chemical refining; the other by steam stripping–vacuum distillation of FFA, known as physical refining. In addition to removing FFA, both processes involve the steps of degumming, dewaxing, and bleaching. Chemical refining involves the additional step of deodorization.

Chemical refining. Problems encountered during refining of RBO are (i) excessive refining loss, (ii) color fixation, (iii) loss of oryzanol, and (iv) loss of bioactives. Refining losses were addressed during the 1990s, but the color fixation problem is still not completely eliminated. The loss of oryzanol and bioactives is generally accepted, as keeping to specification makes these losses unavoidable.

Physical refining. During the mid-1990s, the same technology used to refine palm oil was applied to RBO. This was not very successful owing to a lack of pretreatment technologies that can lower the phosphorus content of crude RBO to below 5 ppm, a prerequisite for physical refining. Since then, several pretreatment technologies have been introduced. The National Institute of Inter-disciplinary Science & Technology (NIIST; Thiruvananthapuram, India—earlier known as Regional Research Laboratory) developed a pretreatment technology known as simultaneous

degumming and dewaxing, in which CaCl_2 is used to remove phosphorus-containing lipids known as phosphatides (or gums). Likewise, the Indian Institute of Chemical Technology (IICT, Hyderabad) developed an enzymatic degumming process to remove phosphorus to desired levels. These pretreatment technologies have revolutionized RBO processing in India. Several new RBO refining plants incorporating these new technologies have been built, the majority of which are based on IICT technology.

Until recently, the issues of higher unsaponifiable matter (>3.5%), increased FFA values (>0.25%), and haziness/cloud point found in physically refined RBO posed problems in marketing of the oil. No such problems were encountered in the marketing of chemically refined RBO, which passed all the tests (values of unsaponifiable matter <3.5% and FFA content <0.25% could be achieved) prescribed by the PFA.

TABLE 3. Chemical composition of rice bran oil and some common vegetable oils^a

Fatty acid ^b (relative area %)	Cereal bran oils		Vegetable oils		
	Rice bran	Corn germ	Ground nut	Sunflower	Soybean
Myristic	0.4–1.0	0–1.7	0–1	0	0–1
Palmitic	12–18	8–12	6–9	3–6	7–11
Stearic	1–3	2–5	3–6	1–3	2–6
Oleic	40–50	14–49	53–71	14–43	15–33
Linoleic	29–42	34–62	13–27	44–75	43–56
Linolenic	0.5–1.0	0	0	0	2–10
Arachidic	0	0	2–4	0–4	0–2
Behenic + lignoceric	0–2	—	0–2	—	—
Unsaponifiable matter (%)	4.20	1.29	0.63	0.59	0.53
Phytosterols	1.80	1.17	0.44	0.39	0.36
4-Methyl sterols	0.40	0.01	0.02	0.11	0.07
Triterpene alcohols	1.20	0.01	0.04	0.07	0.09
Tocopherols	0.08	0.10	0.03	0.06	0.07
Others	0.72	—	—	—	—

^aSource: Gopala Krishna *et al.*, 2012.^bThe fatty acid composition is expressed as relative area % of the individual fatty acids based on the areas of individual fatty acids in the gas chromatogram.

The apparent FFA content of chemically refined RBO is within the permitted limits of 0.25%, but FFA amounts in physically refined RBO are higher. Gopala Krishna *et al.* (2006) investigated the composition of physically refined RBO and its higher FFA value and developed the following formula for calculating real FFA content of vegetable oils containing oryzanol:

$$\text{Real FFA content (\% as oleic)} = \text{observed FFA content} - (\% \text{ oryzanol content} \times 0.425)$$

when phenolphthalein is used as the indicator. This equation clearly indicates that physically refined RBO containing oryzanol show an acidity due to oryzanol, not to FFA. Recently, the PFA amended the rules regarding unsaponifiable matter levels in physically refined RBO, so that physically refined RBO, which contains five to six times the oryzanol found in chemically refined RBO, can be sold. Table 4 on page 264 shows (i) a typical apparent FFA content analysis of chemically and physically refined RBO produced in India and (ii) the corrected value (the real FFA due to oleic acid). This is normal FFA content (real FFA) and, due to the presence of oryzanol, the physically refined RBO which contains oryzanol shows an apparent acidity which should not be mistaken for FFA content due to the presence of oleic acid termed as the real FFA. The real FFA content may be calculated and used for evaluating the physical refined RBO for specification purposes.

FRYING AND BLENDING

Processed RBO that have been refined chemically or physically were studied for frying performance compared to sunflower oil. Although there are claims for low absorption of the RBO during frying, laboratory experiments in the author's laboratory (Gopala Krishna *et al.*, 2005; Rekha *et al.*, 2011) showed that the RBO behaves like other oils, and there is a marginal reduction of oil absorption during frying compared to others such as groundnut, coconut, palm, and sunflower oils and ghee (milk fat).

The Government of India has permitted the blending of oils to extend the oil supply in the country. RBO (20 parts) was blended with either groundnut (80 parts), or mustard (80 parts), or sunflower oils (80 parts) and blends of RBO with the mentioned oils (two-oil blend) in the ratio of 20:80 were prepared. A combination of four vegetable oils (to provide vegetable blends) containing RBO (20 parts), sesame oil (20 parts), and red palm olein (20 parts) were blended with either groundnut (40 parts) or sunflower (40 parts) or mustard oils (40 parts) wt/wt to provide nutritional benefits of the natural antioxidants [oryzanol and tocotrienols in RBO, lignans (sesamin and sesamol) in sesame oil, and β -carotene and tocotrienols in red palm olein] present in them (Shiela *et al.*, 2004). From the work carried out at our laboratory, the oil extracted from parboiled bran showed a

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TABLE 4. Acidity of oryzanol in rice bran oil (RBO) and its contribution to the free fatty acid (FFA) content of the oil

RBO samples used in the study	Observed FFA (% as oleic acid) (phenolphthalein indicator)	Oryzanol (%)	Real FFA (% as oleic) = FFA – (% oryzanol × 0.425) ^a
Chemically refined RBO			
1	0.14	0.1436	0.08
2	0.16	0.1841	0.08
Physically refined RBO			
1	0.40	1.1057	−0.07
2	0.47	1.0875	0.01
3.	0.48	1.0664	0.03
4	0.46	1.2072	−0.05
5.	0.49	1.3194	−0.07
6	0.43	0.5567	0.19
7	0.35	0.6024	0.09
8	0.43	0.5996	0.16
9	0.44	0.7260	0.13
10	0.47	0.7529	0.15
11	0.29	0.6070	0.03
12	0.55	1.3902	0.12

^aFactor for phenolphthalein indicator. Source: Gopala Krishna *et al.*, 2006.

drastic reduction in the tocopherol/tocotrienol levels (Khatoun and Gopala Krishna, 2004). Chemically refined RBO is a poor source of oryzanol (Gopala Krishna *et al.*, 2006) while physically refined RBO has good amounts of oryzanol and tocopherols + tocotrienols to provide health benefits (Raja Rajan and Gopala Krishna, 2009).

PREPARATION FOR NUTRACEUTICAL PURPOSES

RBO produced by either physical or chemical refining processes contains health-improving constituents in amounts lower than those present in crude oil. Studies carried out at our laboratory resulted in the preparation of a nutritionally superior RBO with a light color, a very low wax content, and proven health benefits in experimental animals (Fig. 1, page 260) The oil was found to be equivalent to physically refined RBO in its nutraceutical content, but with low color units. Further developments may yield an even lighter RBO.

SUPERCRITICAL CARBON DIOXIDE (SC-CO₂) AND ENZYMATIC PROCESSES

SC-CO₂ extraction of rice bran has been reported from the Council of Scientific and Industrial Research (CSIR)-NIIST

(Thiruvananthapuram). The phytochemical contents of RBO under optimal conditions were as follows: tocots, 1,500–1,800 ppm; sterols, 15,350–19,120 ppm; and oryzanol, 5,800–11,110 ppm (Balachandran *et al.*, 2008).

Enzymatic (alcalase) treatment of rice bran produced an oil yield of 79% and a protein yield of 68% compared with the amounts originally found in the bran (Hanmoungjai and Niranjana, 2001). RBO processed in this manner had good quality attributes but poor shelf life. Enzymatic processing is an emerging technology and may have commercial value in times to come.

HYPOCHOLESTEROLEMIC EFFECT

Several studies have shown that the effect of RBO on serum cholesterol concentrations is due to the unsaponifiable matter comprising oryzanol, campesterol, and β -sitosterols. Consequently, it could become an important functional food with cardiovascular health benefits. RBO, which is rich in tocopherols and tocotrienols, may improve oxidative stability. Tocotrienols inhibit HMG [hydroxymethylglutaric acid]-CoA reductase, resulting in lower total cholesterol level. The hypolipidemic effect of RBO has also been established in human subjects (Sugano and Tsuji, 1997; Most *et al.*, 2005). Thus, RBO could be a suitable edible oil for patients with hyperlipidemia.

BY-PRODUCTS

More than 75% of the rice bran used for oil extraction is converted into defatted rice bran, which contains fiber, protein, residual antioxidant components, and minerals, and has a production potential of 24.0 MMT (75% of 31.9 MMT; see Table 1 on page 261). Phytochemical extracts have been prepared from defatted bran, but the technology for using them in processed foods still needs to be developed. The present availability in India is about 3 MMT, all of which is being used as feed. To be suitable for human food applications, unhealthful factors such as phytic acid, trypsin inhibitor, and a high silica content would have to be removed. Work on preparation of such a type of full-fat rice bran for use as food supplement is in the concluding stages by the author's research team at the CSIR–Central Food Technological Research Institute (CFTRI), Mysore.

As more industries process edible-grade oil from rice bran, large amounts of waste products such as gum sludge, wax sludge, fatty acid distillate/soapstock, and deodorizer distillate (DOD) are accumulating. Pure products (lecithin, wax, squalene, tocotrienols, phytosterols, and oryzanol) fetch very high prices compared to the prices of sludges/DOD and should be recovered for their health benefits. In India, technologies for value-added products from waste sludges of the industry are available from three CSIR institutions: CSIR-CFTRI, Mysore; CSIR-Indian Institute of Chemical Technology, Hyderabad; and CSIR-NIIST, Thiruvananthapuram.

At present, only about 19% of the RBO that could be produced worldwide is being tapped. The top producer, India, produces only about half of what it could. India could produce another 700,000 MT more, but only if the bran produced in remote areas of India could be stabilized against lipase activity for prolonged storage, so that the resulting oil would have a low FFA content. Similarly, other major rice-growing countries such as China, Indonesia, Bangladesh, Vietnam, Myanmar, Thailand, and Philippines have a great potential for production of RBO. Developments that enable RBO to be used in functional foods are needed as a future strategy to make the benefits of this healthful oil available to more people around the globe.

A complete reference list and additional tables can be found in the digital edition of the April 2013 issue of *inform*. To view them, log in at acocs.org/login, and click the supplements tab to the right of the page.

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A new method for the estimation of olive oil healthfulness

- A growing body of evidence suggests that the healthfulness of olive oils could be classified based on their content of oleocanthal, oleacein, and related secoiridoids. However, such compounds are difficult to measure because they react with the water or methanol used during the mobile phase of liquid chromatography.

- Recently, a new method allowing olive oil polyphenols to be extracted without the use of reacting solvent was developed, making it possible to measure oleocanthal and oleacein levels directly by quantitative ^1H nuclear magnetic resonance (NMR) in CDCl_3 at 600 MHz and 800 MHz.

- Measurements of 300 olive oil samples using this method revealed wide variations in the concentrations of these healthful compounds among extra virgin olive oils.

**Evangelia Karkoula, Eleni Melliou,
and Prokopios Magiatis**

Several epidemiological studies have shown that the traditional Mediterranean diet is associated with a lower incidence of atherosclerosis, cardiovascular disease, neurodegenerative diseases, and certain kinds of cancer. These appreciable health-promoting properties have been partially correlated with the regular consumption of extra virgin olive oil as the principal source of fat. Olive oil is the most famous agricultural product in the Mediterranean, with a history as old as that region's civilization. Olive fruits and olive oil not only are delicious but also have been considered as medicines since ancient times.

Dioscorides (ca. 40–90 CE) and several other ancient doctors claimed that olive oil and other olive-related products had numerous therapeutic applications. In his monumental work “De Materia Medica,” which is the basis of modern pharmacology and pharmacopoeia, Dioscorides clearly stated that olive oil from specific varieties—particularly early-harvested extra virgin olive oil—has anti-inflammatory activities. Ancient recipes described in incredible detail how olive oil could be used as remedies against conditions such as headache and toothache, clear indications of *in vivo* anti-inflammatory activity. Yet, according to descriptions in ancient manuscripts, not all olive oils display such properties. We were intrigued and decided to investigate whether that could be true and why.

In 2005 Beauchamp and co-workers reported in the journal *Nature* that olive oil contains a chemical compound called oleocanthal, which is responsible for the pungency of some olive oils and which has a very strong anti-inflammatory activity with ibuprofen-like cyclooxygenase (COX-1 and COX-2)-inhibiting activity. This may explain the therapeutic properties of virgin olive oil, since inflammation plays a significant role in the development of numerous chronic diseases, such as cardiovascular disease, as well as in certain kinds of cancer.

In addition, recent research has demonstrated that oleocanthal is a promising therapeutic agent for the treatment of inflammatory degenerative joint diseases. Moreover, oleocanthal can be a potentially useful agent for the development of new treatments for neurodegenerative tauopathies (diseases associated with the pathological aggregation of tau protein in the human brain), such as Alzheimer’s disease, or as an agent against *Helicobacter pylori*, which is linked to a majority of peptic ulcers and to some types of gastric cancer. Oleocanthal also exhibits biological properties that can control skin aging and a growing body of evidence suggests that it could be used to treat damaged skin or to reduce a variety of disorders that arise from metabolic syndrome.

Another compound with a similar structure that is related to the bitter taste of some olive oils is the dialdehydic form of decarboxymethyl oleuropein aglycone, known as oleacein. This compound has shown activities similar to those of oleocanthal, but the former has also displayed significant anti-breast cancer properties. Most importantly, oleacein also has potent antioxidant activities, even better than those of hydroxytyrosol, another active compound found in table olives and olive oil. Oleacein can additionally protect low density lipoprotein from oxidation, a health claim already recognized by European Union legislation.

Modern findings about oleocanthal and oleacein and their potential health effects that confirmed the ancient reports prompted us to assume that several varieties of olive oils could be classified on the basis of their content of secoiridoids, such as oleocanthal, oleacein, and related compounds. Toward this end, we investigated the levels of oleocanthal and its related analog oleacein in a large number of Greek and California olive oils of monovarietal origin in relation with the variety, the geographic origin, and the time of harvest. To achieve this target, we recognized the need to develop a new, fast, and accurate analytical method that can circumvent a previously known analytical problem for the oleocanthal and oleacein measurement.

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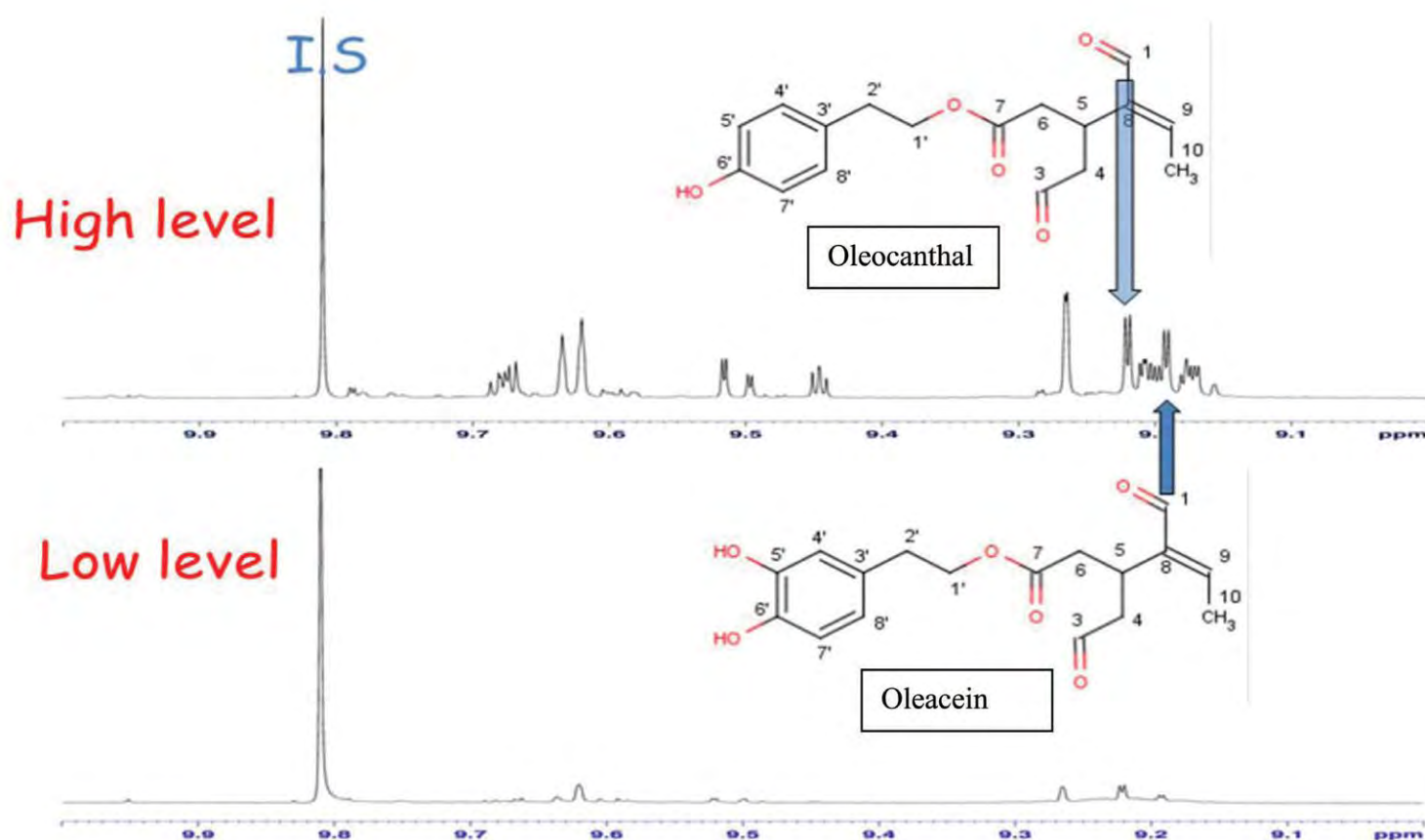


FIG. 1. Example of two ^1H nuclear magnetic resonance spectra of extra virgin olive oils presenting high and low levels of oleocanthal and oleacein. The arrows denote the peaks that are used for the quantification of each compound (IS: internal standard).

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That problem arises because both compounds react rapidly with the water or methanol commonly used in the mobile phase of liquid chromatography, leading to broadened or multiple peaks. This reactivity necessitates the use of derivatization reactions.

For this reason, we developed methods to extract olive oil polyphenols without using any reacting solvent and to measure oleocanthal and oleacein levels directly by quantitative ^1H -NMR in CDCl_3 at 600 MHz and 800 MHz (Fig. 1).

The methods were applied in the study of over 300 olive oil samples. One of the main findings was a highly important variation in the concentrations of oleocanthal and oleacein among the studied extra virgin olive oil samples. The concentrations of both compounds ranged from non detectable to over 500 mg/kg, respectively, and their sum from 0 mg/kg to over 750 mg/kg.

It is important to note that according to the definition established by European Union legislation all the studied samples were considered as extra virgin olive oils. However, the observed important variation of the concentration of the bioactive polyphenolic secoiridoids revealed the need for a new type of classification especially related to possible health claims of

those compounds. For this reason we propose a new index, D1, as the sum of the concentrations of oleocanthal and oleacein.

GREEK OIL SAMPLES

The highest concentrations of oleocanthal and oleacein among the Greek samples were recorded in olive oil samples produced from the Koroneiki cultivar. However, a portion of olive oil samples coming from cv Koroneiki showed significantly low concentrations (Fig. 2). This result in most cases could be attributed either to very late harvest (fully ripe fruit) or to high temperature during malaxation or both.

We also found that there was a group of olive varieties that, independent of geographic origin, harvest time (early or late), or olive mill-related parameters, produced olive oil containing both compounds in low levels (mean value D1 = 49 mg/mg). The olive oil produced by those varieties is traditionally preferred for confectionary owing to its lower sensation of bitterness and pungency. Our findings confirmed their lower content of oleocanthal and oleacein, which are related with those specific organoleptic properties.

Another observation was that the ratio between oleocanthal and oleacein (index D2 = oleacein/oleocanthal) seems to be dependent on the olive tree variety, probably due to genetic reasons, and independent of the olive mill procedure.

We also discovered a positive correlation of oleocanthal and oleacein concentration with the early time of harvest. It is noteworthy that the highest D1 index (750 mg/kg) was recorded for a sample from Koroneiki variety (Antiparos Island) produced in late October 2012. Similarly, the second- and third-highest D1 indexes were recorded for early-harvested (early November) Koroneiki variety from Messini. The same variety from the same olive grove collected after two months and processed in the same olive mill under the same conditions afforded an olive oil with D1 index at 87 mg/kg.

CALIFORNIA OIL SAMPLES

Similarly to the Greek samples, significant differences were also observed for the California olive oil samples. Samples from seven different varieties were studied, and big differences were recorded. For example, the highest variability in D1 index was found for Taggiasca, Leccino and Barouni cultivars, ranging from 45 to 275 to 406 mg/kg, respectively.

Although we measured only two compounds bearing aldehyde groups, the NMR spectrum in the range 9.1–9.8 ppm seems to present a unique recognition pattern especially characteristic for some olive oil varieties. The ¹H-NMR spectrum not only

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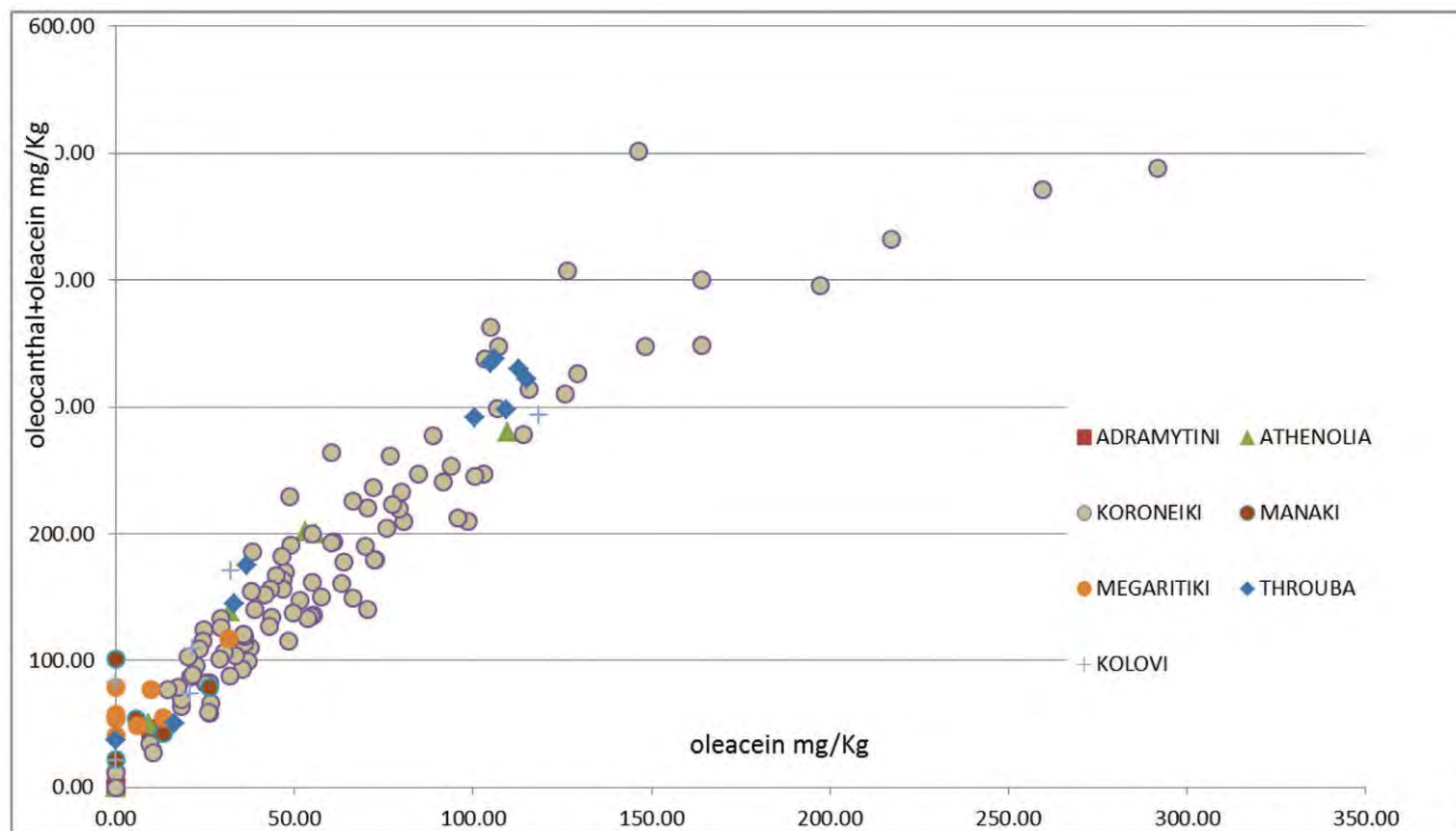


FIG. 2. Diagram showing the wide variability of oleocanthal and oleacein content among the several varieties studied.

offers a method for quantitation but also offers a tool for variety recognition but this finding needs further elaboration.

While there is need for more extensive study, based on our observations the new index for the characterization of extra virgin olive oils—a combination of D1 = oleocanthal + oleacein level with the D2 = oleocanthal/oleacein molar ratio—can be very useful for the estimation of the healthfulness of an olive oil and can be understood easily by consumers.

INDEXES D1 AND D2 IN PERSPECTIVE

In confirming the ancient observations, it was obvious that the oils can be categorized according to their content of bioactive

compounds. The new indexes D1 and D2 reflect such significant differences among the olive oils that although the oils may belong to the official category of extra virgin olive oil, a new subcategory of “super” olive oils with high D1 and D2 can be established. It has to be clear that those indexes mainly concern the support of health claims and are more specific than the total polyphenols (expressed as gallic acid equivalent) related to antioxidant activity.

It is also noteworthy that in preliminary studies the indexes D1 and D2 can predict the pungent and bitter taste of an olive oil. In most cases the highest “healthfulness” is related with increased pungency and bitterness, which are organoleptic properties that are highly appreciated by olive oil experts.

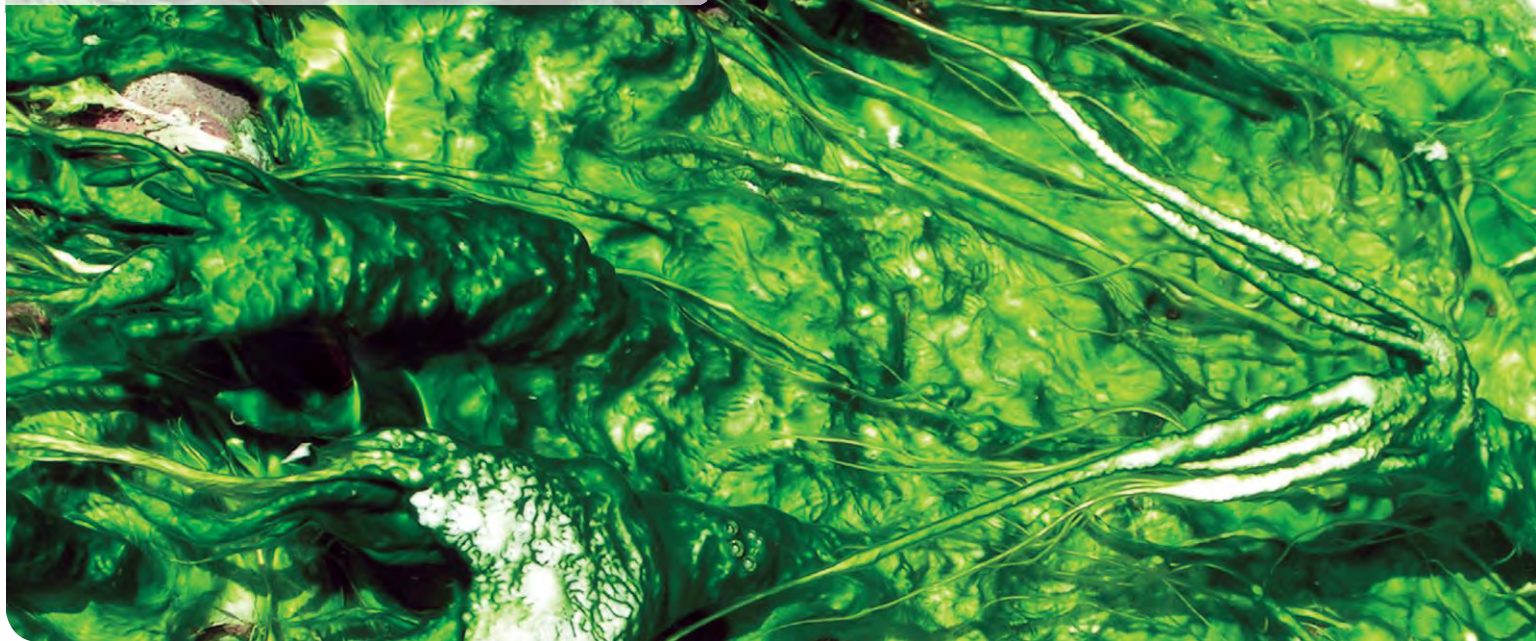
Prokopios Magiatis is an assistant professor in the laboratory of pharmacognosy and natural products chemistry at the University of Athens. He can be contacted at magiatis@pharm.uoa.gr.

Evangelia Karkoula is a graduate student in the laboratory of pharmacognosy and natural products chemistry at the University of Athens.

Eleni Melliou is a visiting scientist at the UC Davis Olive Center at the University of California in Davis, California, USA.

[FAST FACT]

Mayonnaise is said to be the invention of the French chef of the Duke de Richelieu in 1756. While the Duke was defeating the British at Port Mahon, his chef was creating a victory feast that included a sauce made of cream and eggs. When the chef realized that there was no cream in the kitchen, he improvised, substituting olive oil for the cream. A new culinary masterpiece was born, and the chef named it “Mahonnaise” in honor of the Duke's victory. (Copied from <http://www.bestfoods.com/home/about>)



Lack of funding hampers algae for feed progress

Dick Ziggers

When browsing the web on information about the use of algae in animal feeds one almost becomes euphoric about the great versatility of this family of water plants and the great benefits it has for animal performance. Just some statements I came across in poultry:

“Increases egg-laying period from 14 months to 24 months,” “decreases mortality rates from 10% to less than 2%,” and “significantly better taste” (of what?). In cattle there is talk of “increases quantity of milk and healthier and better tasting milk,” “increases ‘good’ butter fat percentage”(?) and a most remarkable one: “prevents and reduces incidence of encephalopathy or mad cow disease.” Indeed a miracle crop, one would think. Despite these (too) broad statements, algae as a feedstock still has a great potential. Algae can be cultivated in human-made ponds on otherwise unusable desert land, requiring only sunlight and seawater to grow. In an optimal situation it’s about 30 times more productive than soy but requires only 1% as much fresh water. It also has a much higher protein content. “If we could use this biomass to replace soybeans, then we could have a lot of soybeans left for human consumption,” explained Xingen Lei, a Cornell professor who’s been testing algae as an animal feed supplement. Lei’s research is funded by a \$5.5

- Current animal feed (corn and soy) is unsustainable, because it directly competes against human food sources.
- Microalgae could be a sustainable alternative, as they contain all the desirable macro- and micro-ingredients that animal nutrition requires.
- However, while algae produce 50 times more oil per hectare than corn, governmental financial support has been far less or even absent compared to the development of the bio-ethanol industry with its co-product DDGS (dried distillers grains with solubles).

million government grant to investigate algae’s role in solutions to alarming food and energy crises. Since the early 1980s, for almost two decades the US government funded research into algae’s potential as a biofuel. It stopped the program in 1996 after concluding

CONTINUED ON NEXT PAGE

that algal biofuels could not be cost competitive with fossil fuels. Current oil prices, however, have renewed attention from investors as a potential fuel source.

SUSTAINABLE PRODUCTION

“Current animal feed directly competes against human food sources and, thus, is unsustainable,” Lei said. “We must develop alternatives to soybean and corn for animal feeds.” Algae produces 50 times more oil per hectare than corn, with a much smaller carbon footprint; uses nutrients more efficiently than land plants, with no runoff; and places no demand on high-quality agricultural land or freshwater supplies.

There are an estimated 1 billion swine worldwide. The average pig consumes about 300 kg of feed by the time it goes to market, Lei said, so replacing just 10% of that feed with algae would save a massive 30 million metric tons. Lei’s preliminary research found that dried defatted algae derived from biofuel production can replace up to one-third of soybean meal in diets for pigs and chickens. It is an attractive source because it is high in protein: 20–70%, compared with about 10% in corn and 40% in soy. Lei and his researchers are now working to determine which algae are best, and the proper ratios of algae, soybean, and corn. They are also discerning whether there are risks or additional health benefits for humans in resultant products, such as meat and eggs.

PILOT PROJECT

Samples are shipped to Lei’s lab from Hawaii, where algae is being cultivated on a few acres near the Kailua Kona Airport (Hawaii,

USA) as part of a \$15 million pilot project by Cellana and a multi-university consortium led by Cornell professors Chuck Greene, professor of earth and atmospheric sciences, and Jeff Tester, professor of chemical and biomolecular engineering.

Ramping it up to commercial scale will require thousands of acres and hundreds of millions of dollars, said Greene.

Which is where Lei can help. Turning a biofuel by-product into a value-added product could be the key to commercial viability and may spawn other new industries. The global animal feed market is expected to exceed 1.5 billion metric tons per year by 2020, 15% of which is protein, Lei said.

Lei’s algae are a dried version of their single-cell species. Their simple structure means it is easier to break down, without the complex cellulose that presents challenges to the production of plant-based biofuels such as corn-derived ethanol. It also has a high lipid, or oil, content—around 30%, compared with 4% in corn—and its own inherent stress response can be harnessed to help in oil production. When starved of nutrients, the algae undergo physiological changes causing it to exude oil—a process being studied by Beth Ahner, professor of biological and environmental engineering, and Ruth Richardson, associate professor of civil and environmental engineering, both of Cornell University.

With further innovations, the process could actually remove substantial amounts of carbon dioxide from the atmosphere, Greene said, and its use in the production of jet fuel could help the US military meet its goal of switching to a 50:50 blend of fossil and biofuels by 2020. Greene said that even with today’s high fossil fuel costs, algal biofuels will likely become cost competitive with fossil fuels only when valuable co-products are simultaneously exploited and commercialized. So, it is similar to the early stages of bioethanol production from corn, where the remaining distillers grains were almost considered a waste product, but when subsidies were lessened they became a valuable material that added to the profitable exploitation of the ethanol plant. Converting the algae biomass that is left behind after extracting the oil to commercially viable feed increases the overall value of algae as a resource. This makes algae’s animal feed application so significant and gives algal biofuel a value-added component that makes it much more attractive to investors. Another benefit of the algae biomass is that, when extracting the oil for fuel, the protein content in the remaining product increases, making it potentially more nearly ideal as a feed source. “Most calculations do not factor in the animal feed application,” Lei said. “If you put that in, the equation would shift significantly. It’s mutually beneficial.” But funding still presents a huge barrier; moving pilot projects to a commercial scale would require hundreds of millions of dollars. If governmental subsidies would shift from bioethanol and biodiesel projects to algae projects these would definitely have a better chance.

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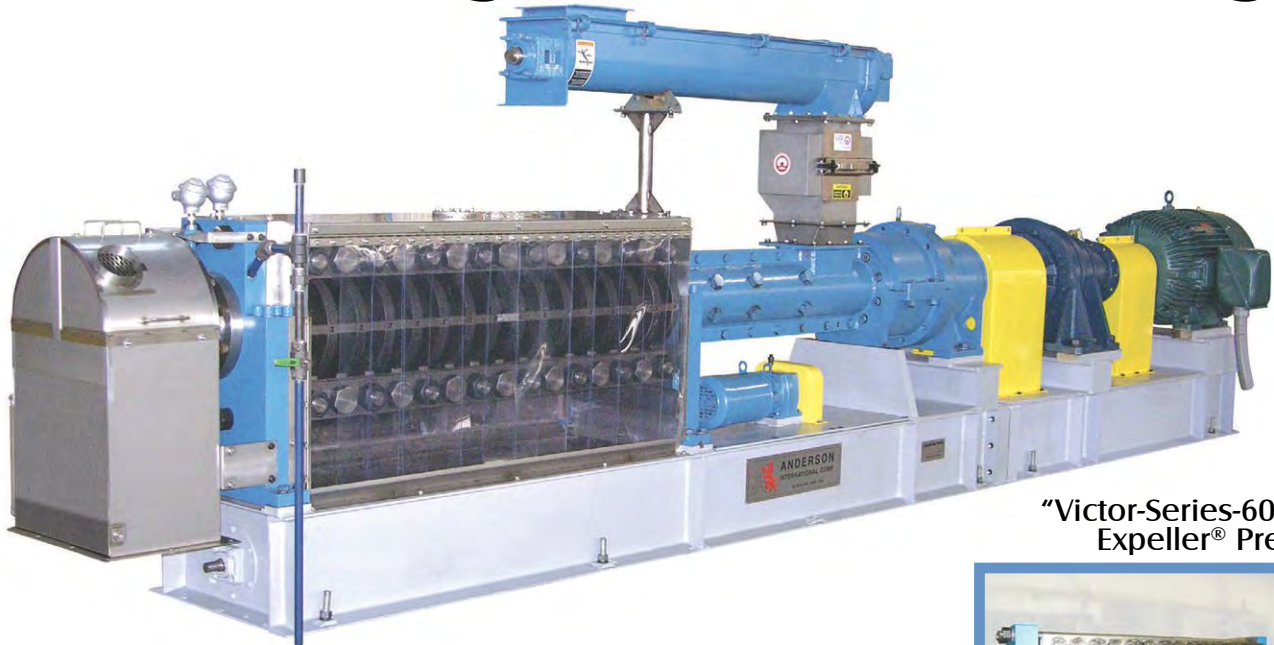
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Dick Ziggers (54) was the editor of All About Feed and other publications of Reed Business Media for many years. He was an expert in the field of agribusiness, especially animal nutrition and related industry. He was known for translating technical information into readable articles and providing fresh perspectives. Ziggers suddenly passed away in November 2012. This article was one of his last.

This article was originally published in the January 8, 2013, issue of All About Feed (<http://www.allaboutfeed.net/Home>). Reprinted with the permission of Reed Business Media.

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- Experts comment on new technique for separating fatty acids in vegetable oils
- Reference list for “Rice bran oil: nature’s healthful oil”
- Additional tables for “Rice bran oil: nature’s healthful oil”



Nanofiltration membrane technique for separating fatty acids in vegetable oils

Inform recently asked a roundtable of experts to comment on the ramifications of a research paper highlighted in this issue of News & Noteworthy (page 217). Douglas G. Hayes, a professor of biosystem engineering at the University of Tennessee, Knoxville, USA, contributed the summary of the paper, which is followed by comments from Hayes and our roundtable of experts.

SUMMARY

The research work by Gupta and Bowden of the University of Iowa, published recently in *ACS Applied Materials and Interfaces* (doi:10.1021/am3025867, 2013), presents transformative preliminary research that demonstrates membranes coated with high cross-linked polydicyclopentadiene can be used to separate a mixture of fatty acids based on degree of (*cis*-) saturation and fatty acyl position. Fatty acids are dissolved in solvent or solvent system (e.g., toluene+hexanes); the upstream side of the membrane is pressurized by N_2 to increase the permeation rate. The process includes complexation of the free fatty acids with a quaternary amine. Amine complexes of saturated and

trans-unsaturated fatty acids more readily permeate the membranes, while *cis*-unsaturated fatty acid complexes possess much slower permeability, with the permeability decreased by an increase of the degree of unsaturation and position of the double in proximity to the fatty acids' carbonyl group. The selectivity of the process is controlled by the "critical area" of the fatty acid-amine complexes, which are greatly affected by the "kinking" of the fatty acyl chain due to the *cis* double bonds. The chemistry of the alkyl groups attached to the amine can be modified to "tune" the selectivity; for example, the use of tri-isobutyl amine enhances separation of oleic (18:1-9c) and stearic acid (18:0), while tri-propyl amine enhanced separation of

oleic and linoleic (18:2-9c,12c). The recovery of fatty acid by this process is high; no fouling of the membranes is evident.

COMMENTS

Douglas G. Hayes, University of Tennessee, Knoxville, USA, offered this assessment:

The method of Gupta and Bowden separates free fatty acids with a similar selectivity as urea fractionation, i.e., discrimination against cis unsaturation, but with higher selectivity. In the near term, the approach has applicability in separations required for higher-value specialty products, such as purified omega-3 fatty acids (e.g., docosahexaenoic acid, DHA, and eicosapentaenoic acid, EPA). Perhaps this method will need to be combined with another separation step; for instance, a primary fractionation step such as molecular distillation would be employed first, followed by the membrane separation, the latter employed as a final, polishing, step.

Whether this approach is sufficiently robust to serve as a primary fractionation step for high-volume fatty acid separations remains to be seen. There are several obstacles that need to be overcome (as described in Ritter, S., Splitting Up Fatty Acids, Chem. Eng. News, 2/11/13, pp 37-38), particularly relating to the high cost of solvent removal and recycling, recovery and reuse of amines, and scalability. What is the minimum amount of solvent that can be used? What is the durability of the membranes? Are they easily fouled? Do minor components in the starting materials, such as oxidation co-products, hinder the performance? There is a lot of research needed along these lines: optimization of solvent system and complex-forming agent, membrane chemistry, operating temperature and pressure, cost analyses, etc. However, this novel technology has many additional potential applications: removal of unsaturated fatty acids during biodiesel preparation (perhaps enabled by replacing methanol as acyl acceptor by one which optimizes selective differences in "critical area" of molecules), removing of fatty acids from oils during refining, and fractionation of neutral lipids and perhaps their products during (bio)-chemical reactions. It will be very interesting to follow the development of this new technology in the years to come.

Doug Root, a senior scientist of biomass & renewable products at the Agricultural Utilization Research Institute in Marshall, Minnesota, USA, shared these thoughts:

The research report from the University of Iowa group is novel and important. Isolation of specific fatty acids or selected groups of fatty acids from vegetable oils could provide a doorway to increased uses of fats and oils for production of industrial chemicals.

The most thought provoking aspects of the research are the potential for industrial scale application and the control of separation efficiency and through-put via selection of a particular

amine and application of a selected pressure difference across the membrane. The degree of membrane cross-linking as well and the choice of membrane material are additional features that may be tailored to a particular separation or isolation task.

This research will almost certainly result in further exploration of systems of fatty acid:cation pairs for separations using a variety of nanoporous membranes. A considerable amount of additional research will be needed before pilot scale or industrial scale projects are considered, but this approach is new and encouraging.

Daniel Pioch, a process engineer of manufacturing bioproducts at CIRAD (Agricultural Research for Development) in Montpellier, France, sent these comments from the Laotian jungle, where he was participating in a cave exploration and discovery expedition. (His comments are based on the C&EN article about the research, as he could not access the original article from such a remote location.):

The industrial problem addressed by this group is a real challenge, because fat splitting under high temperature (and pressure) –the most widely used industrial process– is not suitable for unsaturated and very long chain fatty acids. Enzyme-based processes are not economically suitable for the targeted industrial outlet.

The process looks to suffer some limitations, like the use of amines (often additives in lubricants) and even more of a solvent. Unless they tell something about the kind of solvent (water, ethanol,) this does not look to be suitable for food applications. In addition, the recovery of the solvent and of the amine, could impede the economic viability of the process.

Membrane cost and resistance to solvent, plugging and effect of impurities from oil, life span, are of course topics to be considered that might hinder applications.

Also the way the process is described does not disclose the involved phenomena that could explain the selectivity. I am not convinced with the given explanation; placing the same big group on differing FA is not supposed to bring more selectivity by itself. I think that the abstract you plan to publish should talk a bit about the involved phenomena; these ammonium salts do have surfactant properties, and depending on the solvent etc, they could form micelles; therefore a physicochemical phenomenon could be involved, instead of a physical one shown by the author as an explanation.

In conclusion, the process looks attractive and could/should find interesting applications (maybe not among the listed examples; detergents properties are better when using mixed chain lengths).

CONTINUED ON NEXT PAGE

Laxman P. Naidu, a corporate planning manager at KA PVT LTD, noted the following on LinkedIn:

It's great news for oleo-chemical producers.

Eric Theiner, president and owner of LOGIC, Inc., in Allentown, Pennsylvania, USA, wrote:

In all facets of the industry, certain fatty acid chain length/configurations are generally more desirable than others. What appeals to me from a surfactant point of view is that higher value acids could be removed from raw stock. In this way the lower value acids become lower price as well, which helps to maintain cost competitiveness of renewable surfactants. Furthermore, the separation process allows the surfactant manufacturer to specify tighter constraints on fatty acid makeup, resulting in more control over the final product. This is an exciting development and I hope scale-up goes well for the process.

Randall Weselake, a professor of agricultural biotechnology at the University of Alberta in Edmonton, Canada, had the following reaction:

As we move towards a sustainable bioeconomy, the interest in using fatty acids for industrial applications will continue to increase. Plant oils often contain a mixture of fatty acid chains which can limit the industrial usefulness of the oils as a feedstocks for producing useful compounds. The nanofiltration membrane technique described by Abhinaba Gupta of the University of Iowa provides for a novel process to rapidly separate different molecular species of fatty acid-amine salts from each other thereby resulting in uniform feedstocks for industrial applications. The process appears to be amenable to scale-up. One of the attributes of castor oil is that it can contain over 90% of a single type of fatty acid, namely ricinoleic acid. This has contributed to the success of this oil in serving as a relatively uniform feedstock for many industrial applications including the synthesis of polyurethanes and high performance polyamides.

Alejandro G. Marangoni, a professor in the Department of Food Science at the University of Guelph in Ontario, Canada, offered the following opinion:

The report from Abhinaba Gupta and Ned B. Bowden from the Department of Chemistry at the University of Iowa is very exciting indeed. These authors developed a novel strategy to separate free fatty acids based on their conformation. At an industrial scale, fatty acid fractionation is usually carried out by molecular distillation (short-path distillation) or solvent fractionation. These separations are based on the boiling points or melting points of the individual fatty acids. Even though other strategies such as liquid chromatography, selective hydrolysis and urea complexation are also avenues to achieve separations, these last ones are not very amena-

ble to scale-up. Moreover, the ability to separate free fatty acids based on their molecular conformation is truly unique.

Gupta and Bowden propose to achieve this separation by using a polydicyclopentadiene nanofiltration membrane, which forms very specific "pores" (size and geometry). In a way, these pores are reminiscent, somewhat, to those formed by cyclodextrins. However, the membrane is half the trick! They then prepared bulky trialkylamine salts of the fatty acids. Being bulky now, these acid-base complexes are then slowed down during their passage through the nanopores, and separation was possible. Good separation between linear chains vs. kinked chains (i.e., stearic vs. oleic acids) was reported, which cis chains being slowed down more than linear chains. However, one can use one's imagination to think of possible separations of branched, polyunsaturated, long vs. short fatty acids as well.

The fact that it is an filtration-type technology means that it is amenable to scale-up. Negative points include the fact that one needs to use these amine salts and organic solvents. This limits the food applications of these fractionated fatty acids. However, one should not be too critical of this. Can we find some alternate amine salts to do the job? What about some phospholipids, or basic amino acids, or a peptide rich in lysine, arginine or histidine? One could possibly envision a "dry" version of the filtration process. One would have to deal with a very high viscosity and back-pressure, but a high temperature solution may be one way to go about it.

Regardless of the usual stumbling blocks that one always encounters when dealing with something novel and exciting, the conformation-based separation of fatty acids is an important step forward in our ability to separate/fractionate fatty acids and, who knows, triglycerides eventually.

Tong (Toni) Wang, a lipid professor at Iowa State University in Ames, USA, emailed these comments:

This paper presents a technique of separating fatty acid triisobutylamine salts using synthesized nanofiltration membrane based on polydicyclopentadiene (PDCPD). Because of the salt formation, there are increases both in the effective cross-sectional area of the molecules and in the magnitude of differences among different types of fatty acid salts, particularly between the saturated and unsaturated fatty acids. This leads to an effective separation of the saturates from the unsaturates.

Separation of saturated fatty acid from the unsaturated acids can be feasibly done on industrial scale by using molecular distillation of their methyl esters. This membrane separation study certainly adds another possibility for such separation. However, the most challenging separation is the effective and non-destructive (such as thermal polymerization and oxidation) separation of different types of unsaturated fatty acids, particularly those long chain polyunsaturates with desirable nutritional properties. Although this research does not show separation among these polyunsaturates, the concept of creating molecular adducts that have significantly different effective size may be further tested to achieve such membrane assisted separation of various fatty acids. ■

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Additional tables for Rice bran oil: nature's healthful oil

TABLE 5. Acylglycerol composition of crude, chemically and physically refined rice bran oils, and other commercial vegetable oils^{a,b}

Acylglycerols and TAG molecular species (relative %)	Crude rice bran oil	Chemically refined rice bran oil	Physically refined rice bran oil	Corn germ oil	Ground nut oil	Sunflower oil	Soybean oil
Monoacylglycerols + FFA	6.12	0.4	0.10	—	—	—	—
Diacylglycerols	3.88	5.46	10.52	—	—	—	—
Triacylglycerols							
LLnLn	—	—	—	—	—	1.61	—
LLLn	0.66	0.68	—	—	—	1.42	7.87
LLL	5.3	4.7	5.9	1.23	1.76	19.73	21.73
OLnL	0.96	1.13	0.04	—	—	—	3.44
OLL/LOL	10.6	10.5	10.4	14.61	10.57	27.81	14.74
PLL/LPL	10.6	10.4	10.9	0.54	2.49	9.92	16.36
POLn	0.28	0.37	—	—	—	—	—
OOL/OLO	11.80	12.20	12.10	18.21	18.27	18.11	6.97
PLO/POL	15.7	16.5	15.8	13.41	12.02	12.42	11.86
PPL/PLP	5.0	5.60	—	—	0.30	0.31	—
OOO	8.0	10.10	8.77	17.13	26.63	4.21	2.26
POO	11.60	12.20	11.20	18.72	16.79	4.33	5.31
POP	4.40	4.10	4.20	1.33	1.25	0.22	2.06
GOO	—	—	—	5.42	0.79	—	—
PPP	0.66	0.74	0.47	—	—	—	—
SOO	1.61	2.0	1.58	8.13	6.88	0.12	1.08
SPO/SOP	1.23	1.26	0.91	0.94	0.54	—	0.48
SPP	—	—	—	0.14	1.09	—	—
AOO	—	—	—	0.53	0.82	—	—

^aAbbreviations: A, arachidic acid; G, gadoleic acid; L, linoleic acid; Ln, linolenic acid; O, oleic acid; P, palmitic acid; S, stearic acid; FFA, free fatty acids; TAG, triacylglycerols.

^bSource: Gopala Krishna *et al.*, 2012.

TABLE 6. FSSAI standard for rice bran oil^a (Indian Standard)

Rice bran oil means the oil obtained from the layer around the endosperm of rice obtained from paddy of *Oryza sativa* Linn., FamilyGramineae, which is removed during the process of rice milling and is generally known as rice bran.

The oil shall be clear and free from rancidity, adulterants, sediments, suspended and other foreign matters, separated water and added coloring and flavoring substances. The clarity of the oil shall be judged by the absence of turbidity after keeping the filtered sample at 35°C for 24 hr. Rice bran oil shall be sold for human consumption only after refining. Refined rice bran oil shall be obtained from solvent-extracted oil, neutralized with alkali, bleached with bleaching earth or activated carbon or both and deodorized with steam. Alternatively, deacidification, bleaching and deodorization may be done by physical means. It shall conform to the following standards, namely:

Moisture and volatile matter	Not more than 0.1% by weight
Refractive index at 40°C	1.4600–1.4700
Butyro-refractometer reading at 40°C	51.0–66.4
Saponification value	18–195
Iodine value (Wij's method)	90–105
Acid value	Not more than 0.5
Unsaponifiable matter, % by weight	(i) For chemically refined, not more than 3.5%; (ii) For physically refined, not more than 4.5%; with oryzanol content not less than 1.0%
Flash point (Pensky-Martens closed cup method)	Not less than 250°C
Test for argemone oil	Negative
Hexane	5.00 ppm

^aReference: <http://tinyurl.com/IndianStandard>. Abbreviation: FSSAI, Food Safety and Standards Authority of India.

TABLE 7. Codex Alimentarius Commission standard for rice bran oil^a

Rice bran oil (rice oil) is derived from the bran of rice (<i>Oryza sativa</i> L.)	
Chemical and physical characteristics	
Relative density(20°C/water at 20°C)	0.910–0.929
Refractive index (n_D at 40°C)	1.460–1.473
Saponification value (mg KOH/g oil)	180–199
Iodine value (g I ₂ /100 g oil)	90–115
Unsaponifiable matter (g/kg)	≤65
Levels of desmethylsterols as a percentage of total sterols in crude rice bran oil	
Cholesterol	ND ^b –0.5
Brassicasterol	ND
Campesterol	11.0–35.0
Stigmasterol	6.0–40.0
β-Sitosterol	25.0–67.0
δ-5-Avenasterol	ND–9.9
δ-7-Stigmastenol	ND–14.1
δ-7-Avenasterol	ND–4.4
Others	ND
Total sterols (mg/kg)	10,500–31,000
Levels of tocopherols and tocotrienols in crude rice bran oil (mg/kg)	
α-Tocopherol	49–583
β-Tocopherol	ND–47
γ-Tocopherol	ND–212
δ-Tocopherol	ND–31
α-Tocotrienol	ND–627
γ-Tocotrienol	14–790
δ-Tocotrienol	ND–59
Total (mg/kg)	191–2349
Fatty acid composition (relative area percentage)	
C6:0	ND
C8:0	ND
C10:0	ND
C12:0	ND–0.2
C14:0	0.1–0.7
C16:0	14–23

CONTINUED ON NEXT PAGE

C16:1	ND–0.5
C17:0	ND
C17:1	ND
C18:0	0.9–4.0
C18:1	38–48
C18:2	29–40
C18:3	0.1–2.9
C20:0	ND–0.9
C20:1	ND–0.8
C20:2	ND
C22:0	ND–0.5
C22:1	ND
C22:2	ND
C24:0	ND–0.6
C24:1	ND

Other quality and composition factors

Matter volatile at 105°C	0.2% m/m
Insoluble impurities	0.05 % m/m
Soap content	0.005 % m/m (for refined rice bran oil)
Iron (Fe)	1.5 mg/kg (for refined rice bran oil) 5.0 mg/kg (for crude rice bran oil)
Copper (Cu)	0.1 mg/kg (for refined rice bran oil) 0.4 mg/kg (for crude rice bran oil)
Acid value	0.6 mg KOH/g oil (for refined rice bran oil) 4.0 mg KOH/g oil (for crude rice bran oil)
Peroxide value	Up to 10 meq of active oxygen/kg oil (for refined rice bran oil) Up to 15 meq of active oxygen/kg oil (for crude rice bran oil)

The γ -oryzanols in crude rice bran oil should be in the range of 0.9–2.1%.

^aReference: www.fao.org/docrep/004/Y2774E/y2774e04.htm#bm4.1. Codex Standard for Named Vegetable Oils, CODEX STAN 210-1999, adopted 1999, revisions 2001, 2003, 2009, Amendment 2005, 2011, pp. 1–16.

^bND, nondetectable

EXTRACTS & DISTILLATES

Wild edible fruits as a potential source of phytochemicals with capacity to inhibit lipid peroxidation

Morales, P., et al., *Eur. J. Lipid Sci. Technol.* 115:176–185, 2013.

The edible fruits of four wild small trees or shrubs (*Arbutus unedo*, *Crataegus monogyna*, *Prunus spinosa*, and *Rubus ulmifolius*) traditionally consumed in the Iberian Peninsula were studied to evaluate their potential for human nutrition, considering their content in bioactive compounds. Lipophilic phytochemicals, such as fatty acids and tocopherols, as well as some hydrophilic antioxidants, such as vitamin C and organic acids, were analyzed. In addition, the antioxidant activity, measured as lipid peroxidation inhibition (β -carotene/linoleate and thiobarbituric acid-reactive substance assays), was evaluated in each fruit. As far as we know, this is the first report relating to bioactive compounds in wild fruits with relation to the lipid peroxidation inhibition. Data revealed that these wild edible fruits are good sources of bioactive compounds such as organic acids, vitamin C, tocopherols, and polyunsaturated fatty acids. They could be considered as functional foods or potential sources of bioactive compounds with antioxidant synergism effect, to be included as antioxidant food ingredients or in dietary supplements, mainly *Rubus ulmifolius*, due to its high content in tocopherols. This study provides useful and relevant information that justifies tocopherol influence in the prevention of lipid peroxidation, due to the strong correlation observed ($r > 0.95$) between these lipophilic bioactive compounds and the antioxidant activity.

Enzymatic production of zero-*trans* plastic fat rich in α -linolenic acid and medium-chain fatty acids from highly hydrogenated soybean oil, *Cinnamomum camphora* seed oil, and perilla oil by lipozyme TL IM

Zhao, M.-L., et al., *J. Agric. Food Chem.* 61:1189–1195, 2013.

In the present study, zero-*trans* α -linolenic acid (ALA)- and medium-chain fatty acids (MCFA)-enriched plastic fats

were synthesized through enzymatic interesterification reactions from highly hydrogenated soybean oil (HSO), *Cinnamomum camphora* seed oil (CCSO), and perilla oil (PO). The reactions were performed by incubating the blending mixtures of HSO, CCSO, and PO at different weight ratios (60:40:100, 70:30:100, 80:20:100) using 10% (total weight of substrate) of Lipozyme TL IM at 65°C for 8 h. After reaction, the physical properties (fatty acids profile, triacylglycerol [TAG] composition, solid fat content [SFC], slip melting point, contents of tocopherol, polymorphic forms, and microstructures) of the interesterified products and their physical blends were determined, respectively. Results showed that the fatty acid compositions of the interesterified products and physical blends had no significant changes, while the content of MCFA in both interesterified products and physical blends increased to 8.58–18.72%. Several new types of TAG species were observed in interesterified products (SSL/SLS, PLO/LLS, and OLLn/LnLO/LOLn; where S = stearic; L = linoleic; P = palmitic; O = oleic; and Ln = linolenic). It should be mentioned that no *trans* fatty acids were detected in all products. As the temperature increased, the SFC of interesterified products was obviously lower than that of physical blends. The SFC of interesterified products (60:40:100, 70:30:100, and 80:20:100, HSO:CCSO:PO) at 25°C were 6.5%, 14.6%, and 16.5%, respectively, whereas the counterparts of physical blends were 32.5%, 38.5%, and 43.5%, respectively. Meanwhile, interesterified products showed more β' polymorphs than physical blends, in which β' polymorph is a favorite form for production of margarine and shortening. Such zero-*trans* ALA- and MCFA-enriched fats may have desirable physical and nutritional properties for shortenings and margarines.

Effects of garlic oil on milk fatty acid profile and lipogenesis-related gene expression in mammary gland of dairy goats

Zhu, Z., et al., *J. Sci. Food Agric.* 93:560–567, 2013

Garlic oil (GO) has blood lipid-lowering effects. Milk fatty acid (FA) originates partly from plasma and can be affected by the mammary lipogenesis. This study aimed to investigate GO effects on milk FA profile and mammary lipogenesis-related gene expression. Early-lactation goats were randomly allocated to four treatments with six goats each, and offered corn silage *ad libitum* and fixed amount of 0.79 kg day⁻¹ dry matter (DM) concentrate mixed with GO (0, 0.57, 1.14, 1.71 g kg⁻¹ DM) for 30 days consisting of 26-day adaptation. Intake of corn silage reduced ($P \leq 0.05$) as GO level increased in the concentrate. Lipase activity and lactose content linearly increased, while non-esterified FA concentration quadratically decreased with increasing GO level ($P \leq 0.05$). The proportions of short- and medium-chain (C14:0, C15:0, and C16:0) and saturated FA decreased, whereas C18, *cis*-9,*trans*-11 conjugated linoleic acid (*c9,t11* CLA), *t10,c12* CLA, monounsaturated and polyunsaturated FA,

and some $\geq C20$ FA proportions increased in a linear manner with increasing GO level ($P \leq 0.05$). The mRNA abundance of genes remained unchanged ($P > 0.1$) as GO level increased. Garlic oil altered milk FA profile, and these effects may not be related to the mammary lipogenesis-related genes expression.

Lipase activity, mesocarp oil content, and iodine value in oil palm fruits of *Elaeis guineensis*, *Elaeis oleifera*, and the interspecific hybrid $O \times G$ (*E. oleifera* \times *E. guineensis*)

Cadena, T., et al., *J. Sci. Food Agric.* 93:674–680, 2013

One factor affecting crude palm oil quality is the formation of free fatty acids (FFA), often attributed to the hydrolytic action of mesocarp lipase. The aim of this work was to evaluate the enzyme behavior and to look toward new genotypes with low FFA production, high yield, and better oil quality. Lipase activity was strongly activated at low temperatures (5°C). At this temperature PLL, SOO, POL, and POO (P, palmitic; L, linoleic; S, stearic; O, oleic) were the most hydrolyzed triacylglycerols in *Elaeis guineensis* fruits. Ethylene production decreased from $36 \text{ nL g}^{-1} \text{ h}^{-1}$ at room temperature to $2 \text{ nL g}^{-1} \text{ h}^{-1}$ at 5°C . Lipase activity of *E. guineensis*, the *E. oleifera* \times *E. guineensis* ($O \times G$) hybrid, and *E. oleifera* were 52.7%, 32.9%, and $<0.6\%$ FFA, respectively. The *E. guineensis* showed oil in the mesocarp of 54.7%, followed by the $O \times G$ hybrid (47.0%), and *E. oleifera* (13.6%), and the iodine values were 52.0, 66.3, and $77.4 \text{ g I}_2 (100 \text{ g})^{-1}$, respectively. This work allowed the identification of interspecific $O \times G$ hybrids as promising crosses with less lipase activity and higher iodine value than *E. guineensis*. Although $O \times G$ crosses produce less oil in the mesocarp than commercial *E. guineensis*, this feature could be improved by further breeding to introduce new genes from *E. oleifera* into the hybrids.

Inconsistencies in a highly polar capillary gas chromatography column and necessity of column performance checks for *trans* fatty acid measurement

Tsuzuki, W., *J. AOAC Int.* 95:1740–1743, 2012

Gas chromatography with a capillary column (60–100 m length) is widely used to measure *trans* fatty acids in dietary fats and biological tissues. Recently, we have occasionally observed that isothermal operation of an SP-2560 column at 180°C results in incomplete separation of gondoic acid (11c-20:1) and one of the geometric isomers of α -linolenic acid

(9t,12c,15c-18:3), although it has been known to produce their baseline separation in American Oil Chemists' Society Official Method Ce 1h-05, as well as in previous studies. Thus, *trans* isomer (9t,12c,15c-18:3) is one of the main components of *trans* fatty acids in refined edible oils, and the baseline separation of this peak from that of 11c-20:1 is indispensable. We demonstrate in this study that an isothermal operating temperature of 175°C for an SP-2560 column results in satisfactory resolution of these two fatty acids. Because of the inconsistency in the separation provided by SP-2560 columns, careful monitoring of the relative elution order of different fatty acid methyl esters using standards is necessary for the exact evaluation of *trans* fatty acid contents in oils and fats.

Influence of dairy product and milk fat consumption on cardiovascular disease risk: a review of the evidence

Huth, P.J., and K.M. Park, *Adv. Nutr.* 3:266–285, 2012

Although evidence has linked the consumption of saturated fat (SF) to increased low density lipoprotein (LDL) levels and an increased risk of the development of cardiovascular disease (CVD), recent findings have indicated that the link between CVD and SF may be less straightforward than originally thought. This may be due to the fact that some food sources high in SF contain an array of saturated and unsaturated fatty acids, each of which may differentially affect lipoprotein metabolism as well as contribute significant amounts of other nutrients, which may alter CVD risk. The purpose of this review is to examine the published research on the relationship between milk fat-containing dairy foods and cardiovascular health. The findings indicate that the majority of observational studies have failed to find an association between the intake of dairy products and increased risk of CVD, coronary heart disease, and stroke, regardless of milk fat levels. Results from short-term intervention studies on CVD biomarkers have indicated that a diet higher in SF from whole milk and butter increases LDL cholesterol when substituted for carbohydrates or unsaturated fatty acids; however, they may also increase high density lipoprotein (HDL) and therefore might not affect or even lower the total cholesterol/HDL cholesterol ratio. The results from the review also indicate that cheese intake lowers LDL cholesterol compared with butter of equal milk fat content. In addition, the review highlights some significant gaps in the research surrounding the effects of full-fat dairy on CVD outcomes, pointing to the need for long-term intervention studies. ■