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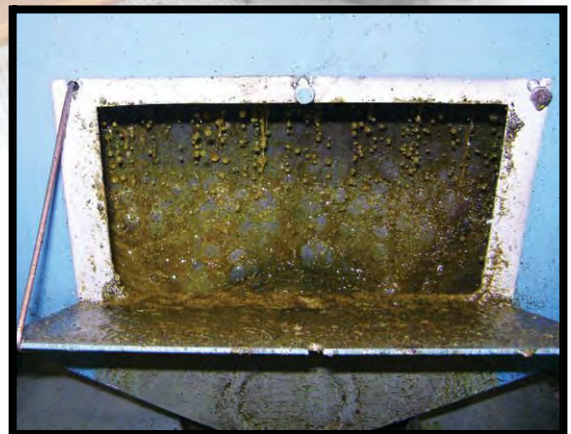
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JULY/AUGUST 2013

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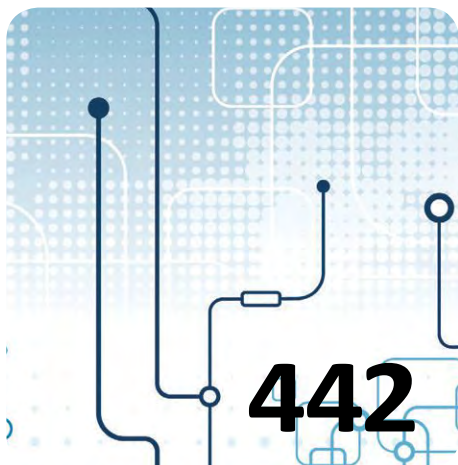
With more than 600 technical presentations, 80 exhibitors, and 210 posters, the 104th AOCS Annual Meeting & Expo (AM&E) in Montréal, Canada, stretched the limits of what's technically and commercially possible in fats and oils chemistry. Relive it or experience it for the first time through *Inform's* extensive coverage and supplementary photo tour, available via the new *Inform* app. Go to <http://bit.ly/informapp>.

454 Structure: the ultimate expression of nature's complexity

Alejandro G. Marangoni, the 2013 Stephen S. Chang Award winner, explains how microscopy plays a central role in developing an understanding of the relationships between molecular composition and phase behavior, solid state structure, growth mode, static and dynamic structure, external fields, and macroscopic properties that can contribute to the engineering of fat and oleogel structure.

460 Plant oils: the perfect renewable resource for the chemical industry?!

Michael Meier, the 2013 AOCS Young Scientist Research Award winner, describes how new developments in catalysis and efficient chemical functionalization protocols are making it possible to synthesize novel fatty acid derivatives from plant oils that are especially interesting for polymer chemistry.

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2013 AOCS Annual Meeting & Expo stretches the limits

Kathy Heine

Beautiful spring weather, cobblestone streets, French bistros, the Notre-Dame Basilica . . . the 104th AOCS Annual Meeting & Expo in Montréal, Canada, April 28–May 1, was a little like April in Paris—only it was on the banks of the Saint Lawrence River instead of the Seine. Granted, there was no view from the Eiffel Tower, but with 600 technical presentations,

an Expo showcasing the novel technologies of more than 80 international companies, and six Forum on Emerging Technologies sessions that addressed critical issues impacting fats and oils, the Palais des congrès de Montréal offered the meeting's nearly 1,500 attendees a comprehensive view of the industry they will never forget.

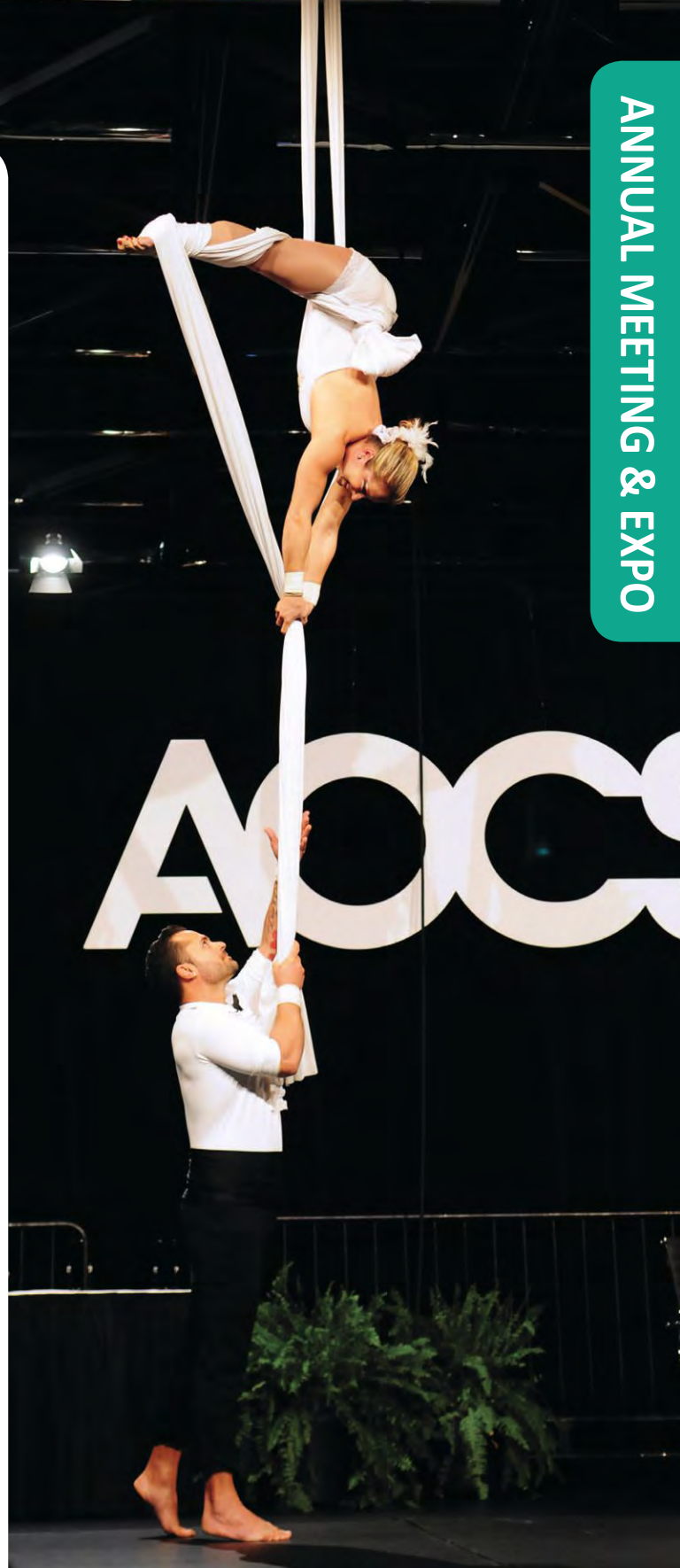
The energy and excitement that developed during the short courses on Saturday and the division meetings and Opening Mixer on Sunday grew with each subsequent event. The Newcomer Speed Networking event drew so many attendees that one chair after another had to be added; the Annual Student Common Interest Group (CIG) Silent Auction raised almost \$6,000 for student programs; and the Forum on Emerging Technologies session that offered helpful strategies for dealing with recent changes in US patent law struck such a chord that a line formed for individual questions after the session.

Guests at the AOCS Annual Business Meeting/Luncheon on Monday were not only treated to the traditional passing of the gavel and presentation of the Award of Merit, AOCS Fellows, and Corporate Achievement awards. They also learned about the new technology platform AOCS is building in 2013 to expand knowledge and networking opportunities and help AOCS grow. Many were not aware that the information management platform AOCS uses to run the society was installed almost 15 years ago. "Can you imagine trying to run your business with a technology platform from 1999?" AOCS CEO Patrick Donnelly asked. "We must upgrade our technology platform. We simply don't have an option."

When the business portion of the meeting ended, two aerial specialists from the local company Cirque Carpe Diem pushed the limits of human physics by performing a series of gravity-defying acrobatics on two silk drapes suspended from the ceiling. It was a difficult act to follow, but followed it was by a chance to socialize over bite-sized Napoleans, tarts, cheesecakes, and *genoise* at the Sweet Retreat in the Expo Hall before attendees headed into the afternoon technical sessions.

This year's technical sessions were a virtual three-day *dégustation* of presentations by researchers and business leaders who, like the trapeze artists of Cirque Carpe Diem, were stretching the limits of what's technically and commercially possible in fats and oils chemistry. Attendees learned about algal oils that are stable after 10 days of frying (and even longer if tocopherols are added); a zero-waste process for extracting palm oil with ultrasound; the first quantification and separation of fatty acids in marine oils; a process for making biodiesel with enzymes that tolerates the presence of water; a one-step method for lipid extractions from food samples and animal tissues that requires no pipetting, no centrifugation, no solvent measurement, and is four times faster and significantly less expensive per sample than the

CONTINUED ON NEXT PAGE



TOP: The AOCS Annual Business Meeting/Luncheon featured a captivating aerial performance by the Montréal-based company Cirque Carpe Diem.

OPPOSITE PAGE: The 2013 Annual Meeting & Expo was held at the colorful Palais des congrès de Montréal, within walking distance of the Saint Lawrence River and Old Port, as well as the historical district of Old Montréal.



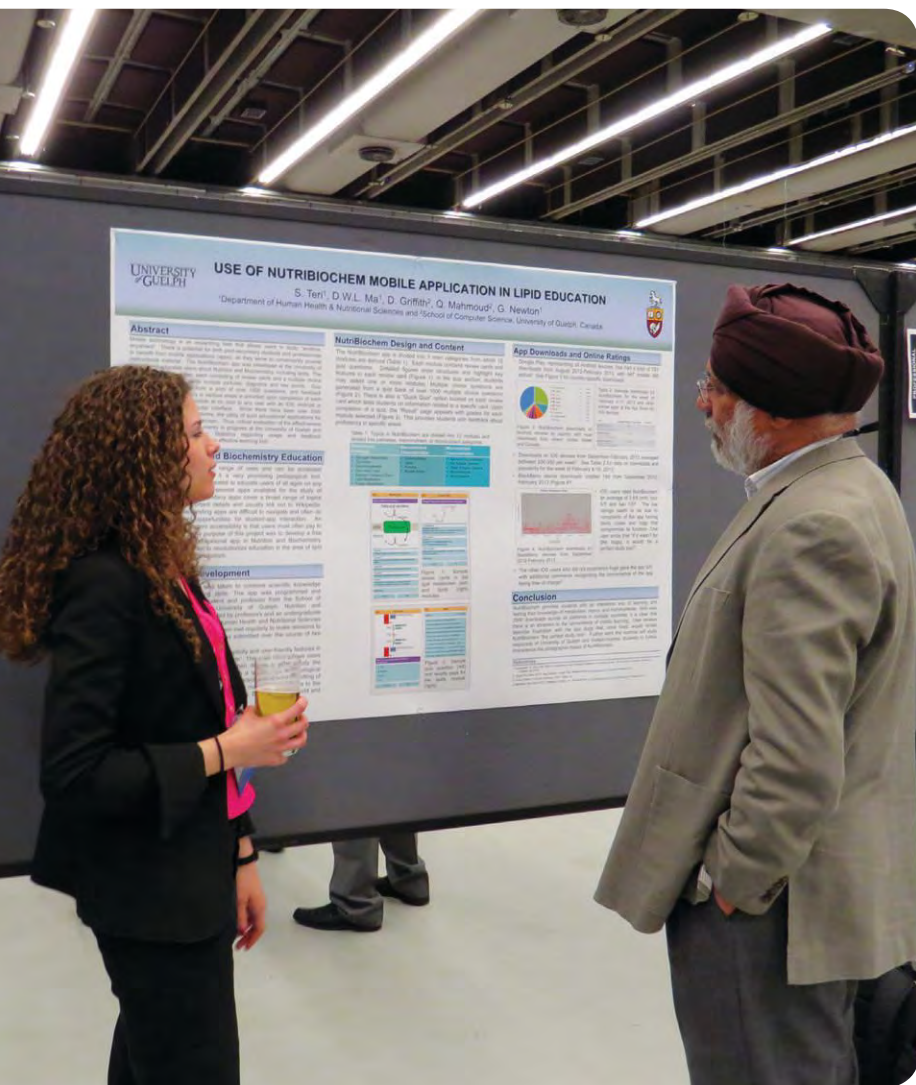
conventional Folch method; and ice creams that are still intact after sitting at room temperature for more than an hour!

Those who attended the Awards Plenary and Recognition saw the first example of a polymer oleogel of triglyceride oils that could potentially be used to stabilize fat-structured materials at high temperatures and to replace animal fat in meat products (see article on page 454) and heard about novel fluid nano delivery vehicles for enhanced and targeted release of nutraceuticals.

Newcomers who had never attended an AOCS Annual Meeting and Expo before were quickly won over by the value of live interaction with colleagues in the same interest area. It was a chance to meet that often cited author face-to-face, to shake hands with a distinguished award winner, to discuss the state of the industry with corporate professionals over a glass of beer, or to establish ties with other new professionals who are doing similar work within different organizations. Scheduled events for newcomers, such as the Newcomer Speed Networking on Sunday evening, the New Professionals Networking on Monday afternoon, the Career Fair on Tuesday that gave job seekers a chance to meet with seven hiring companies, and the Student Common Interest Group Meeting and Mentoring luncheon on Wednesday that attracted approximately 100 participants, provided plenty of opportunities for newcomers.

Those who wanted to attend the meeting but could not were able to follow the proceedings from afar via AOCS's extensive Twitter coverage, which gained 24 followers and was "favorited" by StudentEnergy, a global non-profit organization that is creating a movement of young leaders committed to transitioning the world to a sustainable energy future. Several followers tweeted that they have already marked their calendars to attend the 105th AOCS Annual Meeting & Expo, in San Antonio, Texas, May 4–7, 2014. See y'all there!

Kathy Heine is managing editor of Inform. She can be contacted at kheine@aocs.org.

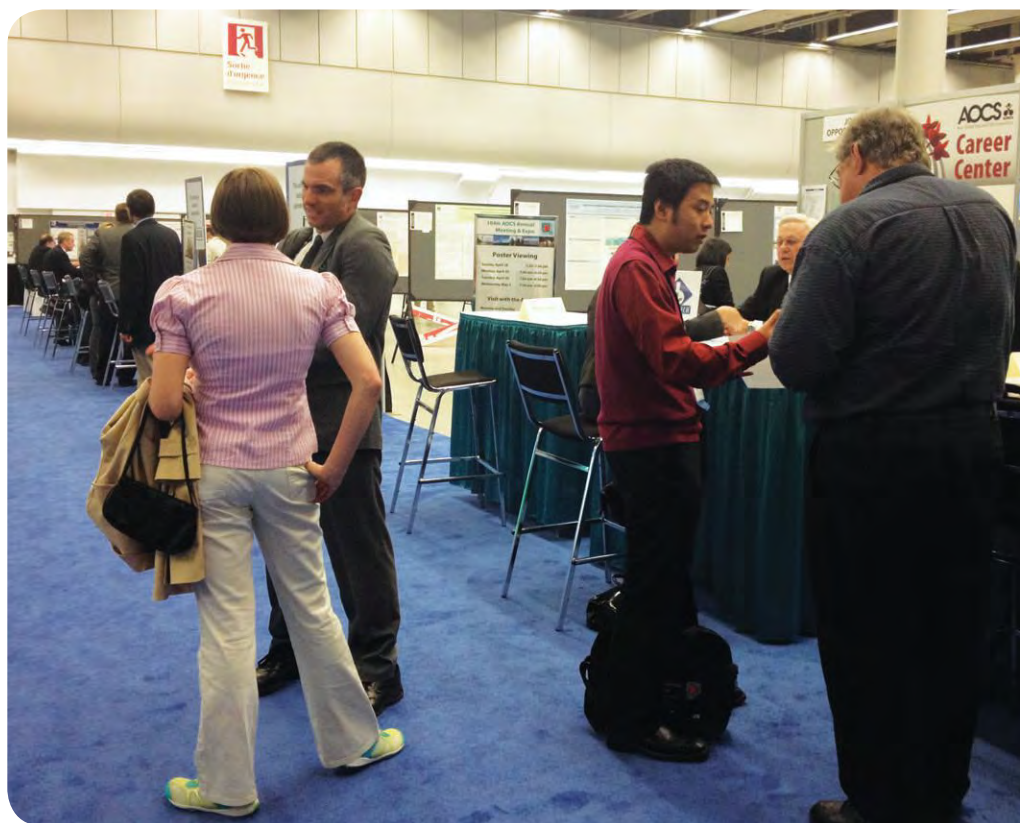


BOTTOM:

The meeting featured a total of 210 posters, which attendees could view and discuss with one another over refreshments during the Opening Mixer on Sunday and Networking Receptions on Monday and Tuesday evening.

TOP:

Almost 1,500 people from 47 countries attended the 104th Annual Meeting & Expo, where more than 80 international companies exhibited the latest fats- and oils-related technologies and equipment.



TOP:

About 70 donors contributed 110 items to the Annual Student Common Interest Group (CIG) Silent Auction, which raised almost \$6,000 to support AOCs student programs. One of the more interesting items was an encaustic painting of a soybean made using vegewax, which was featured in the July/August 2012 issue of *Inform* 23:473–474.

LEFT:

Representatives from seven hiring companies met with job seekers during the Career Fair.



**TOP:**

Attendees could choose from among nearly 600 technical presentations on topics covering everything from the industrial applications of surfactants to the food applications and nutritional aspects of algal oil. The most popular sessions were standing room only.

RIGHT:

The gavel was passed to incoming AOCS President Timothy G. Kemper. In his first address as President, Kemper spoke of how WiFi, smart phones, tablets and other technologies allow today's professionals to communicate globally in real time. As more of the world's knowledge becomes instantly available, AOCS can either turn its head away from change and stick to tradition or "we can embrace this change, ride the wave, and grow as an even more impactful society," he said.

OPPOSITE PAGE, BOTTOM:

During the Annual Business Meeting/Luncheon, AOCS' CEO Patrick Donnelly explained that AOCS must upgrade its technology platform to realize the growth it needs to thrive in the future. He then asked the audience if they would consider a gift of \$25 to help with the upgrade, and he sweetened the pot by offering donors a chance to win a new iPad. AOCS members responded by pledging more than \$6,000.





More complete photographic coverage of the meeting can be found via the new *Inform* app. Go to <http://bit.ly/informapp>.



TOP:

AOCS Fellow Steven E. Hill (left) presented Alejandro G. Marangoni (right) with the jade galloping horse, a symbol of progress presented each year to the winner of the Stephen S. Chang Award. Marangoni, Professor and Tier 1 Canada Research Chair in Food, Health, and Aging at the University of Guelph, Canada, is the 22nd recipient of the award, established by AOCS Past President Stephen S. Chang and his wife, Lucy D. Chang. Marangoni is internationally recognized for his work in food chemistry and physics, particularly as it relates to lipid structure and functionality. In 2012 he was named among the “10 Most Influential Hispanic Canadians” by Guillermo Rishchynski, Canada’s ambassador to the United Nations. An article based on his award presentation, “Structure: the ultimate expression of nature’s complexity,” appears on page 454.

**TOP:**

Michael A.R. Meier, a professor at the Karlsruhe Institute of Technology in Germany (left), received the 2013 Young Scientist Research Award. The award, which is sponsored by Vijai K.S. Shukla and the International Food Science Centre A/S of Denmark, recognizes a young scientist who has made a significant and substantial research contribution in one of the disciplines represented by AOCS Divisions. Meier's scientific work in the area of lipid polymer chemistry has been published in more than 100 original publications and review articles. He is pictured here with AOCS President Timothy G. Kemper. An article based on Meier's award presentation—"Plant oils: the perfect renewable resource for the chemical industry?!"—appears on page 460.

**RIGHT:**

Is there room for one more? So many people joined the Newcomer Speed Networking event that they had to squeeze in shoulder-to-shoulder.





Nissim Garti, The Ratner Chair of Chemistry, Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, Israel (left), was this year's winner of the Supelco/Nicholas Pelick-AOCS Research Award. The award—given to honor significant original contributions in fats and oils research—is sponsored by Pelick and Supelco, Inc., a subsidiary of Sigma-Aldrich Corp. Garti is internationally recognized for his development of novel lipid-based fluid nano delivery vehicles for enhanced and targeted delivery of drugs and nutraceuticals. He is pictured with Leonard Sidisky of Supelco, Inc.

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A Joint World Congress with the Japan Oil Chemists' Society

Bunge North America has opened a new packaging facility at its expanded refinery in Decatur, Alabama, USA. The plant produces soybean-based salad oils, shortenings, and specialty blends for food processing and foodservice customers, Bunge said, as well as for bakeries and confectioners. The facility is one of Bunge's two integrated crush, refining, and packaging plants.

■ ■ ■

Major rice bran oil (RBO) producers met in Thailand in May 2013 and agreed to form an international organization "to create awareness among edible oil consumers across the world about the health-related advantages of using RBO." The decision to form the group was made during a conference on rice bran oil at Naresuan University of Thailand. Delegates from a number of RBO-producing countries, including Japan, Thailand, India (the largest producer), China (the second-largest producer), and Vietnam participated. News about the founding of the organization was released by the Solvent Extractors' Association of India; no further details were announced.

■ ■ ■

Russia will invest about 42 billion rubles (\$1.4 billion) to develop that country's aquaculture industry by 2020, according to a statement on Russia's government website. The investment will be in the form of loans and subsidies for producers. Aquaculture production in Russia "has increased significantly over the past two years, from 134,000 metric tons (MT) in 2011 to a projected 200 MT in 2013," according to allaboutfeed.com.

■ ■ ■

The US Food and Drug Administration has released a software program designed to help owners and operators of food facilities—ranging from primary production and manufacturing to retail and transportation—to develop customized plans to minimize the risk of intentional contamination at their plants. The Food Defense Plan Builder guides users through a series of questions in order to develop a food defense plan for their facilities, including a vulnerability assessment, broad and focused mitigation strategies, and an action plan. To download the tool free of charge, visit www.fda.gov/food/fooddefense. ■

NEWS & NOTEWORTHY



Indirect methods for 3-MCPD/GE validated

AOCS' Technical Department recently completed a collaborative study to compare various direct and indirect methods of detecting mono- and di-esters of both 3-MCPD and glycidol (GE) in vegetable oils.

Fatty acid esters of 3-monochloro-1,2-propanediol (3-MCPD) and glycidol (2,3-epoxy-1-propanol) are potentially carcinogenic process contaminants generated during the production of vegetable oil, most probably during deodorization. Development of a validated direct method became a priority following the 2009 announcement by Germany's risk assessment agency that esters of 3-MCPD and glycidol were a possible safety risk.

In May 2012, AOCS and the Japan Oil Chemists' Society (JOCS) released the first validated direct method for GE in edible oils, AOCS/JOCS Official Method Cd 28-10. The joint method determines GE in edible oils using two solid-phase extraction steps and liquid chromatography-mass spectrometry.

Results of the most recent collaborative study were presented to the AOCS Expert Panel on Process Contaminants on Tuesday,

April 30, 2013, at the 104th AOCS Annual Meeting & Expo (AM&E). This study compared three indirect methods and found that all of them performed well in analyzing standards with a range of 3-MCPD mono- and diesters and GE. Users of AOCS Cd 28-10 were also able to demonstrate the continued reliability of this method.

Also at the AM&E, the AOCS Uniform Methods Committee agreed that the three indirect methods validated for the analysis of esters of 3-MCPD and glycidol by the collaborative study will begin moving through the AOCS method development process for eventual designation as official methods.

The three indirect methods tested were developed by Unilever, SGS, and the German Society for Fat Science (DGF). Further work on them and other research pertaining to process contaminants were presented at an analytical session during the meeting. Among the presentations:

- Shaun MacMahon of the US Food and Drug Administration examined the detection of GE and several species of esters of MCPD in edible oils by liquid chromatography tandem mass spectrometry (LC-MS/MS).

CONTINUED ON NEXT PAGE

- Karel Hrnčirik of Unilever spoke about the analysis of intact fatty acid esters of glycidol in vegetable oils using gas chromatography-mass spectrometry (GC-MS). The method consists of a simple extraction of GE from the lipid matrix, purification via liquid-liquid extraction, and isolation of GE by normal-phase LC.
- Alessia Ermacora, who was an Analytical Division student award winner for her work with Hrnčirik at Unilver, discussed progress in the analysis of MCPD esters and GE from refined oils to oil-based foodstuffs. A method for the simultaneous determination of MCPD esters and GE developed in the Unilever laboratory "can be successfully applied to the analysis of both bulk oils/fats and, for the first time, also various fat-based products," she said.
- Hirofumi Sato of Japan's Osaka Municipal Technical Resarch Institute examined the interconversion between monochloropropanediols and glycidol in the use of DGF Standard Method C-VI 18 (10).
- Michael Granvogl of the German Research Center for Food Chemistry compared the stability and reactivity of esters of glycidol, 2-, and 3-MCPD to free glycidol and free 2- and 3-MCPD.
- Thomas Wenzl of the Joint Research Centre (JRC) of the European Commission discussed a JRC comparison study on direct and indirect methods for the detection of GE and MCPD esters in edible oils.

For more information about the Expert Panel on Process Contaminants or the latest collaborative study, contact Richard Cantrill, AOCS chief science officer and director of Technical Services (rcantrill@aoocs.org).

BASF unveils new catalysts, bleaching clays

BASF Corp. (Iselin, New Jersey) announced several additions to its portfolio of catalysts and adsorbents at the recent 104th AOCS Annual Meeting & Expo in Montréal, Québec, Canada.

Two new highly activated calcium bentonite bleaching clay products were introduced: Grade F 76 and Grade F 72 FF. The bleaching clays are acid-activated using sulfuric acid with improved dispersion characteristics and deliver enhanced bleaching efficiency for all types of oil tested, according to BASF. The clays allow for an overall lower dosage for better adsorption characteristics, added Melissa L. Marchese. Marchese is the company's global business manager, catalysts and adsorbents for oleochemicals.

The company also introduced two new hydrogenation catalysts: Nysosel 880 (for edible oils) and Nysofact 125 (for fatty acids). These precipitated nickel droplet solutions offer flexibility to the customer, because less nickel is required. Therefore, using

CONTINUED ON PAGE 420







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SUSTAINABILITY WATCH

The Hershey Co. (Hershey, Pennsylvania, USA) set a goal in October 2012 of sourcing 100% of its chocolate from sustainable cacao farms by 2020 and set benchmarks for this mission in March 2013 with the “21st Century Cocoa Plan.” Hershey’s self-imposed milestones come as a result of criticism from nongovernmental organizations that the company has not done enough to promote sustainable cacao farming.

The plan outlines three sustainability goals for certified sustainable cacao supply—10% sustainable supply by the end of 2013, 40–50% by the end of 2016, and 100% by 2020. The company plans to invest \$10 million toward cacao farms sustainability by 2017, which is another initiative the company began in 2012.

Other objectives of the “21st Century Cocoa Plan” include:

- Expanding the CocoaLink program, which sends text messages to farmers containing information on sustainable farming;
- Funding the Hershey Learn to Grow farmer and family development center to aid in cacao tracing and certification; and
- Continuing the Mexico Cocoa Project, which started in 2012 as a 10-year initiative to reintroduce cacao growing in southern Mexico and restore the country’s cacao crop

■ ■ ■

Sunflowerseed husks, a huge waste product of the vegetable oil and food industry, could be used as an environmentally friendly filler, or aggregate, for concrete according to Turkish researchers writing in the *International Journal of Environment and Waste Management* (12:203–212, 2013). The team demonstrated that the use of husks reduces the density of concrete as well as boosting the material’s resistance to cracking after exposure to icy then thawing conditions.

Engineers Can Burak Sisman and Erhan Gezer of Namik Kemal University in Turkey, explain how the accumulation of unmanaged wastes from the food industry, particularly in

developing countries, is becoming increasingly problematic. As such, researchers are hoping to find new applications for such waste in the creation of environmentally friendly materials and composites in the road-building and construction industries. This is particularly pertinent given the rising cost and chronic shortages of conventional materials. Engineers are thus being challenged to convert industrial wastes into replacements for certain materials.

Concrete is perhaps one of the most energy- and resource-intensive materials and researchers have investigated and applied waste rubber, glass powder, and paper waste sludge as alternative fillers and bulking agents. The addition of such materials can significantly affect the properties of concrete, altering its strength, density, and water resistance detrimentally in some instances.

The team has turned to the sunflowerseed, and more specifically to its inedible husk, as a possible alternative material for concrete. Turkey is the ninth-largest sunflower producer in the world, generating almost a million metric tons (MT) of product from 584,000 hectares (more than 14 million acres), the bulk of which is used in the manufacture of sunflower oil in the Thrace region. The by-product is approximately 300,000 MT of fibrous seed husk. The team has therefore experimented with different formulations of seed husk in a concrete mix.

They produced concrete samples with a density of around 2,000 MT/cubic meter; the lowest density could be classified as “lightweight.” Some samples had low compressibility, which is suitable for use in construction, although higher husk content meant the resulting concrete could be used only for insulation applications. The team suggests that the sunflowerseed concrete would be most suitable for the construction of agricultural buildings that are usually only one floor and do not need to be as sufficiently load bearing as domestic or office buildings.

■ ■ ■

The European Commission announced in early May 2013 that it will institute a two-year ban on three neonicotinoid pesticides in order to protect honeybees. The action came despite the inability of member states to reach a majority for or against the ban. The restrictions on clothianidin, imidacloprid, and thiamethoxam will go into effect in December 2013. Bayer CorpScience, manufacturer of clothianidin and imidacloprid, called the action “a setback for technology, innovation, and sustainability,” adding that “clear scientific evidence has taken a backseat in the decision-making process.” ■

the same nickel dosage as in the past will lead to a shorter reaction time.

"If you are completely constrained in production," Marchese suggested, "you can reduce your cycle time and get an increase in capacity. They can be used for higher throughput or, essentially, to debottleneck without an additional capital investment."

Alternatively, the same reaction time can be achieved with a smaller nickel dosage. The third possibility is to use the same nickel dosage for the same reaction time at a lower temperature, which will lower the amount of *trans* fats produced, she said.

Arkema forms castor JV

France's Arkema specialty chemical company is forming a joint venture (JV) with castor oil and derivatives producer Jayant Agro-Organics Ltd. of Mumbai, India. Arkema also recently acquired a 25% stake in Jayant's Mumbai-based subsidiary and castor oil producer Ihsedu Agrochem. Arkema remains one of the leading consumers of castor oil for the manufacture of polyamides (PA) 10 and 11, Doris de Guzman's Green Chemicals Blog (greenchemicalsblog.com) notes.

The company has been for almost 60 years the sole producer of PA11 under the Rilsan brand. "Last year, Arkema bought China-based Hipro Polymers, a producer of PA10, and Casda Biomaterials, a producer of sebacic acid (a derivative of castor oil and feedstock for PA10)," de Guzman said. Sebacic acid is used as a feedstock to manufacture PA10.

The JV is expected to be final by the third quarter of 2013.

European crush declines

The oilseed crush in the European Union (including rapeseed, sunflowerseed, and soybeans) will decline in coming months as the bloc's stockpiles shrink and imports decline from South America, according to Oil World market analysts.

Rapeseed processing in the EU-27 may reach almost 6.4 million metric tons (MMT) through the end of June 2013, which is 7.9% less than at the same time last year. Most of the decrease will be in Germany and France, the Hamburg-based researchers said. In the first eight months of the 2012–2013 marketing year, which began July 1, 2012, rapeseed crushing increased by 5.4% from a year earlier to almost 15.6 MMT. But stockpiles of rapeseed in the EU in early March were 800,000 MT smaller than in 2012, the Oil World report said.

The EU is the second-largest importer of soybeans, after China, and the third-largest producer and user of sunflowerseed, after Ukraine and Russia, according to the US Department of Agriculture.

The EU-27 soybean crush in February 2013 was 940,000 MT, down from 950,000 tons in the same month in 2012 and compared with a 12% annual jump in processing in January, the report noted. Lower supplies in South America, where logistical problems have delayed shipments, "decimated" the EU crush in February and March.

Supplies of soy meal have tightened "significantly," Oil World said, primarily because of delayed shipments of meal from South America. "Supply relief can only be expected in the European



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Union from the end of May or early June onward. Argentine and Brazilian soybean crushings were unusually small until March but have reportedly started to recover pronouncedly in April.”

The sunflowerseed crush, according to Oil World, totaled just over 1 MMT in January and February in the EU, down 16% from last year, bringing the total processed since August to almost 4 MMT, which is 10% less than the previous season. The estimated crush from March through July is 2.2 MMT, or 200,000 MT below this period last year.

Table 1. Fatty acid profile of two *Plukenetia* species^a

	<i>Plukenetia huayllabambana</i>	<i>Plukenetia volubilis</i>
Fatty acids	%	%
Saturated	5.6	7.3
Palmitic acid (16:0)	4.21	4.3
Stearic acid (18:0)	1.39	3
Monounsaturated	9	9
Oleic acid (18:1n-9)	9	9
Polyunsaturated	86.4	76.8
Linoleic acid (18:1n-6)	25.11	32.1
α -Linolenic acid (18:2n-3)	61.29	44.7

^aSource: R. Bussmann.

Researchers strike oil in Peruvian jungle

In August 2012, two researchers struck oil in a farmer's garden deep in the Peruvian Amazon. There, they found a plant that resembled the sacha inchi species (as Peruvians call the family) known formally as *Plukenetia volubilis* and *Plukenetia huayllabambana*, both of which are rich in α -linolenic acid (ALA; 18:3n-3). (“Sacha inchi” translates to “forest peanut.”)

The new plant, named *Plukenetia carolis-vegae*, is bigger and has larger seeds than its vegetal cousins. Its discoverers—Rainer W. Bussmann and Carlos Vega—hope to see it become a “conservation crop” that can grow in the shade beneath the forest canopy, without destruction of the rainforest itself.

Bussmann, an ethnobotanist at the Missouri (USA) Botanical Garden in St. Louis, and his group discovered *P. huayllabambana* in 2008 in the same area of the Peruvian Amazon. Vega is head of the Institute for Sustainable Local Development and Andean Amazon Cultural and Biological Conservation in Trujillo, Peru.

“We only have the [fatty acid] profile for *Plukenetia huayllabambana* so far,” Bussmann told *Inform*, adding “we still need to test *P. carolis-vegae*.” A comparison of *P. huayllabambana* and *P. volubilis* (see Table 1) shows levels of ALA that are similar to flax/linseed (35–66%) and chia (63–69%).

Bussmann told www.emaxhealth.com that oil from the *Plukenetia* plants has a nutty green taste “evoking the flavors of peanut and cucumber.” ■



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According to research funded by the United Soybean Board through soybean checkoffs in the US states of Minnesota, Nebraska, North Dakota, and South Dakota, biodiesel made from soybean oil contributed to a \$15 billion increase in soybean oil revenues between 2006 and 2012. It also raised the price of soybeans by \$0.74 per bushel (\$0.027 per kilogram). Soybean oil use for biodiesel production increased from 670,000 pounds in 2005 to 4.1 billion pounds in 2012 (304 metric tons to 1.8 million metric tons). For further information see <http://tinyurl.com/SoyCheckoff-Biodiesel>.

■ ■ ■

The Biodiesel Bible, a book for the do-it-yourselfer who wants to make biodiesel, became available in April 2013. The 342-page publication by Keith Addison has 217 illustrations and is available for download as a PDF for \$38.50. For further information see <http://journeytoforever.org/books/biodiesel-bible.cgi>.

■ ■ ■

The Algae Biomass Organization (ABO) has published a new map of the algae industry in the United States. Locations of algae-related companies, research institutions, national laboratories, demonstration and commercial projects are shown. The ABO, which has made the map available at www.algaebiomass.org/algae-industry-map, intends to update the map continually.

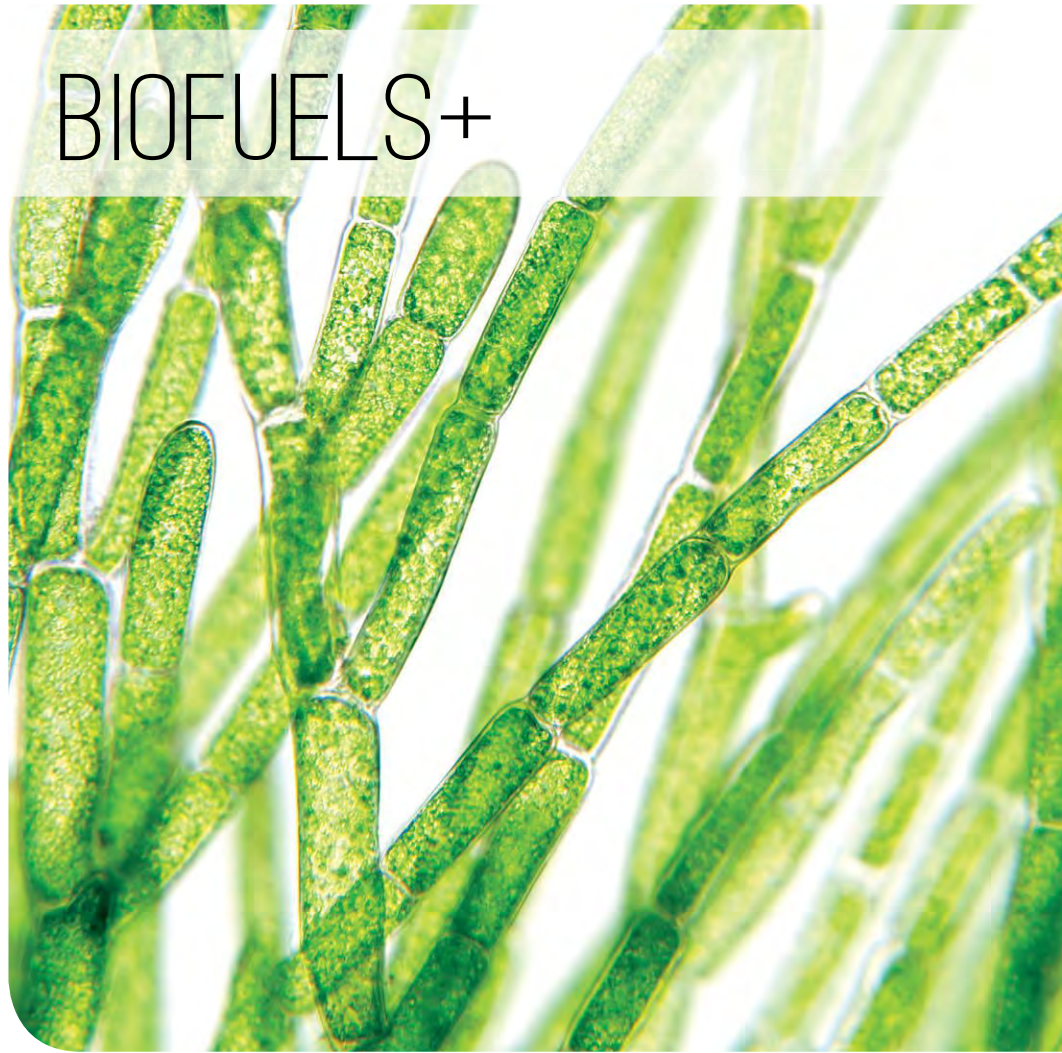
■ ■ ■

Beijing-based Sinopec, China's top oil refiner, announced in April that an Airbus A320 owned by China Eastern Airlines had successfully completed the first test flight of the company's newly developed aviation biofuel product. The biofuel was made from palm oil and recycled cooking oil. Later in April, China Eastern Airlines announced it would begin operating commercial flights fueled by 100% biofuel.

■ ■ ■

In mid-April 2013 the National Renewable Energy Laboratory (NREL; Boulder, Colorado), part of the US

BIOFUELS+



Heliae announces new technology

In late April 2013, Heliae Inc., a platform technology company that uses sunlight and waste carbon to produce high-value products from algae, announced the availability of its patent-pending microalgae production platform, Volaris™. The Gilbert, Arizona (USA) company has worked for five years to reach this point.

Volaris combines the best of existing algae production pathways, using both sunlight and waste carbon feedstocks to optimize facility economics. Heliae's Vice President of Research and Development Lee Tonkovich commented, "Phototrophy and heterotrophy both have their weaknesses—namely, contamination and low growth rates in phototrophy and extremely high capital and operating expenses in heterotrophy. We've developed a hybrid mixotrophic pathway which drives down capital costs, reduces contamination, and increases productivity

to dramatically improve the economics of algae production."

The productivity gains Volaris provides should considerably reduce the amount of land required for a commercial facility. Heliae is scheduled to open a new 20-acre commercial facility in Gilbert, Arizona late in the third quarter of 2013.

Heliae is being circumspect regarding the details of their technology. BiofuelsDigest.com speculated that a V-shaped photobioreactor system, providing entry points for gases used to mix the algae, is part of the operation (<http://tinyurl.com/BioDig-Volaris>). As quoted by BiofuelsDigest, Helia claims, "The gas delivery systems are placed strategically along or near the axis defined by the bottom of the V to keep solids in suspension and to provide improved mixing of the culture medium. Mixing rate of the culture medium can be controlled by the gas delivery system alone, or in combination with other agitation means."

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Department of Energy, announced that the most recent national survey of 100% biodiesel (B100) "blend stock" samples found that 95% of the samples from 2011–2012 had met ASTM International fuel quality specifications. In NREL's 2007 survey, less than half of the samples of B100 biodiesel met quality specifications. The data are available at <http://tinyurl.com/BiodieselSpecs>.

■ ■ ■

A website devoted to customers and users of lubricants and hydraulic oils who are interested in environmentally friendly alternatives became available in May (www.biolubricants.eu). Big purchasers such as public works, water and landscape managers can find guidance there for formulating requirements for contractors and suppliers involved in building and maintaining infrastructural works. The website has been developed by IVAM Research and Consultancy on Sustainability UvA BV (Amsterdam, Netherlands) and the Product Board for Margarine, Fats and Oils (Zoe-termeer, Netherlands) in cooperation with Rijkswaterstaat, part of the Dutch Ministry of Infrastructure and the Environment. ■

The company is also developing a two-solvent system to extract polar and neutral lipids, intending to market the former for use in surfactants, detergents, and food additives and the latter for making renewable fuels.

Heliae states that it is in the top three of US patent holders in the algae space (<http://tinyurl.com/Heliae-patents>).

In early May, Heliae announced it had raised \$15 million in funding from international conglomerate Salim Group's agribusiness company, PT. PP London Sumatra Indonesia, through its wholly-owned subsidiary, Agri Investments Pte. Ltd. (<http://tinyurl.com/Heliae-Indonesia>). Funding will be used in part for a research and development center in Indonesia, with a goal of commercial production in 2014 (<http://tinyurl.com/Heliae-investment>).

Using *E. coli* to make fuel

Scientists with the University of Exeter (UK), with support from Shell Research Ltd., recently reported on their efforts to develop a method to make bacteria produce petroleum-replica fuel molecules. They started from the premise that current biofuels (alcohols and biodiesels) require downstream

processing and may not be fully compatible with modern, mass-market internal combustion engines.

The ideal biofuel would be structurally and chemically identical to the petroleum-based fuels it is intended to replace. That is, the fuel would contain aliphatic *n*- and *iso*-alkanes and alkenes of various chain lengths.

John Love and his Exeter research team modified *E. coli* bacteria to incorporate the activity of the fatty acid (FA) reductase complex from *Photorhabdus luminescens* (a Gram-negative gamma proteobacterium belonging to the family Enterobacteriaceae) coupled with aldehyde decarbonylase from *Nostoc punctiforme* (a cyanobacterium) to use free FA as substrates for alkane biosynthesis.

This combination of genes allowed the researchers to manipulate the FA pool to alter the number of carbon atoms in alkane chains that the organism produces. The authors commented, "Rather than simply reconstituting existing metabolic routes to alkane production found in nature, these results demonstrate the ability to design and implement artificial molecular pathways for the production of renewable, industrially relevant fuel molecules (Howard, T.P., *et al.*, *Proc. Natl. Acad. Sci.* 110:7636–7641, 2013; doi:10.1073/pnas.1215966110. The paper is available open access.).



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As reported in *The Sunday Times* (<http://www.driving.co.uk/news/11021>), the process has a way to go: "At the moment it takes about 24 hours to make a teaspoon [3.5 mL] of diesel from 100 liters of bacteria." Love pointed out, however, that since the bacteria double in number every 20 minutes, the only limiting factors are the size of the processing plant and the amount of feedstock (e.g., plants, animal waste, sewage) available.

ExxonMobil/ Synthetic Genomics modify plans

In July 2009, ExxonMobil Research and Engineering (EMRE) Company and Synthetic Genomics, Inc. (SGI; La Jolla, California, USA) jointly announced a five-year research and development agreement for the creation of next generation biofuels from algae. As part of the agreement EMRE was to contribute as much as \$600 million (*Inform* 20:577, 2009), toward this goal.

For its part, Synthetic Genomics was to identify and modify natural algal strains that yield high amounts of oils. According to J. Craig Venter, CEO of SGI, problems arose when an algal strain that made enough oil in a California greenhouse to meet a required milestone in the contract failed to perform in a pond at an Exxon-Mobil facility in Texas.

Venter counted on EMRE to fund SGI research on synthetic organisms to produce oil. A synthetic organism can be defined as an organism designed to carry out only certain tasks, such as synthesizing lipids that can be used to manufacture liquid fuels, or converting sugar to ethanol. Natural algae, though, have additional priorities, such as replication (<http://tinyurl.com/SynthOrganism>).

Bloomberg.com reported in April 2013 that ExxonMobil has recast its contract with Synthetic Genomics, resulting in layoffs of more than half the SGI employees working on the algae project with ExxonMobil. The effort is now on long-term research and development rather than commercial production, according to SGI (<http://tinyurl.com/BloombergSGI-EMRE>).

In a company statement, Venter said, "We look forward to working with Exxon-Mobil to undertake this in-depth focus on the basic science research to better understand and enhance algae." He added, "The new agreement gives us an opportunity to really focus on improving algal strains using our core synthetic biology technologies to develop biofuels." The search will be on to develop strains that reproduce quickly, produce a high proportion of lipids, and effectively withstand environmental and operational conditions.

Financial details of the agreement were not disclosed.

Catalyst for generating H₂ derived from soybeans

Researchers at the US Department of Energy's Brookhaven National Laboratory (BNL) recently described details of a low-cost, stable, effective catalyst that could replace costly platinum in the production of hydrogen. The catalyst is made from soybeans and molybdenum metal, produces hydrogen in an environmentally friendly, cost-effective manner, potentially increasing the use of this clean energy source.

Kotaro Sasaki, one of leaders on the project, explained, "By splitting liquid water (H₂O) into hydrogen and oxygen, the hydrogen can be regenerated as a gas (H₂) and used directly as fuel. We sought to fabricate a commercially viable catalyst from earth-abundant materials for application in electrolysis" (<http://tinyurl.com/BNL-MoSoy>).

According to BNL's James Muckerman, another researcher on the project, the team has developed "the best-performing, non-noble-metal-containing hydrogen evolution catalyst yet known—even better than bulk platinum metal."

To make the catalyst, the team ground soybeans into a powder, mixed the powder with ammonium molybdate in water, then dried and heated the samples in the presence of inert argon gas. "A subsequent

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high temperature treatment (carburization) induced a reaction between molybdenum and the carbon and nitrogen components of the soybeans to produce molybdenum carbides and molybdenum nitrides,” explained Wei-Fu Chen, also a research coordinator for the project.

Electrochemical tests of the separate ingredients showed that molybdenum carbide was effective for converting H_2O to H_2 , but it was not stable in acidic solution, whereas molybdenum nitride was corrosion resistant but not efficient for hydrogen production. A nanostructured hybrid of these two materials, however, remained active and stable even after 500 hours of testing in a highly acidic environment.

“We attribute the high activity of the molybdenum-soy catalyst (MoSoy) to the synergistic effect between the molybdenum-carbide phase and the molybdenum-nitride phase in the composite material,” Chen said.

The researchers concluded, “This study unambiguously provides evidence that a cheap and earth-abundant transition metal such as molybdenum can be turned into an active catalyst by the controlled solid-state reaction with soybeans. . . . The preparation of the MoSoy catalyst is simple and can be easily scaled up. Its long-term durability and ultra-low capital cost satisfy the prerequisites for its application in the construction of large-scale devices” (Chen, W.-F., *et al.*, Biomass-derived electrocatalytic composites for hydrogen evolution, *Energy Environ. Sci.* 6:1818–1826, 2013; doi: 10.1039/C3EE40596F).

Felda Global buys biodiesel refinery

Felda Global Ventures Holdings Bhd. (FGV), via its subsidiary Felda Global Ventures Downstream Sdn. Bhd., signed an agreement in April 2013 with Mission Biotechnologies Sdn. Bhd. to

buy Mission’s assets including a biodiesel refinery at Kuantan Port, Malaysia, for \$11.5 million. The refinery produces 100,000 metric tons (MT) of biodiesel annually and is sited on 2.42 hectares of prime land. The assets also include 16,000 MT of tank storage and pipelines to a deep water jetty. Plans were for the plant to be fully operation by July 1, 2013.

According to FGV President Sabri Ahmad, the acquisition allows the company to move itself further downstream, thus protecting its upstream business. Furthermore, the biodiesel refinery will consume more palm oil and support the Malaysian government’s promotion of B5 and B10 biodiesel (petrodiesel containing 5% and 10% biodiesel, respectively)—and help reduce the current national stockpile of crude palm oil.

Algal oils in paints

In mid-May 2013, Solazyme, Inc. (South San Francisco, California, USA) and AkzoNobel, a global paints and coatings company, announced their intention to develop advanced tailored oils to replace petroleum-derived chemicals for use in paints. Solazyme will provide commercial supplies of multi-thousand ton quantities of algal oil from its Solazyme Bunge Renewable Oils Joint Venture oil manufacturing plant in Brazil. Sales of product are anticipated to begin in 2014, with pricing to be competitive and based on Solazyme’s cost of manufacturing.

“We think the tailored triglycerides developed by Solazyme can offer valuable new technology for our Surface Chemistry and Decorative Paints businesses, and we are excited about our partnership,” said Graeme Armstrong, corporate director for research, development and innovation for AkzoNobel.

Product development efforts are anticipated to begin in the second half of 2013 and are focused on a number of AkzoNobel’s end market applications, specifically surfactants and paints and coatings. ■

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BRIEFS

The European Food Safety Authority (EFSA) has released its Comprehensive Food Consumption Database, which details food consumption across the European Union (EU). The database will play a key role in the evaluation of the risks related to possible hazards in food in the EU, EFSA says, as well as the assessment of nutrient intakes of the EU population. Guidance regarding the use of the database is available at <http://tinyurl.com/EFSA-DB>.

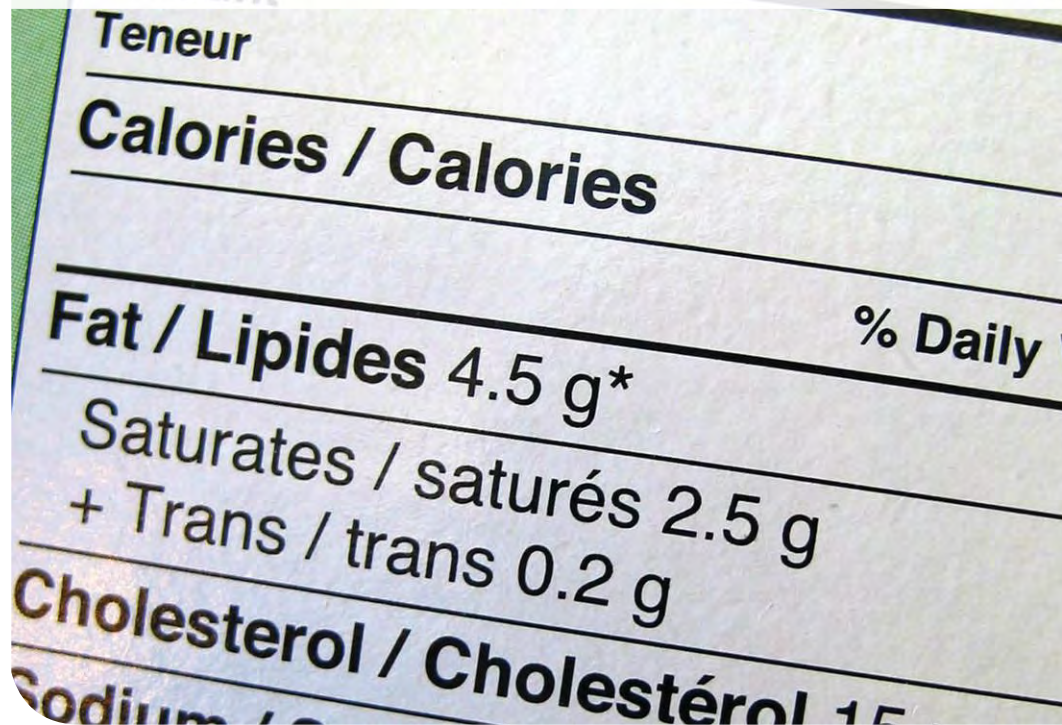
■ ■ ■

Omega-3 fatty acid supplement users want more alternatives to existing sources, according to a survey conducted for Norwegian krill oil producer Aker BioMarine by Discovery Research Group. The survey indicated that 66% of supplement users in Germany want alternatives, along with 55% in France and 47% in the United Kingdom. Reasons given by respondents for stopping omega-3 supplementation included large capsule size, reflux, bad aftertaste, and expense. A US study conducted in 2012 found that 37% of supplement users wanted an omega-3 source other than fish oil, according to *Natural Products Insider (NPI)* magazine. "Krill supplements in the United States now account for 12% of all omega-3 sales," *NPI* noted.

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"Excessive" consumption of vitamin E does not present a health risk, according to a review of 181 research papers in the *Journal of Lipid Research* (doi:10.1194/jlr.R032946, 2013). The review was conducted by Maret G. Traber of the Linus Pauling Institute at Oregon State University in Corvallis. It notes that unlike vitamins A and D, the fat-soluble form of vitamin E known as α -tocopherol does not accumulate to toxic levels in or outside the liver. The mechanisms for the metabolism of α -tocopherol are the focus of Traber's review, which concludes that α -tocopherol is the most efficient and safest of the eight forms of vitamin E synthesized by plants. ■

HEALTH & NUTRITION



Have dietary fats been needlessly vilified?

A review article in *Advances in Nutrition*, which is published by the American Society for Nutrition, is calling for a reevaluation of dietary recommendations for minimizing saturated fat consumption.

Titled "Dietary fats and health: dietary recommendations in the context of scientific evidence," the review examines evidence culled from more than 100 studies. According to review author Glen D. Lawrence, "the influence of dietary fats on serum cholesterol has been overstated, and a physiological mechanism for saturated fats causing heart disease is still missing." Lawrence is a professor of chemistry and biochemistry at Long Island University in Brooklyn, New York, USA.

He points out that a number of studies published in the 1960s and 1970s, including the seminal Framingham Heart Study, linked dietary fats, particularly saturated fats, to heart disease. (It should be noted—although

Lawrence does not do so—that some early researchers have been accused of cherry-picking data to support a connection among saturated fat, cholesterol, and heart disease.)

In recent years, analyses of these older studies, coupled with new findings, have begun to call the purported negative health consequences of dietary fats into question. The *Advances in Nutrition* review (doi:10.3945/an.113.003657, 2013) examines studies of several dietary factors, including saturated fat, polyunsaturated fat, α -linolenic acid, total fat, meat, eggs, and milk. None of these studies provides sufficient evidence to support a positive (or negative) association between fat consumption and heart disease, Lawrence suggests.

For example, he points to a recent analysis of 20 individual studies with more than one million subjects collectively that found that red meat in general was not associated with heart disease (*Circulation* 121:2271–2283, 2010). Processed meats, however, were associated with increased risk of heart disease. This suggests, an American Society for Nutrition's media alert indicates, that

CONTINUED ON NEXT PAGE

saturated fat itself does not lead to heart disease but, rather, other factors such as preservatives or processing methods may be the real culprits. Similarly, claims that oils with high saturated fat content such as palm and coconut oil increase the risk of heart disease lack scientific evidence to support them. Moreover, countries with high consumption rates of so-called tropical oils have some of the lowest rates of heart disease in the world, the alert notes.

"If diets high in fats, particularly saturated fats, are unhealthy, then, logically, we should see the beneficial effects of low-fat diets," the media alert states. Studies, however, generally have failed to show a health benefit to low-fat diets. (Work by Dean Ornish, on the other hand, suggests that comprehensive lifestyle changes including stress reduction through yoga and a low-fat diet high in plant protein can reverse heart disease.)

In summary, Lawrence's review finds that saturated fats *per se* may not be responsible for many of the adverse health effects with which they have been associated; instead, oxidation of polyunsaturated fatty acids in foods considered primarily to be sources of saturated fat (such as meats) may be the cause of any associations that have been found. In light of this evidence, he says, "it is time to reevaluate the dietary recommendations that focus on lowering serum cholesterol and to use a more holistic approach to dietary policy."

The complete paper can be accessed at <http://tinyurl.com/AiN-sat-fat>.

Omega-3 fatty acids and cancer in mice

US researchers have discovered a key mechanism in mice by which dietary omega-3 fatty acids from fish oils reduce tumor growth and spread of cancer.

The team of 16 scientists led by Guodong Zhang of the Bruce Hammock laboratory at the University of California, Davis Comprehensive Cancer Center discovered cytochrome P450 epoxigenase metabolites of the omega-3 fatty acid docosahexaenoic acid (DHA; 22:6n-3)—or 19,20-epoxy docosapentaenoic acids (EDP)—block blood supply to tumors and thus inhibit tumor growth and metastasis. (EDP is derived via epoxidation of the omega-3 double bond of DHA.)

A soluble epoxide hydrolase inhibitor, a drug that is already under development to control pain and hypertension, further stabilized the naturally occurring EDP.

"Many human studies have shown that omega-3 fatty acids reduce the risks of cancers, but the mechanism is poorly understood," said Zhang, a postdoctoral researcher. "Our study provides a novel mechanism by which these omega-3 lipids inhibit cancer."

"We demonstrated that EDP have very potent anticancer and antimetastatic effects," Zhang said. "Current anticancer drugs that block angiogenesis (the formation of new blood vessels to fuel tumor progression) can cause serious side effects such as hypertension. By blocking angiogenesis by a new mechanism and by widening blood vessels, EDP could block tumor growth with reduced side effects in cancer patients."

The studies also suggest that the combination of a diet high in omega-3s and some anti-cancer drugs such as sorafenib "could

not only be efficacious to treat cancers but reduce potential side effects," Zhang said.

Co-author Hammock said the research shows a great deal of promise. "Basically, what Zhang and his collaborators found is that the epoxides of the omega-3 fatty acid DHA are strongly anti-angiogenic and block tumor growth and metastasis. He used the soluble epoxide hydrolase inhibitors to stabilize these epoxides in mice. In contrast, the epoxides of the omega-6 fatty acid ARA (arachidonate; 20:4n-6) are mildly angiogenic and encourage tumor and wound healing.

"Thus, the effects of the soluble epoxide hydrolase inhibitors have opposite effects depending on whether the background lipid mediators are omega-3 or omega-6," Hammock said. "Assuming that humans are mice (the study involved mice), the prediction is that with some cancer drugs—particularly the ones like sorafenib and regorafenib that are potent epoxide hydrolase inhibitors as well as anti-angiogenic agents—could be more effective with a high omega-3 and low omega-6 background."

Several experts who were not involved with the research were asked for comment by UC, Davis.

"This is an exciting step toward our full appreciation of the impact of bioactive products from the DHA metabolome," said Charles Serhan, an expert on omega-3 and inflammation and Simon Gelman Professor of Anesthesia, Perioperative and Pain Medicine, Harvard Medical School.

Cardiologist Jonathan Lindner of the Oregon Health & Science University also commented on the research.

"The study by Zhang and colleagues has uncovered a previously unrecognized anticancer effect of omega-3 fatty acids which are an important lipid component of diets that have been developed to prevent heart disease and cancer," Lindner said. "The authors have demonstrated that metabolites of these lipids can act to suppress the growth of new blood vessels that are necessary to feed tumor growth. By shutting off the tumor's blood supply, these compounds can act to dramatically slow tumor growth and prevent metastasis. The results from this suggest that new drug strategies for fighting cancer could emerge from knowledge of how the body uses nutrition to promote health."

Professor Ingrid Fleming of the Institute for Vascular Signaling, Center for Molecular Medicine at the Goethe University in Frankfurt, Germany, described the study as "exciting" and offering great potential. "Inhibitors of the soluble epoxide hydrolase (sEH) have potential benefits for the prevention of the metabolic syndrome and the associated cardiovascular complications," said Fleming. "However, interest in the development of these compounds for therapy has been limited by the fact that increased levels of the epoxides of arachidonic acid promote angiogenesis and thus increase tumor growth and metastasis.

"Now researchers report that the epoxides of docosahexaenoic acid do exactly the opposite by inhibiting angiogenesis, and thus decrease tumor growth and metastasis," Fleming said. "Thus, it may now be possible to potentiate the beneficial effects of sEH inhibition by supplementing therapy with dietary omega-3 fatty acids."

Zhang, who focuses his research on lipid mediators on angiogenesis, tumor growth and metastasis, received his doctorate in food science from the University of Wisconsin-Madison.

The research appeared in the *Proceedings for the National Academy of Sciences* (doi:10.1073/pnas.1304321110, 2013). ■

A study published in May 2013 found that Droplet Digital Polymerase Chain Reaction (ddPCR™) technology is suitable for routine analysis of genetically modified organisms (GMOs) in food, feed, and seeds. Dany Morisset, lead author and a researcher at Slovenia's National Institute of Biology (Ljubljana), reported that ddPCR is more accurate and reliable than quantitative PCR (qPCR), the most common technique for quantifying the presence of GMOs. ddPCR is especially suitable at low levels and exhibits greater tolerance to inhibitors found in matrices such as wheat flour and feed. ddPCR also meets international food standards of applicability and practicality.

Morisset determined that ddPCR is less expensive than qPCR owing to the need for fewer PCR reactions per sample, and it does not require reactions for a standard curve or dilutions due to lower anticipated inhibition. The work was published in *PLoS ONE* 8(5):e62583 (doi:10.1371/journal.pone.0062583).

■ ■ ■

On May 23, VG Energy, an agricultural biotech company located in San Marino, California, USA, announced a strategic alliance with DAK Renewable Research to conduct field trials using LipidMax to increase corn oil yield. VG Energy's exclusively licensed compound LipidMax selectively inhibits certain metabolic pathways to increase the oil yield in plants. DAK Renewable Research, headquartered in Brandon, South Dakota, USA, is primarily focused on developing viable and cost-effective green energy solutions. DAK is providing twelve 2,000 ft² (190 m²) plots in South Dakota to measure the effect of LipidMax in corn oil production and to test the robustness of LipidMax in field conditions. The crop will reach maturity in mid-October 2013, and results will be announced shortly thereafter.

■ ■ ■

Arcadia Biosciences, Inc, an agricultural company headquartered in Davis, California, USA, and DuPont Pioneer (Des Moines, Iowa, USA) announced in April a formal collaboration to develop new safflower varieties that produce high levels of arachidonic acid-con-



GMO labeling in US news

Legislation at the state level. In November 2012, voters in the state of California rejected Proposition 37, which would have required companies to disclose if foods sold in the states stores were produced by genetic engineering. Since then, efforts have been intensifying in other states to bring this topic to a ballot. For example, the state of Washington will vote in November 2013 on Initiative I-522, which would require all food containing genetically modified organisms to be labeled. According to the Washington newspaper *The Spokesman-Review*, out-of-state money has provided most of the funding for this effort as of mid-May 2013 (<http://tinyurl.com/I-522-funding>).

On May 23, the Connecticut State Senate voted 35–1 in favor of SB 802, which would require labeling of products with genetically modified ingredients (<http://tinyurl.com/ConnecticutGMO>). At press time, the results of the vote on the same bill in the Connecticut State House of Representatives were not known. The bill would require that three nearby states pass similar bills by July 2015 in order for the Connecticut measure to go into effect. (This requirement has been written to ensure that Connecticut's regulation not make it into an "island" different from its neighbors.) Neighboring state Vermont's House of Representatives on May 10 passed H.112, a bill requiring the labeling of all genetically engineered food sold in Vermont, but the bill first

must be approved by the state Senate, which will probably not get the opportunity to look at the bill until January 2014 (<http://tinyurl.com/VermontGMO>). If it is approved by the Senate, it would not go into effect for two years after it is passed, or 18 months after at least two other states adopt similar bills, whichever comes first. And the Maine legislature's Joint Standing Committee on Agriculture, Conservation and Forestry voted 8–5 on May 22 in support of a bill that would require labeling of GMOs in food. The bill was slated to go to the full legislature for votes in the House and Senate.

On the other hand, through what the *Santa Fe New Mexican* newspaper cited as "a procedural mistake," the legislature of the state of New Mexico rejected requiring the labeling of bioengineered foods sold in the state (*Inform* 24:231, 2013).

Federal legislation. The prospect of inconsistencies in labeling laws from one state to the next led Senator Barbara Boxer (Democrat, California) and Representative Peter DeFazio (Democrat, Oregon) to introduce the Genetically Engineered Food Right-to-Know Act on April 24. It was assigned to the House Committee on Energy and Commerce: Health for consideration. GovTrack.US, a Congress-tracking website (<http://tinyurl.com/Boxer-DeFazio>), estimated the Act's chance of getting past committee and into the House as 3%. (In 2011–2013, only 11% of House bills made it past committee, and only 3% were enacted.)

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taining oil in a concentrated, reliable, and cost-effective way. The collaboration builds on new trait innovation from DuPont Pioneer as well as both organizations' crop development and regulatory expertise.

■ ■ ■

At the 2013 Food Technology & Innovation Forum held in Chicago (USA) in April, Sean Westcott, research and development manager for Nestlé's Food Strategic Business Unit, responded to an audience query for his opinion on genetically engineered crops. According to FoodNavigator-USA.com (<http://tinyurl.com/Nestle-Westcott>), he replied, "Our position on biotechnology is that it's vital." He added, "We feel that we have to embrace these technologies. It's a necessary part of the future."

■ ■ ■

At the annual meeting of Abbott Laboratories (Abbott Park, Illinois, USA) held in April, stockholders voted against a shareholder proposal that the company adopt a policy of removing genetically engineered ingredients from all nutritional products sold or manufactured by Abbott, including Similac infant formula range. According to the company, preliminary estimates showed 2.7% of the votes cast supported the proposal. Abbott said, "As part of our ingredient selection process, it is necessary to consider the availability of ingredient supply. The large-scale production of certain genetically modified crops has made it difficult to obtain enough non-GMO supply to meet global demand" (<http://tinyurl.com/Abbott-GMOvote>).

An anti-GMO group, GMO Inside, approached Nestlé USA and Mead Johnson Nutrition with a similar plea. Mead Johnson replied that its infant formula products "comply with all applicable laws and regulations" in each country where it operates.

Nestlé USA passed the plea on to the International Formula Council (IFC), which represents infant formula manufacturers and marketers. In a statement, IFC said in part, "Billions of people, including infants, have eaten biotech food safely for more than 15 years with no evidence of harm demonstrated anywhere in the world" (<http://tinyurl.com/MeadJohnson-Nestle>). ■

The Boxer-DeFazio bill would require clear labels for genetically engineered whole foods and processed foods, including fish and seafood.

Loren Israelsen, executive director of the United Natural Products Alliance, commented to FoodNavigator-USA.com (<http://tinyurl.com/GMO-USCongress>): "The argument for federal legislation is to preempt the patchwork of different state laws. If you had 15 or 20 state laws different enough that you had to pay attention to all of them, that would be highly cumbersome." He predicted that prospects for passage of Boxer-DeFazio in the current congress are dim.

Commentary. In an interview reported by FoodNavigator-USA.com, former US Food and Drug Association associate commissioner of foods David Acheson observed that the momentum behind GMO labeling just shows what a "small, highly vocal, well organized group of people can accomplish irrespective of the science. . . Science doesn't always win" (<http://tinyurl.com/formerFDAofficial>).

Patent rights and biotech seeds

The Supreme Court of the United States (SCOTUS) heard arguments on February 18, 2013, involving patent infringement with respect to genetically engineered (GE) soybeans. Seed producer Monsanto Co., St. Louis, Missouri, sued Vernon Bowman, an Indiana farmer who had planted the offspring of Monsanto's patented glyphosate (Roundup pesticide)-resistant soybean in contradiction to the contract that Monsanto makes its seed purchasers sign, agreeing to plant the purchased seeds in one (and only one) season. Furthermore, the farmer may not save harvested seeds for replanting, nor may the farmer supply them to anyone else for that purpose.

Bowman's unorthodox approach was to purchase commodity soybeans from the local elevator to plant for a risky late-season crop on which he didn't want to spend much money. He correctly reasoned that many of these commodity beans, which are typically sold as animal feed, would be Roundup resistant. He then saved part of this late-season crop to plant in subsequent years and sold the rest to the local elevator without paying fees to Monsanto. Bowman argued that Monsanto's patent was exhausted when he purchased the commodity beans.

In a unanimous decision, the nine justices of SCOTUS ruled against Bowman and for Monsanto on May 13, 2013. The opinion of the court, written by Justice Elena Kagan, is available at http://www.supremecourt.gov/opinions/12pdf/11-796_c07d.pdf.

Kagan wrote: "Under the doctrine of patent exhaustion, the authorized sale of a patented article gives the purchaser, or any subsequent owner, a right to use or resell that article. Such a sale, however, does not allow the purchaser to make new copies of the patented invention. The question in this case is whether a farmer who buys patented seeds may reproduce them through planting and harvesting without the patent holder's permission. We hold that he may not."

Elsewhere in the opinion, Kagan said: "Under the patent exhaustion doctrine, Bowman could resell the patented soybeans he purchased from the grain elevator; so too he could consume the beans himself or feed them to his animals. Monsanto, although the patent holder, would have no business interfering in those uses of Roundup Ready beans. But the exhaustion doctrine does not enable Bowman to make *additional* [italics in the original] patented soybeans without Monsanto's permission (either express or implied). And that is precisely what Bowman did." Kagan also took care to point out that one of the definitions of "to make" is "to plant and raise (a crop)."

Finally, Bowman argued that "soybeans naturally 'self-replicate or sprout unless stored in a controlled manner,' and thus 'it was the planted soybean, not Bowman' himself, that made replicas of Monsanto's patented invention..

"It was Bowman, and not the bean, who controlled the reproduction . . . of Monsanto's patented invention."

While many companies and organizations involved in biotechnology had hoped that the SCOTUS decision would establish widespread precedents concerning biotech patents, the decision was confined to the case at hand. Kagan wrote: "[O]ur holding today is limited—addressing the situation before us, rather than every one involving a self-replicating product. We recognize that such inventions are becoming ever more prevalent, complex, and diverse. In another case, the article's self-replication might occur outside the purchaser's control. . . . In the case at hand, Bowman planted Monsanto's patented soybeans solely to make and market replicas of them, thus depriving the company of the reward patent law provides for the sale of each article. Patent exhaustion provides no haven for that conduct." ■

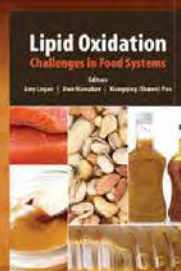
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It's off to a great start thanks to our awareness campaign that began in May with a stirring speech from AOCS CEO Pat Donnelly during the Business Luncheon at the Annual Meeting & Expo.

Attendees were astonished when they learned the current system was installed almost 15 years ago in 1999.

We would like to thank everyone who donated during the meeting and welcome those who may have missed the kickoff opportunity to join in making a difference!



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Industrial Specialty Chemicals Inc.
Institute for Food Safety & Health
Integro Foods Australia Pty. Ltd.
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Attended the Annual Meeting

The US Environmental Protection Agency (EPA) needs a better strategy to reform its toxic chemical regulations, according to report released by the Government Accountability Office (GAO). It would take a decade at EPA's current pace for it to finish assessments of the 83 chemicals it has prioritized for risk assessment, GAO said. The report also suggested EPA should consider requiring chemical companies to report chemical data that have already been submitted to the European Chemicals Agency under REACH. The report covered EPA activities from December 2011 to March 2013 and is available at <http://tinyurl.com/EPA-reform>.

■ ■ ■

Solazyme and AkzoNobel will develop and market specialty surfactants as well as paints/coatings made from tailored algal oils, the companies announced in May 2013. Commercial supply of Solazyme's tailored algal oil is expected to be produced at the Solazyme Bunge Renewable Oils joint venture manufacturing plant in Moema, Brazil, according to the companies. That 100,000 metric tons per year facility is scheduled to begin operation in the fourth quarter of 2013. "Sales of product from the AkzoNobel partnership are anticipated to commence in 2014 and pricing is said to be competitive and based upon Solazyme's cost of manufacturing," *Biofuels Digest* magazine reported.

■ ■ ■

Denmark's AAK Personal Care has introduced Lipex® SheaLight, which it says is produced entirely from renewable sources. Made from an ester formed by the reaction of shea butter and plant-based alcohol, the ester reportedly delivers a "light and silky soft feel in skin care and other personal care products," according to AAK.

■ ■ ■

Despite strong first quarter earnings, Ecolab Inc. (St. Paul, Minnesota, USA) announced a restructuring plan that will include cutting 500 jobs. The maker of industrial and institutional cleaning products recently acquired Champion Technologies, which manufactures specialty chemicals for oil and gas recovery. That acquisition, together with Ecolab's earlier purchase of Nalco, gives the company a presence in oilfield services. ■

SURFACTANTS, DETERGENTS, & PERSONAL CARE NEWS



New higher alcohol capacity to create competitive surfactant market

The higher alcohols market has expanded rapidly in the past seven years to 2.5 million metric tons (MMT) in 2012 as new supply has come onstream, according to a study by Colin A. Houston & Associates, Inc. (CAHA), a consulting firm in Aiken, South Carolina, USA. Higher alcohols, which are alcohols with 12 or more carbon atoms, are mainly used in the production of surfactants and detergents.

CAHA reports that global consumption of higher alcohols has expanded at a rate of more than 4.5% per year between 2005 and 2012. This impressive performance has been the result of new supplies reaching markets after a similar massive addition of oleo-based alcohol capacity between 2005 and 2010. Supply is forecast to grow at twice the rate of demand between 2012 and 2015.

"Over the next few years, use of alcohol-based anionic surfactants may be favored in detergent formulations, as nonionics and alkylbenzene sulfonates face respective supply constraints and competitive cost pressure," noted CAHA President Joel Houston. "Purified ethylene oxide capacity expansions are not keeping up with the new oleo-alcohol capacity, hindering the growth of ethoxylated products in the short term," he added. (Common surfactants produced by ethoxylation include alcohol ethoxylates and alcohol ethoxysulfates.)

Demand for alcohol-based products in Asia has exhibited strong growth over the past few years, with new demand developing from the additional requirements of liquid laundry detergent products, which are formulated from alcohol-based anionic surfactants. Greater consumption of alcohols in personal care products continues to drive growth as well. Although surplus alcohols are currently being exported to Western markets, trade barriers, duties, and new technology could disrupt this trend, CAHA says.

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TABLE 1. Announced capacity additions for C₁₂ and higher detergent alcohols by producer (thousand metric tons)^a

Producer	Location	Type	2013	2014+	Net addition
Codexis	United States	Micro		60	60
Wilmar	Netherlands	Davy	150		150
Jiaxiang Sanjiang	China	Oleo	100		100
Wuhan/HoTung JV	China	Oleo		160	160
KLK Oleomas	Malaysia	Davy	100		100
Ecogreen	Indonesia	Davy		180	180
Musim Mas	Indonesia	Davy	111		111
Bakrie Sumatra	Indonesia	Davy	40		40
Wilmar	Indonesia	Davy	120		120
Pilipinas Kao	Philippines		34		34
SABIC	Saudi Arabia	Lurgi	85		85
		TOTAL	740	400	1,140

^aSource: Colin A. Houston & Associates.

The recent separation of prices between oil palm biofuels and distillate fuels such as kerosene has resulted in a growing advantage for oleo-based chemicals vs. other chemical intermediates of significance. Shale gas economics in North America have improved the cost position of synthetic alcohols to oleos. The shale gas opportunity is generating new investments (particularly by Sasol and Shell) in projects that will continue to support the cost position of synthetic alcohols. CAHA has evaluated recent process developments in sugar-based higher alcohols. Several of these new projects, including those undertaken by LS9 and Codexis, are on the brink of commercialization, and offer a new supply chain route for the future.

A wave of new capacity is set to come onstream during the next 18 months, which will create a flood of alcohol products, the CAHA report suggests (see Table 1). Some producers are slating output to selectively produce mid-cut alcohols, avoiding short- and long-chain co-product economic challenges. More than 1 MMT of planned capacity is expected to start up, and other capacity potentially will be added. It remains to be seen if older, less economical units will be forced out of service.

The degree of integration in the alcohols arena has been expanding through forward integration, according to CAHA. Oil palm planters have expanded into alcohol production. In addition, Asian alcohol producers such as Ecogreen, Emery, KLK Oleomas, Musim Mas, and Wilmar have increased participation in the surfactant space through acquisition and grass root activities. Furthermore, the acquisition of Cognis by BASF has brought together their respective strengths in alcohols and ethylene oxide, while expanding the company's product offerings into a range of specialty products.

Three surfactants accounted for over two thirds of the 2.5 MMT of higher alcohols consumed in 2012: alcohol ether sulfates (38%), alcohol ethoxylates (21%), and alcohol sulfates (13%);

and they will continue to dominate alcohol use in every region. The balance of products includes tertiary amine derivatives (betaines, amine oxides, and quaternary ammonium compounds), and other derivatives including alkyl polyglycosides and methacrylate esters, as well as direct end-use compounds.

The higher alcohols market is expected to grow at a base level of 4.9% per year to 2025, but any substitutions for linear alkylbenzene and methyl ester sulfonates will drive the market above this rate, the CAHA study notes. The 700-page report, titled *Higher Alcohols to 2025*, is available in both print and electronic versions. For more information, visit www.colin-houston.com.

Awards presented in Montréal

What is it about certain surfactants that make them so attracted to water and fats? Or, in scientific terms, how do we better understand the connection between molecular structure and the relative hydrophilic-lipophilic nature of a surfactant?

Scientists Charles E. Hammond and Edgar Acosta's research into this complex topic was recognized as the best paper published in 2012 in the *Journal of Surfactants & Detergents*. The Distinguished Paper Award is an annual honor presented by the American Cleaning Institute[®] (ACI) at the Annual Meeting & Expo of the American Oil Chemists' Society (AOCS), held this year on April 28–May 2, 2013, in Montréal, Québec, Canada.

The work of Hammond and Acosta showed how a surfactant can be altered to disperse more efficiently while increasing its cleaning performance.

"The structure-property relationship presented in this work will help detergent makers facilitate the design of surfactants or surfactant mixtures, better manage feedstocks, and help deter-

mine how to compensate for feedstock variability, especially when using sustainable feedstock sources,” Hammond said.

Hammond is IOR fellow and operations manager at CESI Chemical, a Flotek Company, although his award-winning research was performed while he was with Sasol North America. Acosta is an associate professor at the University of Toronto’s Department of Chemical Engineering and Applied Chemistry.

Their paper, “On the characteristic curvature of alkyl-polypropylene oxide sulfate extended surfactants,” was published in the *Journal of Surfactants and Detergents* 15:155–165, 2012. The abstract is available at <http://tinyurl.com/ACI-Award>.

A related award—this one jointly given by ACI and the National Biodiesel Board (NBB)—was presented at the 104th AOCS Annual Meeting & Expo. The ACI/NBB Glycerine Innovation Award recognizes outstanding achievement for research into new applications for glycerine, with particular emphasis on commercial viability.

The 2013 Award recipient is B.L.A. Prabhavathi Devi from the Centre for Lipid Research at CSIR-Indian Institute of Chemical Technology, Hyderabad, India. Prabhavathi and her group have been researching how glycerol can be used for the development of novel value-added products.

The researchers developed glycerol-based catalysts, including waste from the fat-splitting industry, to replace chemicals more traditionally used in manufacturing processes, such as sulfuric acid and alkali catalysts. The use of such glycerine-based

products can enhance the economies of the oleochemical and biodiesel industries.

“Our catalyst-based reactions may lead to cleaner industrial processes and reduced pollution,” said Prabhavathi.

The Glycerine Innovation Award includes a plaque and a \$5,000 honorarium. ■

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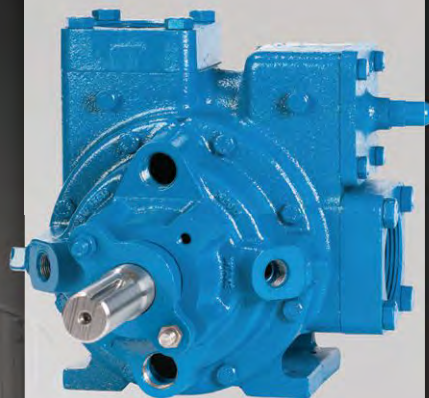
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PEOPLE NEWS

SCI award to Byrdwell



Byrdwell

The Lipids Group of the Society of Chemical Industry (SCI) in collaboration with Ghent University (Belgium) and the Euro Fed Lipid Physical Properties Division held a conference on the compositional analysis of lipids in Ghent on June 20–21, 2013. For this meeting, AOCS member **W. Craig Byrdwell** was chosen to present SCI's Julius Lewkowitsch award lecture. The award commemorates Julius Lewkowitsch (1857–1913), a chemist, entrepreneur, and authority in the field of oils and

fats. Byrdwell spoke on "Three and four mass spectrometers in parallel for lipid analysis—how many instruments are enough?" on June 20.

Byrdwell is an AOCS member and a research chemist in the Food Composition and Methods Development Laboratory, Beltsville (Maryland) Human Nutrition Research Center, Agricultural Research Service of the US Department of Agriculture.



Dunford

Grant to study algae

The Oklahoma Center for the Advancement of Science and Technology has awarded **Nurhan Dunford**, a specialist in oils and oilseeds with Oklahoma State University (Stillwater, USA), \$100,000 for a two-year project entitled "Evaluation of Oklahoma Native Algae Strains for Bioproduct Manufacturing." She and her research group will screen 18 native Oklahoma algal strains to find ones with high biomass productivity and

oil content. She intends to use the results from the project as a springboard for Oklahoma's biosciences industry.

Manitoba-based company wins award

Hemp Oil Canada Inc. (HOCI), located in Ste. Agathe, Manitoba, Canada, received the 2013 Canada Brand Business Award at the Agri-Food Export Gala in April. The award was initiated by Agri-Food Export Group Québec–Canada, the largest Canadian association of agri-food exporters.

AOCS member **Shaun Crew** is president and CEO of HOCI. He commented, "We are very excited by this recognition; this is the first year that we've been nominated."

HOCI currently exports hemp food products and ingredients to 15 different international destinations including the

United States, Italy, Slovakia, Japan, Korea, France, Australia, New Zealand, Mexico, South Africa, United Kingdom, Finland, Ireland, Israel, Trinidad and Tobago. The company is in the planning stages to build a larger-capacity facility just outside the town of Ste. Agathe.

MacDonald retires from Purina PetCare



MacDonald

At the end of Q1 2013, **John MacDonald** retired as group manager of the Organic Laboratory at Nestle Purina PetCare of Nestle Purina Analytical Laboratories (NPAL). During his 30-year career he was a leader in applying gas chromatography, mass spectrometry, liquid chromatography, and spectroscopy to determining nutrients and contaminants in food, feeds and ingredients.

During his career with Purina PetCare, MacDonald developed and improved methods for determining mycotoxins, amino acids, fatty acids, vitamins, and food contaminants.

MacDonald joined AOCS in 2005.

After MacDonald's retirement, **Kathy Phillips** took over his position and became head of the entire chemistry group within NPAL. **Judy O'Brien** continues as head of analytical and research microbiology.

Monks joins Rivertop Renewables

John Monks joined Rivertop Renewables in April as vice president of business development. He has been involved with performance chemicals and biotechnology for more than 30 years with companies such as ICI, DSM, and Genencor.

Rivertop is developing glucaric acid products as effective and cost-competitive replacements for phosphates in the global detergent industry and other large markets (see *Inform* 22:550–552,584, 2011). The company opened a multi-million dollar laboratory expansion and semi-works site last fall at its headquarters in Missoula, Montana, USA. It has also introduced its Riose™ detergent builder into the automatic dishwashing market and sells its Headwaters™ corrosion inhibitor into the road de-icing market.

Walton recognized

Alan Walton, senior general partner at Oxford Bioscience Partners, received the Chemical Heritage Foundation's 2013 Richard J. Bolte, Sr., Award for Supporting Industries in April 2013. In the award citation, Bolton's contributions as a

CONTINUED ON PAGE 440



CORPORATE MEMBER PROFILE

This profile has been provided by the following Bronze Level AOCS Corporate Member:

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MSM Milling is a privately owned Australian oilseed company in Manildra, New South Wales (NSW). Based in the heart of the canola-growing belt, MSM specializes in oilseed crushing; refining; and packaging of canola oil, high-oleic canola oil, and canola meal. The company's on-site packaging plant, Manildra Packing, allows for expedited processing, packaging, and delivery.

MSM Milling was founded by Peter and Bob Mac Smith in 1991, when the two started a small canola seed crushing operation on their family farm in Cudal, NSW. The Mac Smith's formed a joint venture with the Manildra Group in 2006 and began on-site packaging in 2011.

MSM Milling prides itself on manufacturing for a world market. The company has a HACCP (hazard analysis critical control point) management system independently certified

by NCS International (an auditing, assurance, and certification organization). All MSM Milling products are halal and kosher approved, and the company does not produce genetically modified oils or meal.

The company's goal is to be the leading supplier of healthy and sustainable Australian oilseed products to customers in Australia and overseas. To accomplish this, MSM has pledged to continuously improve all aspects of business operations and engage in ethical and sustainable practices.

As a benefit of corporate membership, companies are entitled to provide a 250-word profile for inclusion on a space-available basis in Inform magazine. For more information, contact Nicole Philyaw at nicolep@aocs.org.

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AOCS MEETING WATCH

August 8–10, 2013. International Conference on Emerging Trends in Oleochemicals & Lipids Expo 2013, Hyderabad, India. www.aocs.org/oleo2013

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. www.aocs.org/australasian

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

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

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

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

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biotechnology pioneer were pointed out. He was also commended for financing Martek (subsequently purchased by DSM in 2011), the company that found that docosahexaenoic acid (DHA) was a vital component of mother's milk and that DHA was lacking in infant formula. DHA is now added to infant formula around the world.

Mecpro receives award

The Ministry of Small & Medium Enterprises (MSME) of the Government of India presented its National Award in the R&D category to Mecpro Heavy Engineering Limited (New Delhi, India) at a function in Vigyan Bhawan on April 3, 2013. AOCS member Rajan Skhariya, managing director of Mecpro, received the award from Pranab Mukherjee, the president of India.

Mecpro is a turnkey plant and machinery supplier and technology provider in the edible oil industry.

New appointments at Bunge

Effective June 1, **Todd Bastean** became chief executive officer (CEO) of Bunge North America (St. Louis, Missouri, USA). He was promoted to this position from his previous position as chief financial officer. He succeeded **Soren Schroder**, who became CEO of Bunge Limited on the same date; Schroder replaced **Alberto Weisser**, who retired after 15 years leading the company. ■

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Professional Pathways

Professional Pathways is a regular column in which AOCS members answer questions about their professional experiences and share advice with young professionals who are starting to establish their own careers in oils and fats chemistry.

Our first subject is Jerry King, a former professor and current consultant based at the University of Arkansas in Fayetteville (USA). King has more than 40 years of experience in oils and fats chemistry that includes industry, academia, and government work.

Why did you join AOCS?

I joined AOCS in 1988 during my time at the US Department of Agriculture (USDA). At the time I was required to be part of organizations such as AOCS as part of promoting my professional image, but not all government agencies require this.

Describe your career path.

I earned a bachelor's degree (1965) and master's degree (1969) from Butler University (Indianapolis, Indiana, USA) before completing my Ph.D. at Northeastern University (Boston, Massachusetts, USA). I started out in academia as a postdoctoral scholar at Georgetown University (Washington, DC, USA) for a year, followed by working as an assistant professor from 1974–1976 at Virginia Commonwealth University (Richmond, USA). My first job outside of academia was with Arthur D. Little, Inc. in Cambridge, Massachusetts, as a research chemist. From 1978–1980, I worked at the American Can Company in Barrington, Illinois, USA, as a research associate devel-

oping packaging technology. From 1980–1986, I worked at CPC International in Argo, Illinois, as a food research chemist/engineer. Then I moved to Peoria, Illinois, to work as a lead scientist at the Agricultural Research Service (ARS) of the USDA from 1986–2002. From 2002–2005, I was with the Los Alamos National Laboratory's Chemistry Division in New Mexico, USA, as program manager/senior scientist/engineer. Starting in 2005, I was a professor of chemical engineering at the University of Arkansas in Fayetteville.

How has your industry changed since you entered the field?

Since I have experienced a multi-faceted career—academia, industry, and government—it's a rather complex question to answer. It seems academia has abandoned a lot of its basic principles that have traditionally focused on research and teaching for the benefit of the students. There is far too much emphasis in major universities in pursuing money at all costs

in order to support research, and something has been lost in the process. Although I have been away formally from industry for some time, my sense is that research is no longer being supported as it was 30–40 years ago and that long-term commitment and loyalty to employees (and vice versa) of companies is lacking in the current atmosphere. Government employment today is compromised consistently by funding issues, such as sequestration and delays in congressional budget approval, which impact on the morale and effectiveness of public servants conducting research and development. I feel the continual privatization of government laboratories also impacts negatively on the professionalism the chemist or engineer can attain.

All this being said, I think these changes challenge individuals to be more diverse and flexible in their career goals. It may take several professional positions for one to find a niche that is compatible with their desires—and this can be a decade-long period of time.

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

The most important quality to develop, whether you go into industry, academia, or government, is communication and writing skills.

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

There will be less basic research—this at best will be done by the few academics involved in this line of work and organizations such as USDA-ARS, and the US Department of Energy laboratories. I think it's important that AOCS as an organization be there to support professionals faced with job and income loss within the next five years.

Describe a memorable job experience.

While at Arthur D. Little, I helped develop analytical/physical methods for the US Environmental Protection Agency, the US Food and Drug Administration, and the National Institute for Occupational Safety and Health, as well as applying polymer chemistry in food, polymer, and flavor projects. We worked on contract, with government agencies, and in private industry, even working on pet food. It was very interesting. It gave a great deal of diverse experience, more so than just industry.

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

I would say my early involvement with Professor J.C. Giddings at the University of Utah was seminal to the path my career and interests would take. It was this academic research setting many years ago that led to me developing along this career

pathway and building a healthy respect for applying fundamental studies to practical problems and situations.

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

Since I am not much into Internet, blog sites, and the like, I advise young professionals to attend many professional meetings, even those outside your specialty. The networking will occur almost automatically. Young professionals should also publish and review manuscripts. It's a surreptitious way of getting around to interacting with people, including those in the publishing world. Take advantage of interview opportunities: by that, I mean contributing more generic brief publications in widely read or dispersed professional magazines (e.g., *R&D Magazine*).

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

My basic academic training occurred in physical-analytical chemistry, an area in which there is always demand for well-trained individuals. With this type of background you can contribute to chemical and food processing engineering or food technology since analytical chemistry is seminal to all of these fields. So I recommend that you get some training in this discipline, whatever your field. It also opens up opportunities in marketing, service engineering, and related areas.

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

In academia you receive a great degree of freedom when you achieve tenure, and you can leave behind your mark in a way that you can't accomplish in industry. Industry is interesting, but it is there for one purpose and that is to make money. It doesn't always help one's professional growth.

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

I feel that I have benefitted substantially from being rather interdisciplinary in my orientation and experience. I personally feel this is important when defining yourself as an engineer, chemist, or food technologist. All the trends I see embrace this merging of fields.

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

It is necessary, especially in academia. If you are going into a Tier-1 research university, you need a postdoc appointment. ■

PATENTS

Prostaglandin fat emulsion, method for producing the same, method for stabilizing the same, and emulsifying agent

Kamiya, S., *et al.*, Q.P. Corp., US8334321, December 18, 2012

A fat emulsion comprises a prostaglandin as an active ingredient, the fat emulsion comprising a phospholipid that comprises phosphatidylcholine (PC) and phosphatidylglycerol (PG) and has a ratio of PC to PG (PC/PG) of 85:15 to 99.7:0.3.

Cold flow improver

Maehling F., *et al.*, Basf Aktiengesellschaft, US8338344, December 25, 2012

The invention relates to the use of polymers which comprise, in copolymerized form, an α -olefin, at least one alkenyl ester and at least one ester of an α,β -unsaturated carboxylic acid with higher alcohols as an additive for fuel oils and lubricants and especially as a cold flow improver in fuel oils; to the fuel oils and lubricants additized with these polymers; and to additive packages comprising such copolymers. The invention also relates to quaternary and higher copolymers which comprise the abovementioned monomers in copolymerized form.

Rinse-off personal care compositions

Tao, B., *et al.*, The Procter & Gamble Company, US8338349, December 25, 2012

The present invention relates to a cleanser composition comprising (i) from about 1% to about 20% of fatty acid soap containing from about 8 to about 16 carbon atoms; (ii) from about 2% to about 20% of a synthetic surfactant; and (iii) water, wherein the composition comprises a metal ion in a level no more than a predetermined amount to provide a turbidity no higher than about 9 NTU [nephelometric turbidity units].

Bio-based oxygenated esters and diesters and method of preparation thereof

Narayan R., *et al.*, Board of Trustees of Michigan State University; Bioplastic Polymers and Composites, LLC, US8349032, January 8, 2013

Fuel oxygenates comprised of fatty acid or fatty acid ester derivatives which have been reacted with ozone; a base; and a lower alkanol (1 to 8 carbon atoms) are described. The oxygenates comprise ester groups at a point of cleavage by the ozone which provide oxygen in the oxygenate.

Aerosol foam composition

Cajan, C., and J. Klutzny, KPSS-KAO Professional Salon Services GmbH, US8349296, January 8, 2013

The present invention relates to aerosol foam composition for styling and conditioning keratin fibers especially human hair. The composition improves hair styling with excellent hold and especially conditions hair with excellent shine, comb-ability, volume and body and also excellent elasticity. The inventors of the present invention have found out surprisingly that an aqueous composition based on at least one hair styling polymer selected from anionic, nonionic, cationic and/or amphoteric or zwitterionic ones which additionally comprises at least one oil or oily compound, at least one fatty acid soap, at least one emulsifier, and at least one propellant shows excellent styling and conditioning benefits and has an appearance like a whipped cream which has not been known in the cosmetic market prior to the present invention.

Polishing liquid

Kamimura, T., Fujifilm Corp., US8338303, December 25, 2012

A polishing liquid for a chemical mechanical polishing of a semiconductor device includes (i) a carboxylic acid compound having one or more carboxy groups, (ii) colloidal silica particles having a ζ potential of -10 mV to -35 mV when used in the polishing liquid, (iii) a benzotriazole derivative, (iv) an anionic surfactant, and (v) an oxidizing agent, and the polishing liquid has a pH of from 5.0 to 8.0.

Decantation improvement in a method of producing alkyl esters from vegetable or animal oil and an aliphatic monoalcohol

Koudil, A., *et al.*, IFP Energies nouvelles, US8350071, January 8, 2013

The present invention describes a method of producing fatty acid alkyl esters and glycerin implementing, in a reaction section, a set of transesterification reactions between a vegetable or animal oil and an aliphatic monoalcohol, and using a heterogeneous solid catalyst, comprising: (i) a stage of recontacting the effluent coming from the reaction section, and separated from the excess alcohol, with a glycerin phase, (ii) a stage of mixing said effluent with said glycerin phase, and (iii) a glycerin phase decantation stage. The supernatant ester phase obtained after decantation is then optionally sent to a coalescer, also allowing separation of the glycerin, then to a purification stage by adsorption on solids.

Modifying agent for plastic fat

Sakai, M., and M. Murayama, Kaneka Corp., US8354133, January 15, 2013

Provided are a modifying agent for a plastic fat to be used in a plastic fat comprising palm oil, which inhibits changes in physical properties of the plastic fat such as hardness or crude crystal

formation and gives an air-containing plastic fat; and a plastic fat using the same. A plastic fat is prepared by using, as modifying agent, an appropriate amount of a fat composition which comprised triglycerides comprising, as constituting fatty acids, a saturated fatty acid (A) having a melting point of 60°C or higher and a saturated fatty acid (B) having a melting point of 40°C or lower, wherein the fat composition contains 40–85 wt%, relative to the total fat composition, of ABB type triglycerides, and the weight ratio (ABB/AAB) of said ABB type triglycerides o AAB type triglycerides is 2–15.

Biodiesel synthesis

Davies, O.M., and R.D. Jackson, Renewable Holdings Ltd., US8350069, January 8, 2013

The present invention provides a method and apparatus for reacting a natural oil with a short-chain alcohol in the presence of alkaline catalyst, in which a mixture of natural oil, short-chain alcohol, and alkaline catalyst is fed in one direction along a pipe reactor under transitional or turbulent conditions, so that the reactants are mixed in a direction normal to the flow direction to a greater degree than in a direction parallel to the flow direction or so that the reactants are mixed in a direction normal to the flow direction, such that the time taken for 90% of the elements of fluid to pass through the reactor is within 20% of the mean residence time of reactant in the reactor. There is also provided a ship, comprising means for storing a raw material used in the synthesis

of biodiesel, a plant for the synthesis of biodiesel, and means for storing the biodiesel synthesized.

Lubricant composition

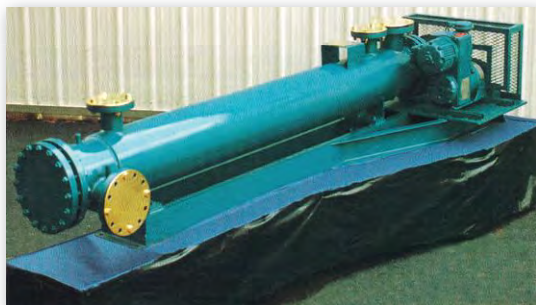
Teshima, K., and H. Kamano, Idemitsu Kosan Co., Ltd., US8349775, January 8, 2013

A lubricating oil composition used in an internal combustion engine is provided. The internal combusting engine uses a fuel that contains at least one fat and oil selected from a group consisting of natural fat and oil, hydrotreated natural fat and oil, transesterified natural fat, and oil and hydrotreated transesterified natural fat and oil. The lubricating oil composition includes: base oil of lubricating oil; a component (A) containing a boron derivative of an alkyl- or alkenyl-substituted succinimide compound having a number average molecular weight of 200 to 5,000; and a component (B) containing an alkaline earth metal-based detergent. The component (A) is contained by 0.01 to 0.2 mass% in terms of boron of a total amount of the composition while the component (B) is contained by 0.35 mass% or less in terms of the alkaline earth metal of the total amount of the composition.

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



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EXTRACTS & DISTILLATES

DHA supplementation improved both memory and reaction time in healthy young adults: a randomized controlled trial

Stonehouse, W., *et al.*, *Am. J. Clin. Nutr.* 97:1134–1143, 2013.

Docosahexaenoic acid (DHA) is important for brain function, and its status is dependent on dietary intakes. Therefore, individuals who consume diets low in omega-3 (n-3) polyunsaturated fatty acids may cognitively benefit from DHA supplementation. Sex and apolipoprotein E genotype (*APOE*) affect cognition and may modulate the response to DHA supplementation. We investigated whether a DHA supplement improves cognitive performance in healthy young adults and whether sex and *APOE* modulate the response. Healthy adults ($n = 176$; age range: 18–45 yr; nonsmoking and with a low intake of DHA) completed a 6-mon randomized, placebo-controlled, double-blind intervention in which they consumed 1.16 g DHA/day or a placebo. Cognitive performance was assessed by using a computerized cognitive test battery. For all tests, z scores were calculated and clustered into cognitive domains as follows: episodic and working memory, attention, reaction time (RT) of episodic and working memory, and attention and processing speed. ANCOVA [analysis of covariance] was conducted with sex and *APOE* as independent variables. RT of episodic and working memory improved with DHA compared with placebo

[mean difference (95% confidence interval, CI): -0.18 standard deviation (SD) ($-0.33, -0.03$ SD) ($P = 0.02$) and -0.36 SD ($-0.58, -0.14$ SD) ($P = 0.002$), respectively]. Sex \times treatment interactions occurred for episodic memory ($P = 0.006$) and the RT of working memory ($P = 0.03$). Compared with the placebo, DHA improved episodic memory in women [0.28 SD ($0.08, 0.48$ SD); $P = 0.006$] and RT of working memory in men [-0.60 SD ($-0.95, -0.25$ SD); $P = 0.001$]. *APOE* did not affect cognitive function, but there were some indications of *APOE* \times sex \times treatment interactions.

Conclusions: DHA supplementation improved memory and the RT of memory in healthy, young adults whose habitual diets were low in DHA. The response was modulated by sex.

Detection of key factors affecting lycopene *in vitro* accessibility

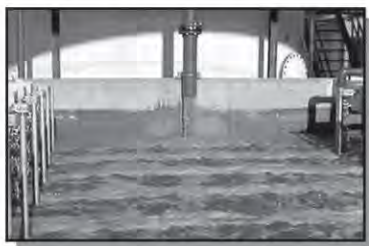
Periago, M.J., *et al.*, *J. Agric. Food Chem.* 61:3859–3867, 2013.

On the basis of a Plackett–Burman experimental design for a resolution IV level obtained via a *foldover* strategy, the effect of 11 factors on lycopene *in vitro* accessibility was investigated. The selected factors were thermal treatment (X_1), olive oil addition (X_2), gastric pH (X_3), gastric digestion time (X_4), pepsin concentration (X_5), intestinal pH (X_6), pancreatin concentration (X_7), bile salts concentration (X_8), colipase addition (X_9), intestinal digestion time (X_{10}), and intestinal digestion speed (X_{11}). Tomato passata [uncooked tomato purée] was used as a natural source of lycopene. Samples were collected after gastric and intestinal digestion, and from the micellar phase, to quantify the (*all-E*)-lycopene and its (*Z*)-isomers by high-performance liquid chromatography. Except for X_3 , X_6 , X_7 , and X_{11} , the other factors studied explained lycopene *in vitro* accessibility, mainly regarding intestinal digestion, with R^2 values ≥ 0.60 . Our results showed that the accessibility of lycopene is influenced by the conditions applied during *in vitro* intestinal digestion.

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Metabolic syndrome, diabetes mellitus, cardiovascular and neurodegenerative diseases: *trans* fatty acids and cardiovascular health: research completed?

Brouwer, I.A., *Eur. J. Clin. Nutr.* 67:541–547, 2013.

This review asks the question if further research on *trans* fatty acids and cardiovascular health is needed. We therefore review the evidence from human studies on *trans* fatty acids and cardiovascular health, and provide a quantitative review of effects of *trans* fatty acid intake on lipoproteins. The results show that the effect of industrially produced *trans* fatty acids on heart health seen in observational studies is larger than predicted from changes in lipoprotein concentrations. There is debate on the effect of ruminant *trans* fatty acids and cardiovascular disease. Of special interest is conjugated linoleic acid (CLA), which is produced industrially for sale as supplements. Observational studies do not show higher risks of cardiovascular disease with higher intakes of ruminant *trans* fatty acids. However, CLA, industrial, and ruminant *trans* fatty acids all raise plasma low-density lipoprotein and the total to high-density lipoprotein ratio. Gram for gram, all *trans* fatty acids have largely the same effect on blood lipoproteins. In conclusion, the detrimental effects of industrial *trans* fatty acids on heart health are beyond dispute. The exact size of effect will remain hard to determine. Further research is warranted on the effects of ruminant *trans* fatty acids and CLA on cardiovascular disease and its risk factors.

Effect of nutrient-based fertilizers of olive trees on olive oil quality

Tekaya, M., *et al.*, *J. Sci. Food Agric.* 93:2045–2052, 2013.

This work was conducted to determine the effects of two nutrient-based fertilizers on the general physicochemical characteristics (including free fatty acid content, peroxide value and ultraviolet spectrophotometric characteristics), fatty acid profile, total phenols, *o*-diphenols, and phytosterol composition of olive oil. Foliar applications were carried out in two successive years and included four treatments: TC (control, without foliar nutrition), T1 (rich in nitrogen, applied at the start of vegetation, 10 days later, and 20 days later), T2 (rich in boron, magnesium, sulfur, and manganese, applied at the beginning of flowering and 10 days later), and T3 (T1 + T2). At the end of the experiment (after 2 years), oils were extracted and analyzed. No effect was found on either general physicochemical characteristics or fatty acid composition. Foliar fertilization caused a significant decrease in both polyphenol and *o*-diphenol contents.



Journal of the American Oil Chemists' Society (June)

- Rapid FT-NIR analysis of edible oils for total SFA, MUFA, PUFA, and *trans* FA with comparison to GC, Mossoba, M.M., H. Azizian, C. Tyburczy, J.K.G. Kramer, P. Delmonte P., A.-R.F. Kia, and J.I. Rader
- Detection of 430 fatty acid methyl esters from a transesterified butter sample, Schröder, M., and W. Vetter
- Physical properties of aqueous solutions of pectin containing sunflower wax, Bäumlér, E.R., A.A. Carelli, and S. Martini
- Pro- and antioxidative effect of α -tocopherol on edible oils, triglycerides and fatty acids, Jerzykiewicz, M., I. Ćwieląg-Piasecka, and A. Jezierski
- The ultrasonic investigation of phase transition in olive oil up to 0.7 GPa, Rostocki, A.J., R. Tarakowski, P. Kiełczyński, M. Szalewski, A. Balcerzak, and S. Ptasznik
- Effect of liquid oil on the distribution and reactivity of a hydrophobic solute in solid lipid nanoparticles, Yucel, U., R.J. Elias, and J.N. Coupland
- No evidence found for Diels–Alder reaction products in soybean oil oxidized at the frying temperature by NMR study, Hwang, H.-S., K.M. Doll, J.K. Winkler-Moser, K. Vermillion, and S.X. Liu
- Fatty acid profile of kenaf seed oil, Razon, L.F., F.T. Bacani, R.L. Evangelista, and G. Knothe
- Growth and biomass characteristics of *Picochlorum oklahomensis* and *Nannochloropsis oculata*, Zhu, Y., and N.T. Dunford
- Evaluation of potential and real quality of virgin olive oil from “Campos de Hellín” (Albacete, Spain), Pardo, J.E., E. Sena, M.A. Cuesta, J.D. Granell, J. Valiente, and M. Alvarez-Ortí
- Effect of UV processing treatments on soy oil conjugated linoleic acid yields and tocopherols stability, Yettella, R.R., B. Henbest, and A. Proctor
- Shear and rapeseed oil addition affect the crystal polymorphic behavior of milk fat, Kaufmann, N., J.J.K. Kirkensgaard, U. Andersen, and L. Wiking
- Pro-oxidant effects of β -carotene during thermal oxidation of edible oils, Zeb, A., and M. Murkovic
- Tribological properties of biobased ester phosphonates, Biresaw, G., and G.B. Bantchev
- Coloration process in the sulfonation of fatty acid methyl ester with sulfur trioxide, Niikura, F., M. Omine, Y. Kimura, H. Konta, M. Kageyama, N. Tobori, and K. Araki
- Synthesis of chloro alkoxy and alkoxy derivatives of methyl oleate, Lowery, B.A., B. Andersh, and T.A. Isbell
- Chemo-enzymatic synthesis of novel β -hydroxy- β -methylbutyric acid (HMB)–medium chain triacylglycerol (MCT) complexes, Cheong, L.-Z., K. Widzisz, Y. Wang, H.H. Jensen, P.K. Theil, Z. Guo, and X. Xu

Lipids

Lipids (June)

- Small high-density lipoprotein (HDL) subclasses are increased with decreased activity of HDL-associated phospholipase A₂ in subjects with prediabetes, Filippatos T.D., E.C. Rizos, V. Tsimihodimos, I.F. Gazi, A.D. Tselepis, and M.S. Elisaf
- Egg consumption modulates HDL lipid composition and increases the cholesterol-accepting capacity of serum in metabolic syndrome, Andersen, C.J., C.N. Blesso, J. Lee, J. Barona, D. Shah, M.J. Thomas, and M.L. Fernandez
- Plasma HDL reduces nonesterified fatty acid hydroperoxides originating from oxidized LDL: a mechanism for its antioxidant ability, Kotosai, M., S. Shimada, M. Kanda, N. Matsuda, K. Sekido, Y. Shimizu, A. Tokumura, T. Nakamura, K. Murota, Y. Kawai, and J. Terao
- Oxidized lipoprotein(a) increases endothelial cell monolayer permeability via ROS generation, Wei, D., X. Zhang, R. Wang, J. Zeng, K. Zhang, J. Yang, S. Li, X. Lin, Z. Jiang, G. Wang, and Z. Wang
- Ezetimibe impairs uptake of dietary cholesterol oxidation products and reduces alterations in hepatic cholesterol metabolism and antioxidant function in rats, Terunuma, S., N. Kumata, and K. Osada
- Lipid lowering and antioxidant effect of miglitol in triton treated hyperlipidemic and high fat diet induced obese rats, Shrivastava, A., U. Chaturvedi, S.V. Singh, J.K. Saxena, and G. Bhatia
- Amaranth oil increased fecal excretion of bile acid but had no effect in reducing plasma cholesterol in hamsters, de Castro, L.Í.A., R.A.M. Soares, P.H.N. Saldiva, R.A. Ferrari, A.M.R.O. Miguel, C.A.S. Almeida, and J.A.G. Arêas
- *Celastrus orbiculatus* Thunb. decreases athero-susceptibility in lipoproteins and the aorta of guinea pigs fed high fat diet, Zhang, Y., Y. Si, S. Yao, N. Yang, G. Song, H. Sang, D. Zu, X. Xu, J. Wang, and S. Qin
- Sesamol treatment reduces plasma cholesterol and triacylglycerol levels in mouse models of acute and chronic hyperlipidemia, Kumar, N., J. Mudgal, V.K. Parihar, P.G. Nayak, N.G. Kutty, and C.M. Rao
- New long chain bases in lipophosphoglycan of *Acanthamoeba castellanii*, Karaś, M.A., and R. Russa

Total sterol content was unaffected by foliar fertilization. However, the phytosterol composition of the oil, particularly its β -sitosterol level, was markedly improved after foliar nutrient application. Principal component analysis of the phytosterol composition showed discrimination between the control oil and the oils from T1, T2, and T3 treatments. The results of this study extend the current knowledge of such cross-talk between plant nutrition and quality of oil.

A lycopene-enriched virgin olive oil enhances antioxidant status in humans

Garrido, M., *et al.*, *J. Sci. Food Agric.* 93:1820–1826, 2013.

Lycopene, a bioactive red pigment, represents the most potent *in vitro* antioxidant among carotenoids. Virgin olive oil contains trace amounts of a wide variety of phytochemicals, which have proven to exert beneficial effects on oxidative stress. Since the ingestion of lycopene together with oil reportedly increases its bioavailability, we evaluated urinary antioxidant capacity after the consumption of a lycopene-enriched virgin olive oil (7 mg lycopene day⁻¹) compared with the antioxidant effect produced after the ingestion of a virgin olive oil and a sunflower oil during 5 days, in young (25–30 years of age), middle-aged (35–55 years of age) and elderly (65–85 years of age) subjects. The results showed that the consumption of virgin olive oil increased urinary antioxidant capacity in middle-aged and elderly volunteers, whereas the administration of a lycopene-enriched virgin olive oil produced higher antioxidant effects in all of the three age groups assayed. The incorporation of the lycopene-enriched virgin olive oil into the diet may enhance the health-promoting effects of the virgin olive oil, contributing as a functional tool against several disorders where oxidative stress plays an important role.

Obesity as malnutrition: the dimensions beyond energy balance

Wells, J.C.K., *Eur. J. Clin. Nutr.* 67:507–512, 2013.

The etiology of obesity is seemingly simple to understand: Individuals consume more energy than they expend, with the excess energy being stored in adipose tissue. Public health campaigns therefore promote dietary restraint and physical exercise, and emphasize individual responsibility for these behaviors. Increasingly, however, researchers are switching from thermodynamic to metabolic models of obesity, thereby clarifying how specific environmental factors promote lipogenesis. Obesity can best be explained not by counting “calories in and out,” but by understanding how specific dietary products and activity behaviors perturb cellular metabolism and promote net lipogenesis. This metabolic approach can furthermore be integrated with more

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sophisticated models of how commercial practices drive the consumer trends that promote obesogenic behaviors. Notably, obesity treatment has proven more effective if it bypasses individual responsibility, suggesting that a similar approach placing less emphasis on individual responsibility would improve the efficacy of obesity prevention. Successful obesity prevention campaigns are likely to emerge only when the public receive better “protection” from the commercial practices that are driving the global obesity epidemic. Rather than populations failing to heed governments’ public health advice, governments are currently failing the public by abandoning their responsibility for regulating commercial activities.

Enzymatic hydrolysis of palm stearin to produce diacylglycerol with a highly thermostable lipase

Xu, Y., *et al.*, *Eur. J. Lipid Sci. Technol.* 115:564–570, 2013.

This paper for the first time presents the production of diacylglycerol (DAG) by hydrolysis of high-melting oil by a highly thermostable lipase (T1 lipase). T1 lipase was expressed in recombinant *Escherichia coli* and used to produce DAG by catalyzing the hydrolysis of palm stearin. The optimal conditions were obtained by a water content of 30% wt/wt (with respect to oil mass), T1 lipase at a concentration of 7.5 U/g (U/wt, with respect to oil mass), and at 60°C. Scale-up reaction was attempted based on the optimized conditions, and 28.1% of DAG was achieved. Molecular distillation was employed for purification of DAG from the reaction

mixture, and the final DAG product yielded 42.5% of DAG (27.8% for 1,3-DAG and 14.7% for 1,2-DAG) and 57.5% of triacylglycerol (TAG). During hydrolysis, T1 lipase was discovered to show 1,3-regiospecific activity toward TAG. The results indicated that T1 lipase is a prospective enzyme which can be used in the modification of high-melting oils and fats.

Evaluation of total and saturated monoglyceride content in biodiesel at low concentration

Bondioli, P., *et al.*, *Eur. J. Lipid Sci. Technol.* 115:576–582, 2013.

Monoglycerides represent a reaction residue in renewable biodiesel fuel. Among the possible glyceridic forms, they are poorly soluble and have high melting point. For this reason, during the in-field use of biodiesel neat or in blend with diesel, monoglycerides can cause problems as regards to the cold stability of the fuel and the plugging of filters. The problem of quantitatively evaluating the monoglyceride content in biodiesel has been addressed and solved during the last 20 years, generally by means of gas chromatography (GC). Recently the need for a strong reduction of total and saturated monoglycerides content appeared. In parallel with the technology changes, new analytical methods have to be developed, in order to fulfill the requirement of accuracy and precision at low concentration levels. The technique presented here allows the determination of total monoglycerides content and the separate quantification of glycerol

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monopalmitate and stearate. The proposed method is based on acetylation of hydroxy groups of the sample, followed by micro column solid-phase separation, isolation of polar fraction containing all acetylated glycerides, and GC quantification with internal standard. By using this technique, a low-noise GC path is obtained thus allowing the identification and the quantification of peaks. Our results are discussed in comparison to those obtained with the existing standards and demonstrated a good repeatability even at low concentration levels.

Comparison of catabolic rates of fatty acids using stable isotope and isotope-ratio mass spectrometry

Gotoh, N., *et al.*, *Lipid Technol.* 25:110–112, 2013.

The catabolic rates of individual fatty acids in mice were compared using stable isotope (^{13}C)-labeled fatty acids and isotope-ratio mass spectrometry (IRMS). The catabolic rates were evaluated from the ratio of ^{13}C and ^{12}C in carbon dioxide expired by mice. The results showed that the catabolic rate of octanoic acid is three times faster than that of palmitic acid. This result is consistent with previous reports using radioisotope ^{14}C showing that medium-chain fatty acids are more easily β -oxidized than long-chain fatty acids. The catabolic rates of odd-numbered fatty acids such as pentadecanoic acid and heptadecanoic acid were significantly lower compared to those of even-numbered fatty acids such as palmitic acid. These findings support previous reports that

show odd-numbered fatty acids easily accumulating in body fat. The high accumulation of odd-numbered fatty acids in body fat thus directly reflects a low degree of β -oxidization. The combination of stable isotope-labeled compounds and IRMS serves as a powerful tool in lipid analysis.

Quality analysis of commercial fish oil preparations

Ritter, J.C.S., *et al.*, *J. Sci. Food Agric.* 93:1935–1939, 2013.

Fish oil supplements have grown in popularity in recent years owing to their multiple health benefits, leading to rapid growth in the number of fish oil supplements available for consumers. When choosing a product, it is important that label claims for eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are met, especially when a specific dosage is required. In this study the amounts of EPA and DHA in 16 of the top-selling liquid fish oil products from the American marketplace were analyzed and compared with their label claims. Peroxide value, a measure of oxidation, was also determined, along with lipid class. This study found that over half of the supplements did not meet their label claims for EPA and DHA, and a quarter exceeded recommended limits for peroxide value. These results suggest that more stringent regulation is required for fish oil products.

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Structure: the ultimate expression of nature's complexity



The following article is based on a presentation by Alejandro G. Marangoni, the 2013 Stephen S. Chang Award winner. Marangoni delivered this address on April 30 at the 104th AOCS Annual Meeting & Expo in Montréal, Québec, Canada.

Alejandro G. Marangoni

The process of creating a supramolecular structure does not entail simply finding a thermodynamic global free energy minimum. Kinetic factors play a key role in determining which local free energy minima are achieved along the formation pathway. Environmental effects become even more important (than molecular effects) beyond the microscopic world, where heat and mass transfer effects will strongly influence the formation of nanostructures, microstructures, and eventually a network.

Over the past 20 years, our research group has observed that several soft materials of industrial interest, such as triglyceride crystal networks (Marangoni *et al.*, 2012), self-assembled fibrillar networks (SAFIN), and polymer oleogels (Co and Marangoni, 2012; Marangoni and Garti, 2011), display such structural

- The macroscopic properties of soft materials cannot always be directly related to their molecular structure.
- Understanding the relationships between molecular composition and phase behavior, solid state structure, growth mode, static and dynamic structure, external fields, and macroscopic properties will contribute to the engineering of fat and oleogel structure.
- Microscopy plays a central role in developing this understanding.



hierarchy and that the macroscopic properties of such materials are highly dependent on their underlying nanostructure and mesoscale structure. Some of these macroscopic properties include hardness (elastic modulus), plasticity (yield stress), and oil-binding capacity (oil diffusivity).

Furthermore, the final morphology of these microstructures is strongly influenced by heat and mass transfer phenomena. For example, when triglycerides are cooled from the melt to a temperature below their melting point, that is, when they are supercooled, they undergo a liquid-solid transformation to form primary nanoplatelets with characteristic polymorphism. These primary nanoplatelets aggregate, or grow into each other, to form clusters, which further interact, resulting in the formation of a continuous three-dimensional network. The solid-like character of fats, in particular elasticity, is highly dependent on the structure of the underlying microstructural network. This structure is a function of the amount of solid fat, the size and shape of crystals, crystal aggregates' intercrystalline separation distance, the strength of van der Waals' interaction between these structures, as well as the spatial distribution of network mass (Marangoni and Wesdorp, 2012; Marangoni, 2012).

To truly understand, and eventually predict, the macroscopic properties of these soft materials, one must characterize and define the different levels of structure present in the material and the relationship of those structural levels with macroscopic properties. In our experience, the macroscopic properties of soft materials cannot always be directly related to molecular structure. Rather than always invoking “molecular interpretations” to explain the macroscopic properties of materials, relationships between the appropriate level of structure and macroscopic properties should be sought first. Eventually, knowledge of the relationships between molecular composition and phase behavior, solid state structure, growth mode, static and dynamic structure, external fields, and macroscopic properties will allow for the engineering of fat and oleogel structure.

Microscopy plays a central role in developing our understanding of the structure and properties of fats and oleogels. Humans are very visual animals, and I believe it to be true that a picture is worth a thousand words. In this short essay, I will highlight some of the most interesting structures we have come across in our work.

The idea for considering fat crystals as fractal objects originated from various microstructural studies. In many of these, we could observe large crystal clusters that resembled classic fractal object found in the scientific and popular literature. Figure 1 is a false-color 50:50 overlay of a phase contrast and a polarized light micrograph of the high-melting fraction of milkfat in triolein (30:70) cooled slowly. The general size and shape of the crystals as well as mysterious needle-like structures in-between could be identified. These two structures could represent different triglyceride families and/or polymorphs. Do both structures form networks? If so, do they affect the rheological properties of the material?

Many fats crystallize into spherulites, such as the one shown in Figure 2. This false-color phase contrast micrograph of a palm oil spherulite reveals the exquisite fine structure of this nonequilibrium structure. Notice the palm leaf-like structure of the crystalline structures that make up the spherulite, their periodic branching, and the fact that the center seems hollow! One can only ponder about the physical processes responsible for the formation of such structure.

Several materials science researchers, ourselves included, have demonstrated the fractal nature of spherulitic structures. Interestingly, the view of a milkfat spherulite imaged using confocal laser scanning microscopy (CLSM) and Nile red (oil dye)

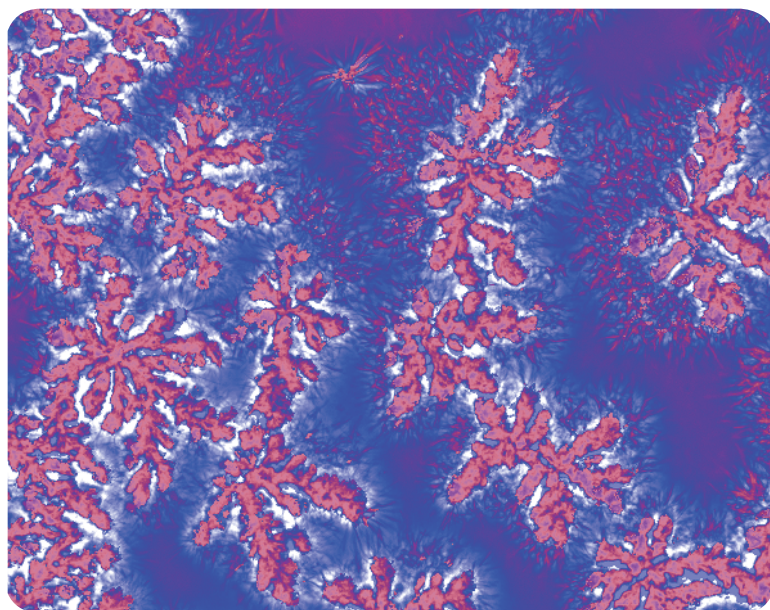


FIG. 1. Phase contrast-polarized light micrograph of the high melting fraction of milkfat in triolein.

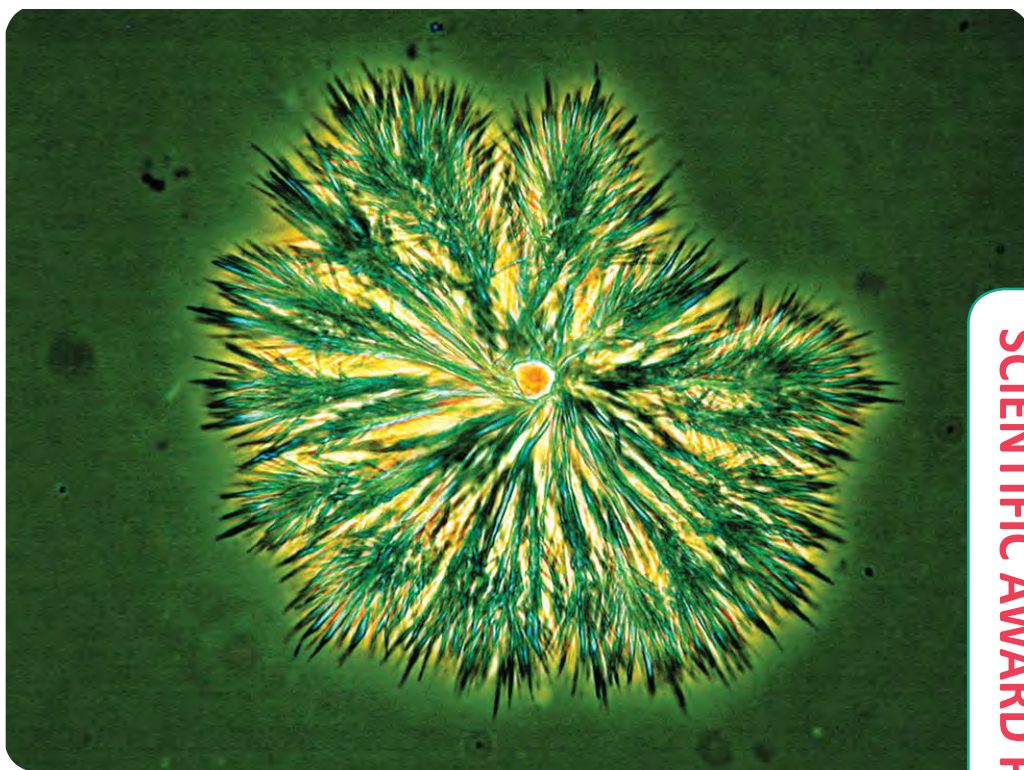


FIG. 2. Phase contrast micrograph of a palm oil spherulite.

is not as interesting. (See Figure 3, which is available via the new *Inform* app. Go to <http://bit.ly/informapp>.) The fine structure of the object is not as clear as that of the milkfat fraction, and the spherulite resembles a sea urchin more than anything else. Notice how the dye partitions into the liquid oil phase and is thus excluded from the crystal. The spherulitic structure observed is

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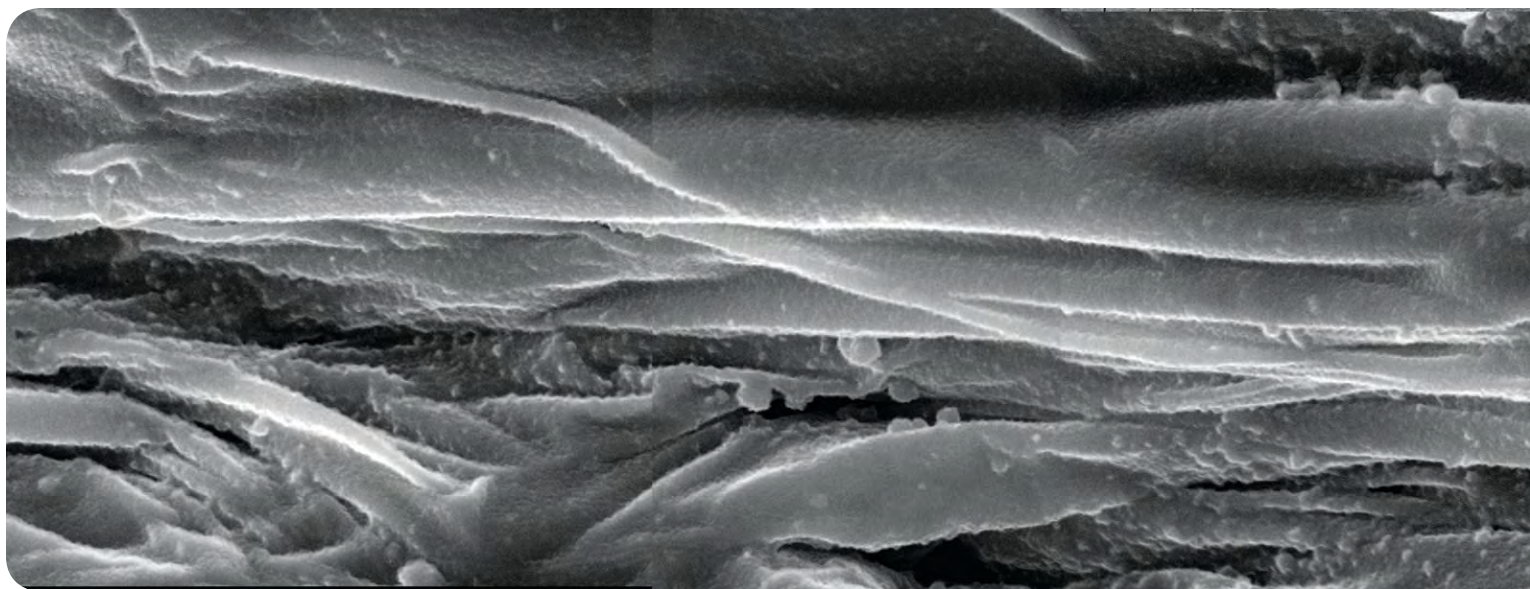


FIG. 9. Cryogenic scanning electron micrograph of a de-oiled 12-hydroxystearic acid–canola oil oleogel.

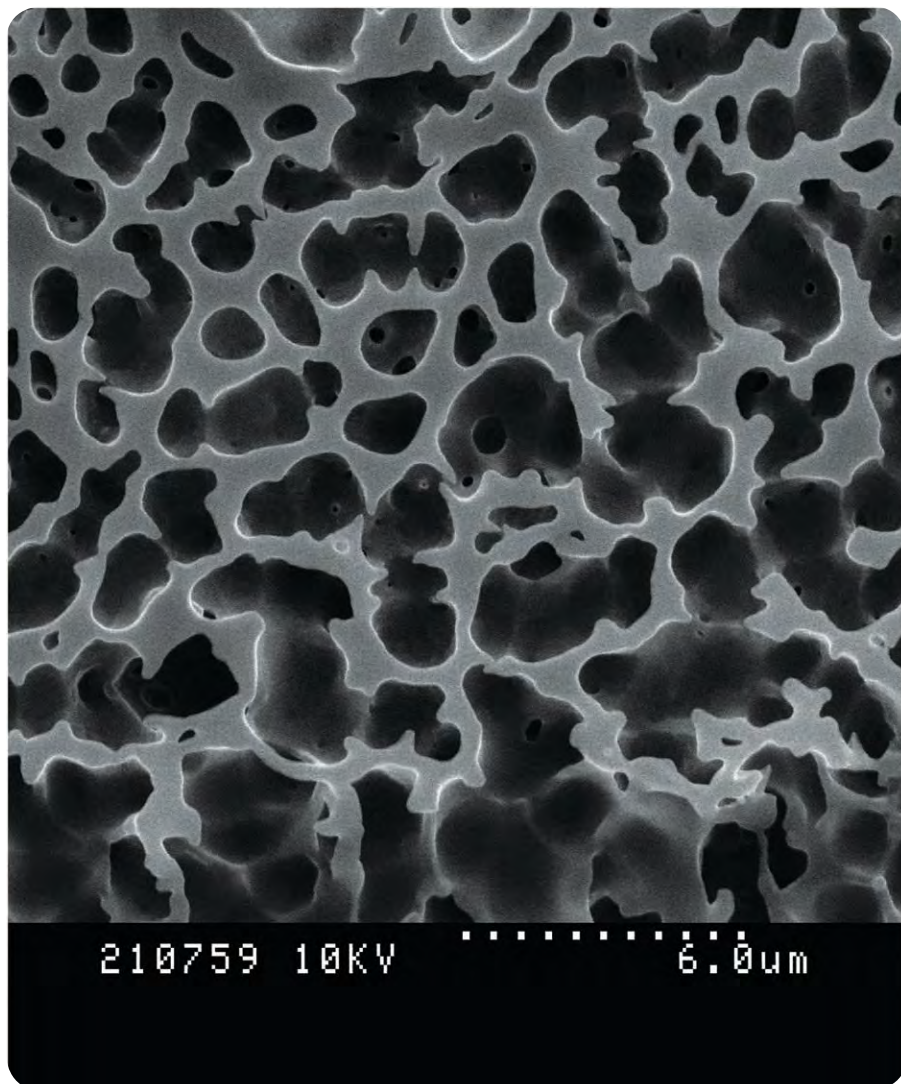
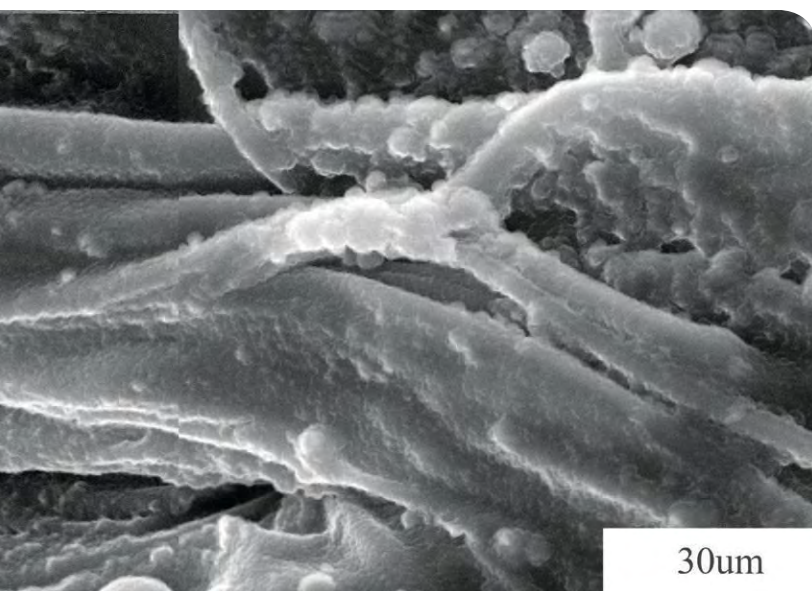


FIG. 10. Cryogenic scanning electron micrograph of a de-oiled ethylcellulose oleogel.

therefore a negative image of the real thing. This should reinforce the concept that different types of microscopy should be used in order to come to valid conclusions about the structure of natural objects. One question one may add is whether a spherulite is more efficient than a large number of crystalline needles in binding oil or providing elasticity, plasticity, or brittleness.

Recent work in our laboratory (Marangoni *et al.*, 2012; Marangoni, 2012) by Nuria Acevdo, now at Iowa State University (Ames, USA), demonstrated the existence of a nanoscale level of structure in fat crystal networks. The breathtaking cryogenic transmission electron micrographs, after extraction, isolation and de-oiling, demonstrated that a crystalline nanoplatelet lies at the base of fat supramolecular structure. (See Figure 4, which is available via the new *Inform* app. Go to <http://bit.ly/informapp>.) This remarkable micrograph even clearly shows molecular triglyceride bilayers of 4.5 nm! This dimension agrees quantitatively with powder X-ray diffraction estimates. The entire hierarchy of structures, from nanoplatelets to clusters, had been imaged by our group some 15 years earlier by atomic force microscopy. (See Figure 5, which is available via the new *Inform* app. Go to <http://bit.ly/informapp>.) However, our understanding of their interrelationships was not clear at that time.

A very interesting microscopy technique that I used back in 1997 was multiple photon excitation fluorescence microscopy, a cousin of CLSM. Figure 6 is an autofluorescence micrograph of milkfat. (See Figure 6, which



30um

is available via the new *Inform* app. Go to <http://bit.ly/informapp>.) A naturally occurring fluorescent compound is distributed within the crystals and allows a unique view of the microstructure of milkfat. This structure remains unexplained.

A major part of our work has focused on the search for alternatives to traditional plastic fats, including fats with reduced saturated and zero *trans* fatty acid content. The structured emulsion Coasun (www.coasun.com) relies on the formation of an oil-in-water emulsion, where the oil globules are stabilized by several hydrated monoglyceride bilayers stacked epitaxially above a monolayer surrounding the oil. This self-assembly process happens spontaneously above the Krafft temperature of the saturated monoglyceride, once all components are in the molten state. The crystalline nature of the hydrated multilayers combined with hydrogen bonding between globules leads to the solidification of this emulsion into a material with the functional properties of a fat. A confocal micrograph of Coasun stained with Nile red (oil) and coumarin (water) reveals the oil-in-water nature of the material. (See Figure 7, which is available via the new *Inform* app. Go to <http://bit.ly/informapp>.)

A remarkable example of structure and functionality is that of SAFIN such as 12-hydroxystearic acid (12-HSA)-stabilized oleogels. (See Figure 8, which is available via the new *Inform* app. Go to <http://bit.ly/informapp>.) This oleogel is formed with as little as 0.5% structuring material. What is remarkable is that the

solidity of the material is provided by a network of macroscopic crystalline 12-HSA fibers formed by self-assembly of this molecule into long crystalline ribbons. Figure 9 is a deoiled (cold isobutanol) cryogenic scanning electron micrograph (SEM) of a 12-HSA SAFIN in canola oil. Notice the thickness of the fibers. Much oil seems to be adsorbed on the surface of these fibers. Possibly this is a mechanism by which these structures bind oil at such low concentrations. The pockets, or pores, formed by the fibers also suggest relatively weak oil binding as well. Only the oil that is adsorbed onto the fiber will be tightly bound; oil trapped in pores is quite free to move.

Recent work from our laboratory has shown that ethylcellulose can gel oils. This is the first example of a polymer oleogel of triglyceride oils. We have since shown its great potential in stabilizing fat-structured materials at high temperatures, that is, heat resistance, and in replacing animal fat in meat products. We can make the most awesome breakfast sausages, hot dogs, and chicken burgers with up to 50% replacement of the animal fat. These translucent molecular oleogels are very similar to hydrogels, minus the water plus the oil, with the polymer forming cells where the solvent (oil) is trapped. The deoiled SEM of an ethylcellulose gel (Fig. 10) provides a good idea of the structure of the gel and its implications for functionality. Moreover, we can now determine the effects of polymer concentration and molecular weight, surfactant addition, oil used, and cooling and heating rates on final microstructure and functionality. Combining a microscopy image with a functional test is very powerful.

This brief overview of the structures found in fat crystal networks, polymer oleogels, and self-assembled fibrillar networks provides, I hope, a framework for understanding the relationship between supramolecular structure and functionality in fats and fat mimetics. The development of microscopy techniques for the visualization and quantification of the static and dynamic structure of these materials will provide valuable insight in order both to optimize existing formulations and functionalities and to help create new ones.

Alejandro G. Marangoni is Professor and Canada Research Chair at the University of Guelph (Ontario, Canada). He may be contacted at amarango@uguelph.ca.

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CALL FOR NO



A. Richard Baldwin Distinguished Service

This is the Society's highest service award. It recognizes long-term, distinguished service to AOCS in positions of significant responsibility.

Nature of the Award: \$2,000, a travel-and-expense allowance, and a plaque provided by Cargill.

Deadline: November 1

AOCS Award of Merit

This award recognizes productive service to AOCS: leadership in committee activities; service that has advanced the Society's prestige, standing, or interests; and service not otherwise specifically recognized.

Nature of the Award: A plaque.

Deadline: November 1

AOCS Fellow

The status of Fellow is awarded to members of AOCS whose achievements in science entitle them to exceptionally important recognition or to those who have rendered unusually important service to the Society or to the profession.

Nature of the Award: Fellow membership status and a plaque.

Deadline: December 1

CALL FOR NOMINATIONS

Each award has its own specific and unique nomination requirements. For award consideration, it is essential that all paperwork be complete and received at AOCS by the nomination deadline. Self-nominations are welcomed and encouraged. Please refer to the website for the nomination requirements and submission deadlines.

ELECTRONIC SUBMISSIONS ONLY!

AOCS is accepting nomination material only by electronic communication. Window based programs (WORD) and PDF material emailed to AOCS must include the award name and candidate name in the email subject line.



Supelco/Nicholas Pelick-AOCS Research

This award recognizes outstanding original research of fats, oils, lipid chemistry, or biochemistry. The recipient must have published the research results in high-quality technical papers regarding fats, oils, lipid chemistry, or biochemistry.

Nature of the Award: \$10,000, a travel-and-expense allowance, and a plaque. The award is sponsored by Supelco, a subsidiary of Sigma Aldrich Corp, and Nicholas Pelick, past president of AOCS.

Deadline: November 1 

Stephen S. Chang

This award recognizes a scientist, technologist, or engineer whose distinguished accomplishments in basic research have been used by industries for the improvement or development of products related to lipids.

Nature of the Award: A cash prize and a jade horse, provided by the Stephen and Lucy Chang endowed fund.

Deadline: October 15 

AOCS Young Scientist Research

This award recognizes a young scientist who has made a significant and substantial research contribution in one of the areas represented by the Divisions of AOCS.

Nature of the Award: \$1,000, a plaque, and a travel-and-expense allowance provided by the International Food Science Center A/S.

Deadline: November 1 

The Schroepfer Medal

Originated by colleagues of George Schroepfer, this award recognizes a scientist who has made significant and distinguished advances in the steroid field. The work may represent a single major achievement or an accumulation of data.

Nature of the Award: An honorarium and a bronze medal.

Deadline: October 15 



ACI/NBB Glycerine Innovation

The Industrial Oil Products Division initiated this award to recognize outstanding achievement for research in new applications for glycerine with particular emphasis on commercial viability.

Nature of the Award: \$5,000 and a plaque provided by the American Cleaning Institute and the National Biodiesel Board.

Deadline: November 1

Samuel Rosen Memorial

Milton Rosen and the Surfactants and Detergents Division initiated this award to recognize a surfactant chemist for significant advancement or application of surfactant chemistry principles.

Nature of the Award: \$2,000 and a plaque.

Deadline: November 1 

Herbert J. Dutton

The Analytical Division initiated this award to recognize an individual who has made significant contributions to the analysis of fats and oils and related products or whose work has resulted in major advances in the understanding of processes utilized in the fats and oils industry.

Nature of the Award: \$1,000, a travel-and-expense allowance, and a plaque.

Deadline: November 1 

Timothy L. Mounts

The Edible Applications Technology Division initiated this award to recognize research relating to the science and technology of edible oils or derivatives in food products, which may be basic or applied in nature.

Nature of the Award: \$750 and a plaque provided by Bunge North America.

Deadline: November 1 

MINATIONS

Edible Applications Technology Outstanding Achievement

This award recognizes a scientist, technologist, or leader who has made significant contributions to the Division's field of interest, or made contributions to the advancement of edible oils.

Nature of the Award: \$500 and a plaque.

Deadline: November 1 

Ralph Holman Lifetime Achievement

The Health and Nutrition Division established this award to annually recognize an individual who has made significant contributions to the Division's field of interest, or whose work has resulted in major advances in health and nutrition.

Nature of the Award: \$500, a travel-and-expense allowance, and a signed orchid print.

Deadline: November 1 

Processing Distinguished Service

The award recognizes and honors outstanding, meritorious service to the oilseed processing industry.

Nature of the Award: Travel-and-expense allowance and a certificate.

Deadline: December 1

Surfactants and Detergents Distinguished Service

The award recognizes outstanding, commendable service to the surfactants, detergents and soaps industry.


Nature of the Award: A plaque.

Deadline: December 1

Alton E. Bailey Award

This award is supported by the USA Section and recognizes research and/or service in the fields of fats and oils and related disciplines.

Nature of the Award: \$750 and a plaque.

Deadline: November 1 



Thomas H. Smouse Fellowship

This award was established by the Archer Daniels Midland Foundation and the family and friends of Thomas H. Smouse. The purpose of this graduate fellowship is to encourage and support outstanding research by recognizing a graduate student pursuing an M.S. and/or Ph.D. degree in a field of study consistent with the areas of interest of AOCS.

Nature of the Award: The Fellowship level is up to \$15,000 (\$10,000 Fellowship, \$5,000 for travel and research expenditures related to the student's graduate program).

Deadline: February 1

Ralph H. Potts Memorial Fellowship

This award recognizes a graduate student working in the field of chemistry of fats and oils and their derivatives. Qualifying research will involve fatty acids and their derivatives, such as long-chain alcohols, amines, and other nitrogen compounds.

Nature of the Award: \$2,000, a plaque, and travel-and-expense allowance. The award is supported by AkzoNobel, Inc.

Deadline: October 15 

Honored Student

This award recognizes graduate students in any area of fats and lipids. To receive the award, a candidate must remain a registered graduate student and must not have received a graduate degree or have begun career employment prior to the Society's Annual Meeting.

Nature of the Award: Travel-and-expense allowance and a certificate.

Deadline: October 15 

Kalustian and Manuchehr Eijadi

Each award recognizes outstanding merit and performance of one Honored Student award recipient and includes a scholarship of \$1,000.

Hans Kaunitz

This award is supported by the USA Section and encourages studies in the sciences relating to fats, oils, and detergent technology. This award is open to graduate students within the geographical boundaries of the USA Section.

Nature of the Award: \$1,000, a travel-and-expense allowance, and a certificate.

Deadline: February 1 

AOCS Division Awards for Students

These awards recognize students at any institution of higher learning, who are studying and doing research towards an advanced degree in fats, oils, proteins, lipids, surfactants, detergents, and related materials.

The following student awards are currently being offered by these AOCS Divisions:

- Analytical Division Student Award
- Biotechnology Student Excellence Award
- Edible Applications Technology Division Student Award
- Health and Nutrition Division Student Excellence Award
- Industrial Oil Products Division Student Award
- Lipid Oxidation and Quality Division Student Poster
- Processing Division Student Excellence Award
- Protein and Co-Products Division Student Poster
- Surfactants and Detergents Division Student Travel Award

Nature of the Award: Awards can consist of \$100 to \$1,000 and a certificate.

Deadline: Varies from October 15 to January 15 



The award recipient must agree to attend the AOCS Annual Meeting & Expo and present an award address.

The 105th AOCS Annual Meeting & Expo will be held in San Antonio, Texas, USA from May 4–7, 2014.

AOCS Awards contact ➤ awards@aocs.org • www.aocs.org/awards

Plant oils: the perfect renewable resource for the chemical industry?!



The following article is based on a presentation by Michael Meier, the 2013 AOCS Young Scientist Research Award winner. Meier delivered this address on April 30 at the 104th AOCS Annual Meeting & Expo in Montréal, Québec, Canada.

Michael Meier

Have we passed peak oil? How long will reserves last? Are hydrocarbons isolated from coal, oil sands, or fracking

sustainable alternatives to obtain the required resources for fuels as well as starting materials for the chemical industry? These alternatives may be industrially feasible and lucrative, but they are certainly unsustainable by any means! Apart from causing environmental hazards such as increased CO₂ emissions or pollution, these “alternatives” to petroleum will last only for a limited time. Our only truly sustainable alternative is thus the use of renewable resources. Plant oils, with their inherent chemical functionality, are a long-established renewable feedstock for the chemical industry with applications in cosmetics, lubricants, detergents, and polymers, to name only a few. New developments in catalysis and efficient chemical functionalization protocols enable the synthesis of novel fatty acid derivatives that are especially interesting for polymer chemistry.

- Plant oils are a long-established renewable feedstock for the chemical industry.
- Their long-chain fatty acids of various composition and chemical functionality offer manifold possibilities for the synthesis of monomers and polymers.
- Additionally, new developments in catalysis and efficient chemical functionalization protocols are making it possible to synthesize novel fatty acid derivatives from plant oils that are especially interesting for polymer chemistry.

Plant oils offer numerous possibilities for the synthesis of monomers and polymers. Their long-chain fatty acids of various composition and chemical functionality allow chemists to take full advantage of nature's synthetic potential. Apart from the more commonly known unsaturated fatty acids—such as oleic acid (1), linoleic acid (2), or linolenic acid (3)—nature provides

us with fatty acids containing functional groups, such as the hydroxyl group of ricinoleic acid (4), which is the major component of castor oil (Fig. 1). The latter is an especially well-established feedstock for the polymer industry, with applications ranging from polyurethanes to Nylon-11, the only fully renewable polyamide on the market, and including several thermoplastic materials based on sebacic acid.

These and other fatty acid derivatives can be used for thermoplastic as well as for thermoset materials. Industrial realities in the field of thermoset materials include, for instance, alkyd resins, which are based on the cross-linking of polyunsaturated fatty acids such as 2 and 3, as well as polyols for polyurethanes that can be prepared via epoxidation of soybean oil and subsequent ring opening with methanol. Additionally, acrylated triglycerides have many applications including fiber-reinforced thermoset materials.

Apart from these thermoset materials, some novel developments involving thermoplastic materials derived from plant oils are worth mentioning. An interesting route is olefin metathesis, which earned the Nobel Prize in chemistry in 2005 for Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock. This reaction allows the synthesis of long-chain α,ω -difunctional fatty acid materials via self-metathesis as well as cross-metathesis.



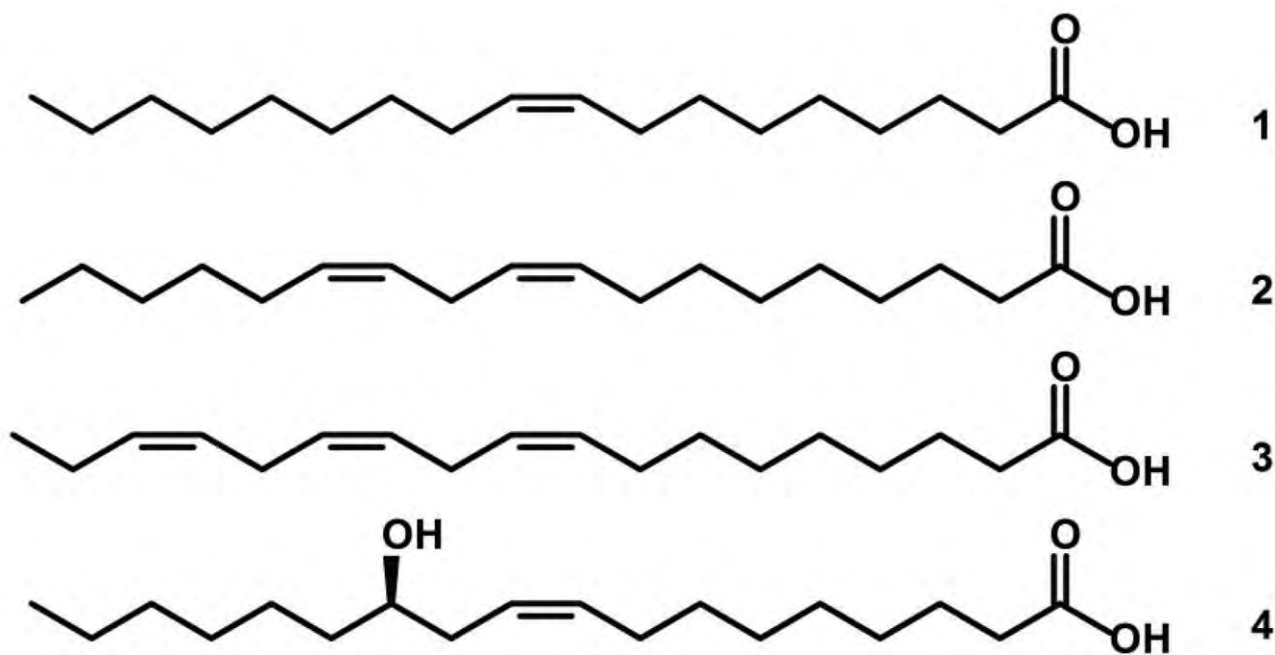


FIG. 1. Fatty acids commonly used in polymer chemistry: (1) oleic acid; (2) linoleic acid; (3) linolenic acid; and (4) ricinoleic acid.

Examples are depicted in Figure 2 (page 462). These reactions are nowadays most often performed with ruthenium-alkylidene catalysts, as initially developed by Nobel laureate Grubbs, because they are very efficient as well as tolerant to moisture, oxygen, and functional groups.

As one can see in Figure 2, the self-metathesis reaction of methyl oleate **5** yields the C18 diester **6**, which would be of interest for the synthesis of polyesters and polyamides, together with the C18 alkene **7**. A problem with this reaction is the equilibrium character of olefin metathesis, which limits the yield of the desired compound **6** to only 25%. Some attempts to shift this equilibrium and thus increase the yield have been made, but only with limited success. Recently, we have shown that the use of highly unsaturated fatty acid methyl esters with high contents of **2** and especially **3** shifts the equilibrium due to the formation of volatile by-products, such as 3-hexene and 1,4-cyclohexadiene. The latter can be removed from the equilibrium by distillation to force the formation of the desired long-chain diester.

Another very promising approach to the synthesis of renewable long-chain diester monomers involves a very selective isomerization/methoxycarbonylation of, for instance, methyl oleate **5** (see Fig. 2), which has been extensively investigated by Stefan Mecking (University of Konstanz, Germany) and David Cole-Hamilton (University of St. Andrews, UK). On the other hand, if the reacting olefin and the reaction conditions are properly chosen, cross-metathesis is not an equilibrium reaction and thus usually results in good yields. The example shown in Figure 2 was first published by our group and yields the C11 diester **9**, useful

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again for the synthesis of polyesters and polyamides, together with the C11 monoester **8**, which would be a suitable starting material for detergent applications. Thus, two useful products are formed at the same time.

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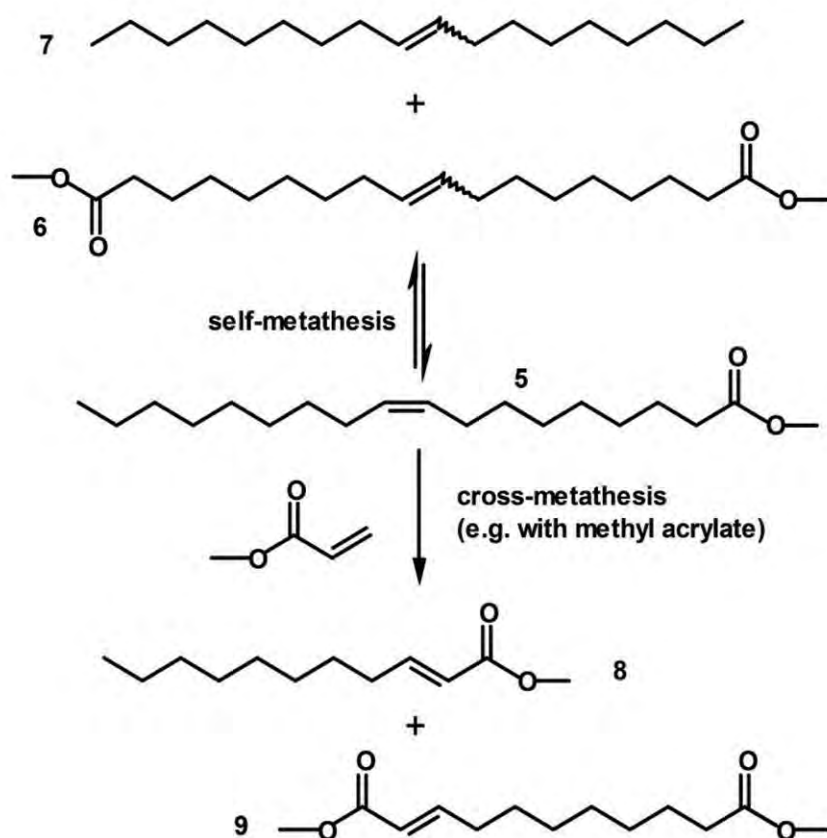


FIG. 2. Self- and cross-metathesis reactions of methyl oleate (5), yielding valuable building blocks for thermoplastic materials and detergents.

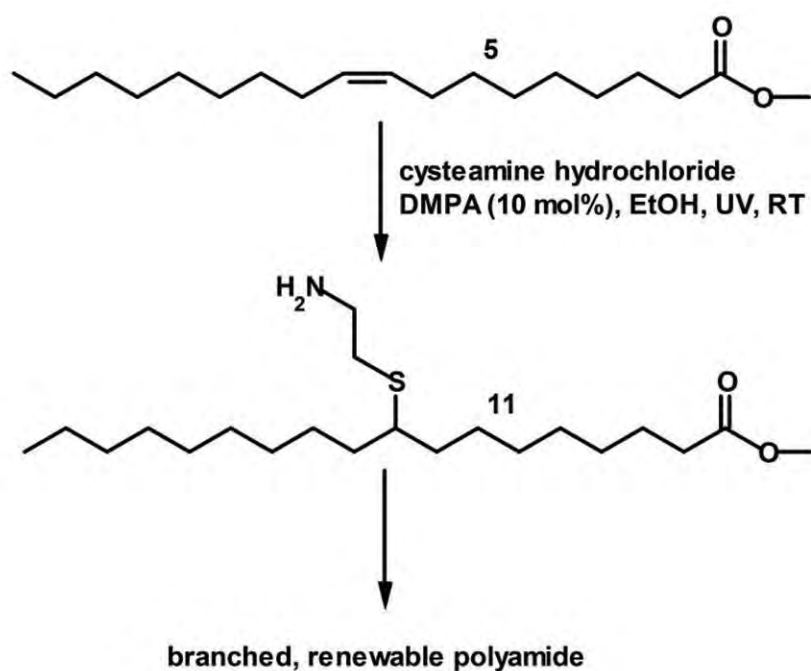


FIG. 3. Thiol-ene route to renewable monomers for polyamides. Abbreviations: DMPA, 2,2-dimethoxy-2-phenylacetophenone; EtOH, ethanol; UV, ultraviolet light; RT, room temperature.

Many groups have studied this and other cross-metathesis reactions in order to introduce many different functional groups. Especially noteworthy in this context is the team of Pierre Dixneuf and Christian Bruneau from the University of Rennes (France), who investigated the cross-metathesis of acrylonitrile with fatty acid derivatives in order to obtain polyamide precursors. Additionally, ADMET (acyclic diene metathesis) polymerization was shown to be a very versatile tool for the polymerization of plant oil-derived dienes as well as for the direct polymerization of triglycerides to yield high molecular weight hyperbranched polymers.

Apart from metathesis, so-called thiol-ene chemistry has recently been applied to fatty acid derivatives. This reaction involves the radical addition of a thiol (via a thiyl radical) to the C=C double bond and can be initiated by ultraviolet light or by using radical initiators. If 10-undecenoic acid methyl ester (10), a derivative of 4 obtained by pyrolysis in a retro Alder-ene reaction, is used as substrate, the reaction meets the criteria of click chemistry due to the high reactivity of the terminal double bond of 10 in this process. The internal double bonds of, for instance, 5 are far less reactive, and harsher conditions and an excess of reacting thiol are required.

Generally, the reaction is very versatile and tolerant toward many reaction conditions and functional groups. Thus, it is not surprising that this reaction was described for the synthesis of monomers derived from 10 and 5, yielding, for example, polyesters and polyamides with promising material properties. Interestingly, the sulfur atom in the polymer backbone provides additional freedom in the design of these materials, since the thio ether can be oxidized to sulfones, which leads to significant enhancements in the thermal properties of these polymers, as recently shown by Filip Du Prez (Gent University, Belgium) and us. An example of monomer synthesis and polymerization developed by our group is depicted in Figure 3. Depending on the plant oil derivative used in this thiol-ene reaction, the resulting polyamides show melting points up to ~140°C, and it is possible to tune the properties of Nylon 6.6 by copolymerization.

In addition to the heavily researched strategies for monomer synthesis from plant oil derivatives just described, many other also highly efficient and versatile approaches are described in the literature (see Refs 1 and 2 for summaries). As a final example, I would like to highlight a recent result of our group. We are able to transform the well-known Lossen rearrangement of hydroxamic acids to a more sustainable catalytic procedure. Applied to fatty acids, this route offers interesting new pathways for the synthesis of renewable non-isocyanate polyurethanes and polyamides. Thus, in summary, plant oil derivatives offer seemingly countless ways to synthesize renewable monomers and polymers in an efficient and sustainable manner. In the future, I would love to see these and other routes transferred to industrial processes in order to contribute to a sustainable development of our society.

Michael Meier has been a full professor at the Karlsruhe Institute of Technology in Karlsruhe, Germany, since October 2010. His scientific work has been published in more than 100 original publications and review articles. In 2010, Meier was awarded the European Young Lipid Scientist Award of the European Federation for the Science and Technology of Lipids, and he received the Outstanding Young Scientists award of the BioEnvironmental Polymer Society in 2012.

[FAST FACT]

Cottoning up to crude (vegetable?) oil

Low-micronaire (immature) cotton, a low-quality fiber not fit for textile processing, may be an “eco-friendly” solution for cleaning up crude oil spills. A study published in *Industrial & Engineering Chemistry Research* (doi:10.1021/ie4005942, 2013) suggests that one pound of low-micronaire cotton can pick up more than 30 pounds of crude oil through absorption and adsorption, and the cotton’s natural waxiness helps to repel water. The immature cotton is effective because its densely packed fibers absorb the oil. It is also biodegradable. The question is: How well does it pick up vegetable oils?



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The other Vitamin E

Laura Cassidy

Many people have turned to personal care products or nutritional supplements that contain vitamin E in hopes that the celebrated antioxidant will prevent wrinkles, minimize scars, or protect against diseases such as cancer and atherosclerosis. The labels of most such products list “alpha-tocopherol (vitamin E)” as an ingredient. Yet alpha-tocopherol is only one of several chemical forms of vitamin E and, as recent research suggests, perhaps not the most beneficial one.

Alpha-tocopherol is the prevalent form of vitamin E in common dietary oils such as sunflower, peanut, sesame, and olive oils and is also the form best absorbed by the body. In the 1940s, reports began to surface that alpha-tocopherol’s ability to scavenge harmful free radicals could treat or prevent a host of health conditions. As alpha-tocopherol gained popularity among researchers and health enthusiasts, the other members of the vitamin E family remained in the shadows. “For years there was



Oil from fruits of the palm tree (Elaeis guineensis) is the richest natural source of tocotrienols.

- The antioxidant properties, prevalence, and bioavailability of alpha-tocopherol have made this form of vitamin E a popular ingredient in nutraceuticals and personal care products.

- Recent research suggests that another class of vitamin E known as the tocotrienols may be better antioxidants and confer greater health benefits, but they are poorly absorbed by the small intestine and rapidly metabolized by the liver.

- Consequently, researchers are trying to increase the bioavailability of tocotrienols by modifying their structure and/or formulation.

a prejudice that alpha-tocopherol was the only form of vitamin E that mattered,” says Paul Sylvester, professor of pharmacology at the University of Louisiana at Monroe (USA).

But in recent years, scientists have discovered that a class of vitamin E known as the tocotrienols are better antioxidants and confer greater health benefits than tocopherols, although they are poorly absorbed into the bloodstream from dietary sources such as palm oil and cereal grains. As a result, researchers are now attempting to improve the bioavailability—the fraction of the ingested vitamin that reaches the target tissues—of tocotrienols. Meanwhile, the reputation of alpha-tocopherol has been tarnished by clinical trials that found no benefit and, in some cases, harm from alpha-tocopherol supplementation for diseases such as diabetes, stroke, and prostate cancer.

STRUCTURE, ACTIVITY, AND BIOAVAILABILITY

Although the eight members of the vitamin E family differ only slightly in structure, these differences translate to striking variations in activity and bioavailability. The two major classes of vitamin E are the tocopherols and the tocotrienols. These molecules share a phenolic OH group crucial for antioxidant activity,

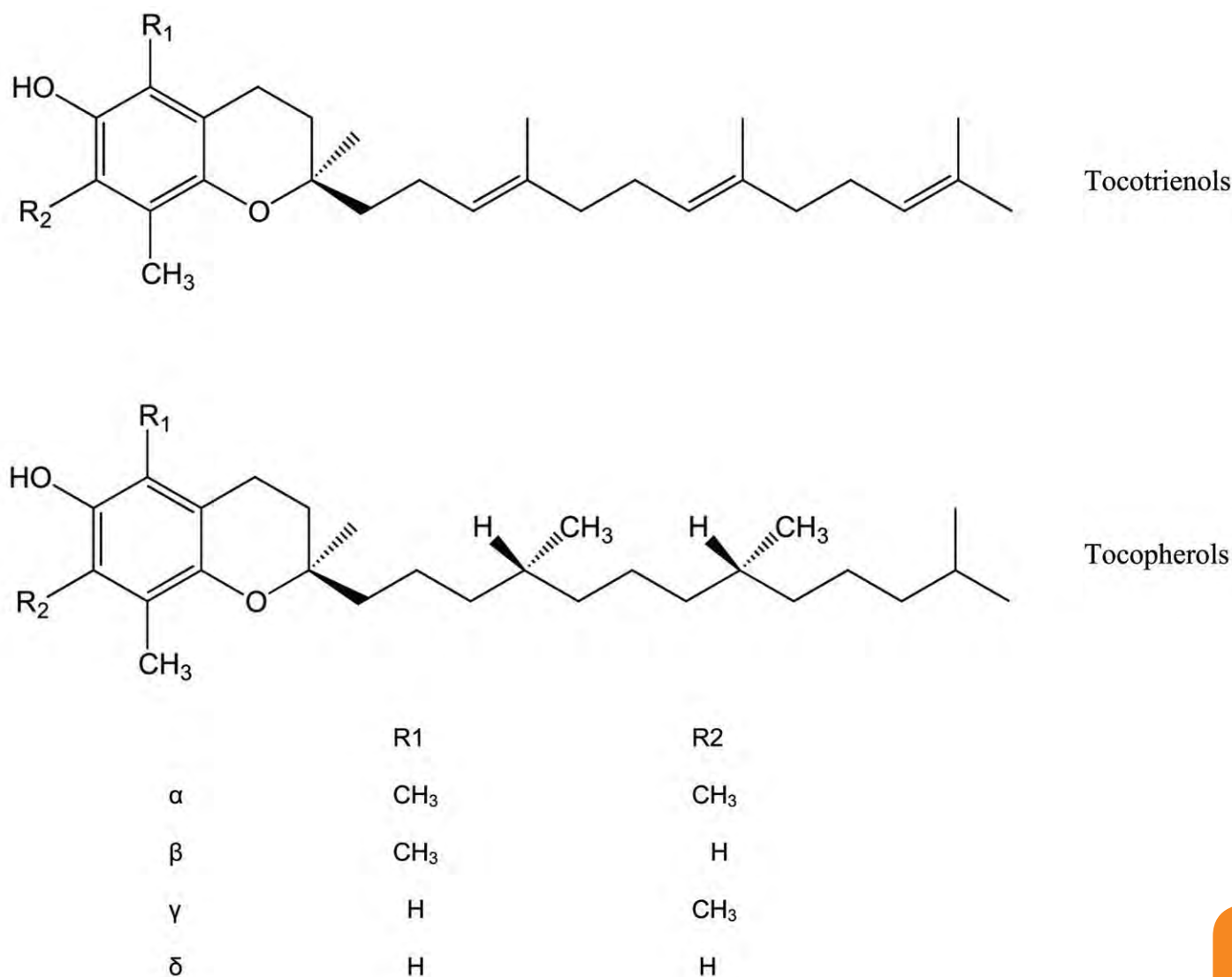


FIG. 1. Chemical structures of vitamin E components.

a chromane ring with variable methylation patterns, and a lipophilic tail that can embed into biological membranes (Fig. 1). Whereas the lipophilic tail of tocopherols is completely saturated, tocotrienols have double bonds at the 3', 7', and 11' positions. The pattern of methyl groups on the chromane ring determines whether the chemical is alpha-, beta-, delta-, or gamma-tocopherol or tocotrienol.

As a post-doctoral student in the 1980s, Sylvester developed an interest in tocotrienols after some surprising data emerged from studies in rats. "We knew that high-fat diets would stimulate the formation of mammary tumors in rats, but we wondered if the kind of fat matters," he says. So Sylvester fed the rats different types of dietary fats such as corn oil, animal fat, and palm oil. All of the fats stimulated tumors, with the exception of palm oil. "We were trying to figure out what's so great about palm oil," recalls Sylvester. "Then we realized that the vitamin E in palm oil is about 80% tocotrienols. When we removed the tocotrienols from the palm oil, the protective effect disappeared, and the rats got tumors" (Sylvester, *et al.*, 1986).

Since then, Sylvester and his coworkers have shown that tocotrienols, in particular delta- and gamma-tocotrienol, are much more potent than tocopherols at inhibiting mammary tumors in animals. At low doses, tocotrienols stop cancer cells from dividing. At higher doses, tocotrienols kill the tumor cells by triggering apoptosis. Additionally, tocotrienols do not harm healthy cells, making them promising candidates for chemotherapy. Moreover, Sylvester's lab has shown that combining gamma-tocotrienol with standard chemotherapy drugs kills cancer cells better than either the tocotrienol or the drug alone (Sylvester, *et al.*, 2011).

Researchers still aren't sure exactly how tocotrienols kill cancer cells or stop them from dividing, but the anticancer effect does not rely on tocotrienols' antioxidant capabilities. According to Sylvester, blocking the phenolic OH group on tocotrienols does not abolish, and in some cases even increases, the compounds' anticancer effects. "Tocotrienols have multiple

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TABLE 1. Health benefits of tocotrienols^a

Benefit	Nature of study	Selected references
Kill cancer cells or inhibit their growth	<i>In vitro</i> (human breast, prostate, melanoma, pancreatic, and cervical cancer cells); rats (chemically induced breast and liver cancer).	Yu, W., <i>et al.</i> , <i>Nutr. Cancer</i> 33:26–32 (1999). Conte, C., <i>et al.</i> , <i>Ann. NY Acad. Sci.</i> 1031:391–394 (2004). Iqbal, J., <i>et al.</i> , <i>Eur. J. Cancer Prev.</i> 13:515–520 (2004)
Lower triglycerides and “bad” (LDL) cholesterol; raise “good” (HDL) cholesterol	<i>In vitro</i> (human hepatocellular carcinoma and fibroblast cells); chickens and mice; double-blind, placebo-controlled human study	Pearce, B.C., <i>et al.</i> , <i>J. Med. Chem.</i> 37:526–541 (1994). Zaiden, N., <i>et al.</i> , <i>J. Atheroscler. Thromb.</i> 17:1019–1032 (2010). Chin, S.-F., <i>et al.</i> , <i>Nutr. Metab.</i> 8:42 (2011).
Lower blood pressure	Rats	Newaz, M.A., and N.N. Newal, <i>Clin. Exp. Hypertens.</i> 21: 1297–1313 (1999).
Prevent or reverse atherosclerosis	Mice; double-blind, placebo-controlled human study	Tomeo, A.C., <i>et al.</i> , <i>Lipids</i> 30:1179–1183 (1995). Li, F., <i>et al.</i> , <i>Atherosclerosis</i> 211:278–282 (2010).
Prevent or improve diabetes	Rats; prospective human population study	Montenen, J., <i>et al.</i> , <i>Diabetes Care</i> 27:362–366 (2004). Budin, S.B., <i>et al.</i> , <i>Clinics</i> 64:235–244 (2009).
Minimize stroke-induced brain damage	Mice, dogs	Mishima, K., <i>et al.</i> , <i>Neurosci. Lett.</i> 337:56–60 (2003). Rink, C., <i>et al.</i> , <i>J. Cereb. Blood Flow Metab.</i> 31:2218–2230 (2011).
Protect against ultraviolet-induced skin damage and stress-induced skin aging	<i>In vitro</i> (human skin fibroblasts), mice	Yamada, Y., <i>et al.</i> , <i>J. Nutr. Sci. Vitaminol.</i> 54:117–123 (2008). Makpol, S., <i>et al.</i> , <i>Arch. Med. Sci.</i> 7:889–895 (2011).
Stimulate hair growth	Double-blind, placebo-controlled human study (unpublished)	Ho, D.S.S., <i>et al.</i> , Hair growth formulation, US Patent 7211274 (2007).

^aThis table shows a sampling of relevant studies and is not intended to be comprehensive. Abbreviations: LDL, low-density lipoprotein; HDL, high-density lipoprotein.

activities besides being antioxidants,” Sylvester explains. His team has shown that tocotrienols block the phosphoinositide 3-kinase/Akt pathway, a relay of molecules that sends powerful growth-stimulating signals to cancer cells. Also, tocotrienols inhibit NF-kappaB, a transcription factor that, when overactive, helps cancer cells proliferate.

In addition to their anticancer effects, tocotrienols have been shown to lower blood cholesterol and blood pressure, reverse atherosclerosis, minimize brain damage after a stroke, regrow hair, and prevent skin aging from the sun (Table 1). Some of these benefits can be ascribed to tocotrienols’ antioxidant effect, whereas others arise from broader actions of the vitamin on cellular proteins and signaling pathways.

COMMERCIAL USE

Although alpha-tocopherol still dominates the nutraceutical and personal care markets, tocotrienols are cropping up in various

products. The skin care company Perricone MD (Meriden, Connecticut, USA) sells firming creams and moisturizers containing tocotrienols, and company founder Nicholas Perricone called tocotrienols the “Super Vitamin E for your skin” in his 2001 *New York Times* bestselling book, *The Wrinkle Cure*.

Other cosmetics companies are also investigating the incorporation of tocotrienols in their products, says Sharon Ling, vice president of scientific affairs in the United Kingdom for Carotech, the world’s largest supplier of tocotrienols. According to Ling, alpha-tocotrienol is 40–60 times more potent as an antioxidant than alpha-tocopherol and, when applied topically, penetrates the skin better than tocopherol.

Carotech, with headquarters in Perak, Malaysia, supplies mixed tocotrienols and other phytonutrients for use in dietary supplements, foods and drinks, and personal care products. In 1990, Malaysian businessman David Ho founded Carotech to extract phytonutrients such as mixed carotene and tocopherols from Malaysia’s abundant supply of red palm oil. When scientists

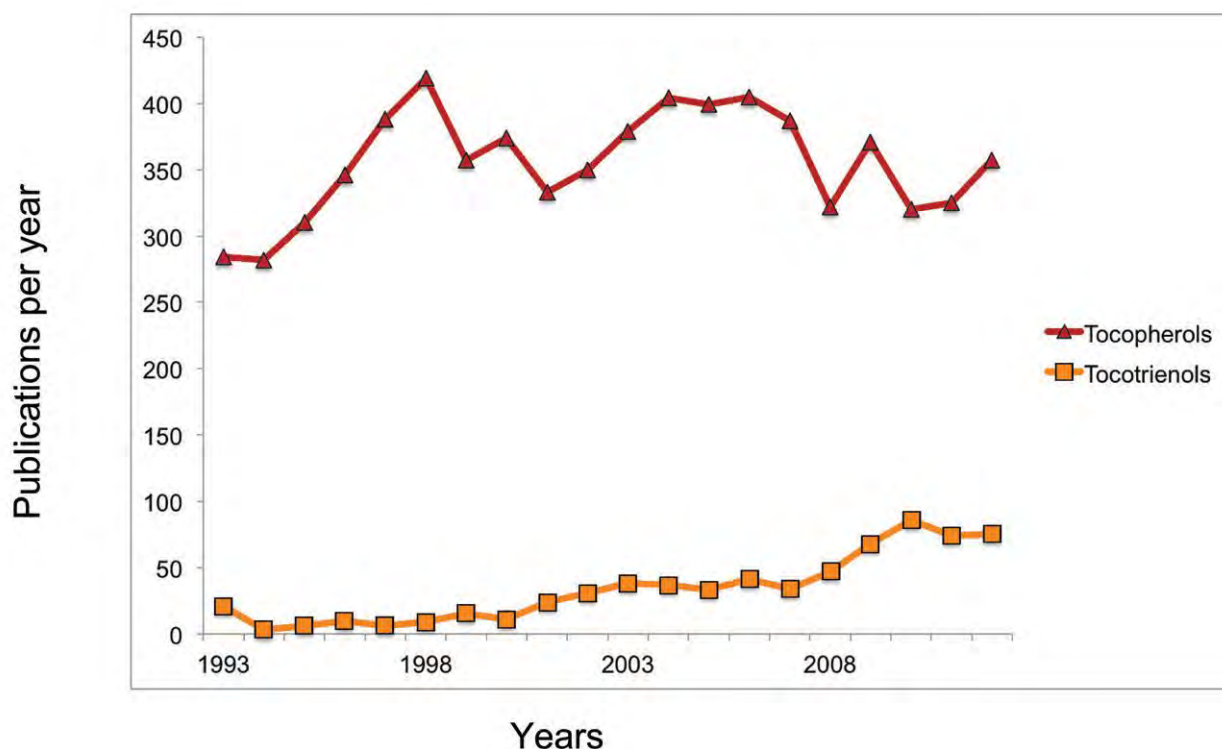


FIG. 2. Twenty years of vitamin E research. Number of publications per year with the word *tocopherol* or *tocotrienol* in the title. Search was performed using Google Scholar for the years 1993 to 2012. Credit: Cesar Compadre, University of Arkansas for Medical Sciences.

began to recognize the unique health benefits of tocotrienols, Ho developed a molecular distillation process to extract a tocotrienol-rich fraction from red palm oil, the richest natural source of tocotrienols. The resulting Tocomin® series of products contains alpha-, beta-, delta-, and gamma-tocotrienols, as well as tocopherols, plant squalene, phytosterols, co-enzyme Q10, and mixed carotenoids.

Given the research thus far showing the benefits of tocotrienols, it may seem surprising that more companies aren't embracing the "other vitamin E." However, because tocotrienols are costlier than tocopherols, companies may be waiting for more published reports on tocotrienols before they make the shift. Indeed, research on tocotrienols has been slow to come. For example, of the total number of publications focused primarily on tocopherols or tocotrienols, only 6% have addressed tocotrienols. Fortunately, the situation is changing, and in 2012 about 21% of the total number of vitamin E publications focused on tocotrienols (Fig. 2).

Further, most published studies that show beneficial effects of tocotrienols have used cell culture or animal models. "The human trials on tocotrienols that have been published are, to be honest, pretty disappointing," says Sylvester. "I think it all relates to the poor bioavailability of tocotrienols."

INCREASING BIOAVAILABILITY

Tocotrienols taken orally are poorly absorbed by the small intestine because the carrier proteins that transport vitamin E from the gut into the blood have a preference for tocopherols. High doses of tocotrienols can slightly increase absorption, but eventually the carrier proteins become saturated and downregulate. "If you take

Stay tuned for special report on novel antioxidants

As consumer preference for all-natural labels continues to grow, Vitamin E, sesamol, and extracts from common herbs and spices offer a natural alternative to synthetic antioxidants in the stabilization of vegetable oils and prepared foods. The 2013 AOCS Annual Meeting & Expo in Montréal, Canada, April 28–May 1, featured some of the latest research in this area and will form the basis of a special report in the next issue of *Inform*.

massive doses of tocotrienols, you will actually absorb less than if you took low doses because there will be fewer carrier proteins," Sylvester explains.

However, by formulating the tocotrienols in an efficient delivery system, researchers can increase their solubility so that they bypass the carrier proteins and passively diffuse through membrane channels from the small intestine into the bloodstream, like other water-soluble nutrients. Sylvester and other researchers have used drug delivery systems such as microemulsions or nanoparticles to enhance the intestinal permeability of tocotrienols (Abuasal *et al.*, 2012). Sylvester notes that tocotrienols for cancer

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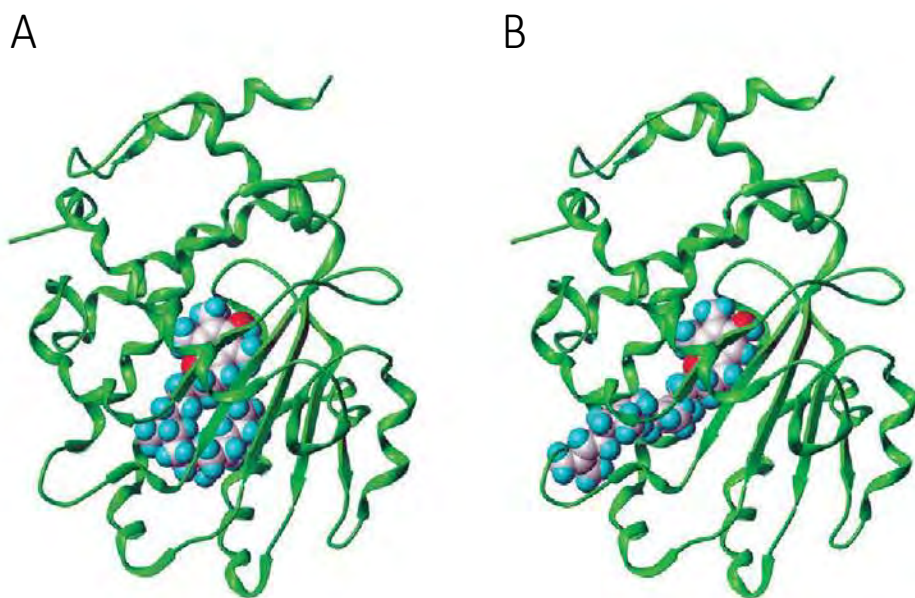


FIG. 3. Binding of alpha-tocopherol (A; blue/grey/red) and gamma-tocotrienol (B; yellow) to the alpha-tocopherol transport protein (A-TTP, green) in liver. Whereas ATTP encloses the alpha-tocopherol molecule, the rigid double bonds in the tail of gamma-tocotrienol prevent efficient binding to ATTP. As a result, less gamma-tocotrienol re-enters the blood-stream. Credit: Cesar Compadre, University of Arkansas for Medical Sciences.

chemotherapy could be encapsulated in nanoparticles and injected into the blood-stream or directly into a tumor, thereby avoiding the problem of intestinal absorption completely.

In 2004, Carotech introduced an improved formulation of their Tocomin tocotrienol complex known as Tocomin SupraBio®. Tocomin SupraBio® has a self-emulsifying delivery system that increases the intestinal absorption of each tocotrienol by an average of 250% compared to regular tocotrienol oil extract, says Ling. Tocomin SupraBio® is now an ingredient in several commercially available tocotrienol supplements.

According to Ling, Tocomin SupraBio® is the only tocotrienol product on the market that has human tissue distribution data (Patel *et al.*, 2012). "This study proved that the tocotrienols in Tocomin SupraBio® are well absorbed and transported to vital human organs," she notes.

Another approach to increasing the solubility of tocotrienols is to chemically modify their structures. For example,

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Sylvester and his collaborators at the University of Louisiana at Monroe have obtained a patent for carbamate ester derivatives of tocotrienols (Sylvester *et al.*, 2012). The derivatives show improved absorption and resistance to breakdown compared with natural forms of the vitamins.

Taking tocotrienols after a meal, rather than on an empty stomach, enhances their absorption because other fats in the diet increase bile excretion and hence the emulsification of tocotrienols. However, ingesting tocopherols simultaneously with tocotrienols reduces tocotrienol absorption because the two forms of vitamin E compete with each other for binding to carrier proteins, Sylvester says.

A SHORT ELIMINATION HALF-LIFE

Increasing the absorption of tocotrienols is only half the problem, says Cesar Compadre, professor of pharmaceutical sciences at the University of Arkansas for Medical Sciences, in Little Rock (USA). “One hurdle is getting tocotrienols into the body; the other is keeping them in,” he says. Compared with tocopherols, tocotrienols have a very short elimination half-life, that is, the time required for half of the tocotrienol that enters the bloodstream to be eliminated (Table 2). For example, the elimination half-life of alpha-tocopherol (44 h) is 10 times that of alpha-tocotrienol (4.4 h).

The reason for the comparatively short half-lives of tocotrienols in blood has to do with a liver protein called

TABLE 2. Elimination half-lives^a of different natural forms of vitamin E^b

Vitamin E isoform	Elimination half-life (h)
Alpha-tocopherol	44
Gamma-tocopherol	13
Alpha-tocotrienol	4.4
Gamma-tocotrienol	4.3
Delta-tocotrienol	2.3

^a Time required for the blood plasma concentration of the vitamin E isomer to reach half its initial level after ingestion.

^b Credit: A. Singh *et al.* (2012).

alpha-tocopherol transporter protein (ATTP). Vitamin E circulating in the bloodstream is taken up by the liver. ATTP preferentially takes alpha-tocopherol out of the liver and secretes it back into the bloodstream. Because tocotrienols have a lower affinity for ATTP than tocopherols, they remain in the liver longer, increasing the chances they will be metabolized or excreted.

The X-ray crystal structure of ATTP reveals why tocotrienols bind poorly to this transfer protein. When ATTP

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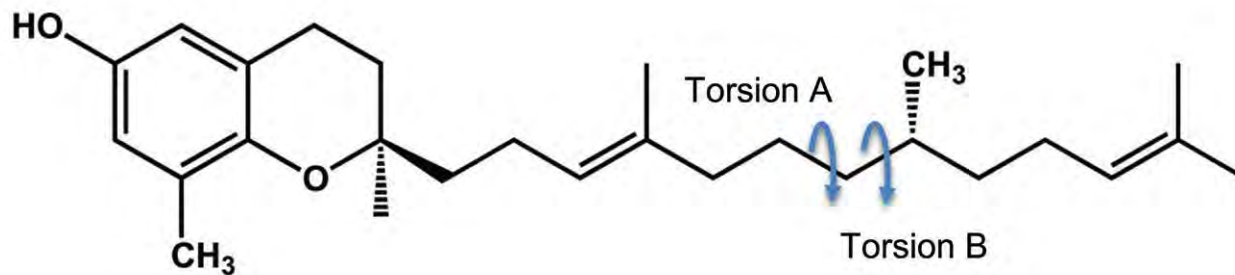


FIG. 4. Synthetic tocotrienols have a more flexible tail (capable of adopting conformations with torsion angles A and B around 60°) than tocotrienols, allowing more efficient binding to ATTP. The optimal structures for tocotrienols were determined by molecular dynamic-based screening. Credit: Cesar Compadre and Philip Breen, University of Arkansas for Medical Sciences.

binds alpha-tocopherol, it closes around the vitamin, causing alpha-tocopherol to fold deeper into the binding pocket of the transporter (Fig. 3A, page 468). In contrast, the more rigid, unsaturated tail of gamma-tocotrienol resists this close embrace, ruling out efficient binding.

Philip Breen, associate professor of pharmaceutical sciences at the University of Arkansas for Medical Sciences, in Little Rock, notes that the literature accompanying many tocotrienol supplements advises taking one pill per day. “Let’s say you take it at 8 in the morning; by noon it’s mostly gone,” he

says. “The other 20 hours of the day, all of the processes that cause oxidative damage, such as sunlight exposure and eating fatty foods, are still going on, and you’re not protected.”

Compadre adds that people would have to take a tocotrienol pill every four hours to get adequate antioxidant protection, which would be not only inconvenient but also expensive. “It’s great that commercial products are beginning to incorporate tocotrienols, but because they get eliminated so quickly, they’re practically ineffective,” he says.

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SYNTHETIC VERSIONS

In hopes of improving tocotrienols' bioavailability, Compadre and Breen designed a class of synthetic tocotrienols that they call "tocoflexols." Tocoflexols have one or two double bonds in their lipophilic tail, rather than the three double bonds of natural tocotrienols (Fig. 4). As a result, the tails are much more flexible and able to fold up for efficient ATTP binding. Breen and Compadre used computer simulations to screen hundreds of thousands of tocoflexol conformations for the ones that bind ATTP with the highest affinity.

So far, the researchers have shown in cell culture studies that tocoflexols protect cells from oxidative damage as well as tocotrienols, and get into the cells about seven times faster than tocopherols (unpublished results). Compadre and Breen are now planning to test the compounds in animal models. The University of Arkansas has filed for patent protection for the tocoflexols (WO/2011/153353 and PCT/US2013/30862), and Breen and Compadre founded a company called Tocol Pharmaceuticals to develop and commercialize the compounds.

To help support their tocotrienol research, Breen, Compadre, and their colleagues received funding from the US Department of Defense's Defense Threat Reduction Agency (DTRA).

The DTRA is interested in tocotrienols because experiments in mice have shown that the compounds protect bone marrow cells from radiation damage (Kulkarni, S., *et al.*, 2010). Therefore, if tocotrienols can be made more bioavailable, they may prove effective radiation countermeasures.

"If, God forbid, there was ever a radiation accident in the United States like the one in Japan during the tsunami, people would have something to do," says Compadre. "Imagine if everybody had a bottle of tocoflexol in their medicine cabinet. They could have it on hand in case anything nasty happens."

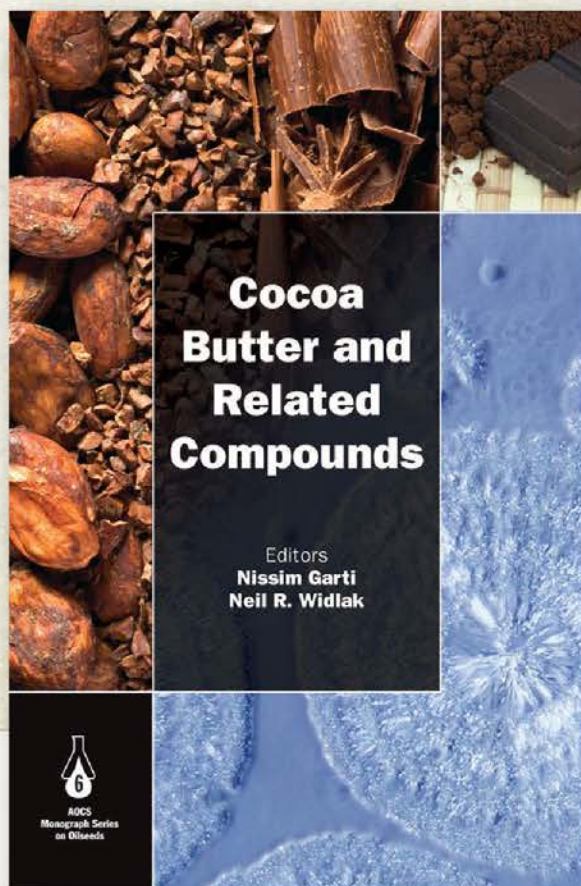
But before tocotrienols become trusted staples of the medicine cabinet and the clinic, more research, especially human studies, needs to be conducted on the promising compounds. Further improvements to tocotrienol bioavailability are also needed before these long-neglected members of the vitamin E family can at last realize their full potential.

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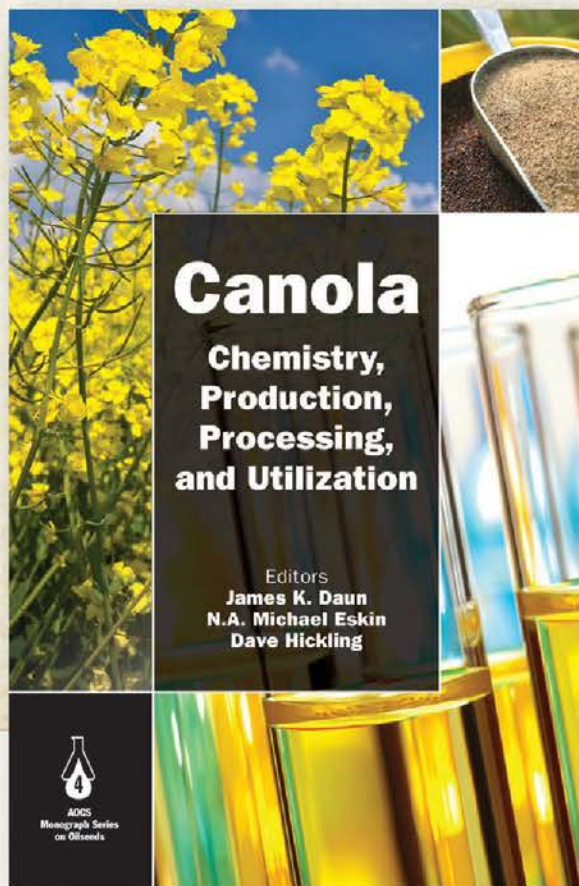
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TSCA and the regulation of renewable chemicals

- While regulators are generally supportive of new chemistries that can replace older, petroleum-based ones, biobased chemicals are subject to the same Toxic Substances Control Act (TSCA) that governs every other chemical substance in the United States.
- Surprisingly, biobased chemicals that are considered to be “new chemicals” may actually receive more scrutiny under this law than established chemicals do.
- The following article provides practical information about the TSCA provisions that are most relevant to biobased chemicals, regulatory outcomes of Premanufacture Notification (PMN) review, and strategies stakeholders can use to assure compliance and successful commercialization of biobased chemicals.

Lynn L. Bergeson, Charles M. Auer, and R. David Peveler

Biobased chemicals represent a multi-billion pound chemical business, and their share of the global chemical industry is expected to grow from 2% to 22% by 2025 [1]. Lux Research reports that biobased chemicals capacity will double in market potential to \$19.7 billion in 2016 [2].

The enthusiasm that supports the commercialization of biobased chemicals in the United States has eclipsed a solid understanding of how the Toxic Substances Control Act (TSCA) applies to them. This article explains how TSCA relates to such products and suggests strategies stakeholders can use to ensure the successful marketing of biobased chemical products.

Biobased products include a broad spectrum, but for TSCA purposes, they can be placed into two broad groupings: biobased chemical products and biofuels. While biofuels may be a more prominent category of products derivative of renewable feedstocks

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(most notably corn and soybeans), biobased chemicals are the primary focus of this article as it is in this product area that TSCA has its greatest potential application.

TSCA OVERVIEW AND RELEVANT PROVISIONS

TSCA is the federal law that governs new and existing chemical substances throughout their production, distribution, use, and disposal [3]. “Chemical substances” are defined broadly to include “any organic or inorganic substance of a particular molecular identity,” excluding pesticides, drugs, and food, which are regulated under other federal laws [4]. That biobased substances are derived from renewable feedstocks does not preclude TSCA’s application to them. We focus here on understanding the provisions critical to recognizing and appreciating how TSCA applies to biobased chemicals.

Three TSCA sections are especially relevant to this discussion: TSCA Section 2, Section 8, and Section 5. TSCA Section 2(b) outlines TSCA policy, and TSCA Sections 2(b)(1) and (2), respectively, discuss that test data need to be developed on the effects of chemicals and that adequate regulatory authority should exist to control chemicals presenting “unreasonable risks” to health and the environment. Section 2(b)(3) clarifies that this authority should be exercised so as not to impede or create “unnecessary economic barriers to technological innovation.” TSCA Section 2(c) states that it is Congress’ intent that the US Environmental Protection Agency (EPA) “consider the environmental, economic, and social impact” of any actions taken. Read in combination, TSCA Sections

2(b) and 2(c) confirm that in taking action to control unreasonable risks, EPA is to consider and balance the risks, costs, and benefits presented.

TSCA Section 8(b)(1) directs EPA to compile and maintain the TSCA Chemical Substance Inventory of each chemical substance that is domestically manufactured or imported into the United States. The initial Inventory was created in 1978–1979 when chemicals were listed on the Inventory automatically, avoiding EPA review of them when listed. New substances are added to the TSCA Inventory through a process that involves submission of a Premanufacture Notification (PMN), which typically accounts for 1,000 to 2,000 new chemical substances each year. EPA reviews the new chemical, imposes any needed regulatory requirements, and adds it to the Inventory once a notice to EPA by the notifier has been filed confirming that manufacture has commenced.

Given that the TSCA Inventory was initiated in the late 1970s, the organic chemicals listed are reflective of the commercial chemistry of that time, which was largely petroleum based. While biobased chemicals were present on the original TSCA Inventory, their number and variety were limited in comparison to petroleum-based substances, with the result that many biobased chemicals will be considered “new chemicals” subject to TSCA Section 5 notification.

It is important for biobased chemical manufacturers and their downstream customers to understand the regulatory implications of the TSCA status of their biobased chemicals. Manufacturers (including importers) of chemical substances considered “new” must notify EPA of the chemical substance through the submission of a PMN. Unless a PMN exemption applies, a company must

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submit a completed PMN form to EPA at least 90 days before commencing the manufacture of a new chemical substance. The EPA review process by statute takes no less than 90 days but can take considerably longer.

Under TSCA Section 5, EPA assesses the PMN to determine if a new chemical presents potential “unreasonable risks.” TSCA Section 5(d)(1) requires that certain information be provided in the notice, including a description of the chemical, estimated annual production volume, intended uses, worker exposure information, and any test data in the possession of the notifier on health and environmental effects, among others. Information provided in the optional “Pollution Prevention” section (e.g., information on expected net benefits such as reductions in risk or releases associated with the new chemical, energy or product efficiency, use of less toxic intermediates, and related factors) is also requested.

REGULATORY OUTCOMES OF PMN REVIEW

If EPA's review reveals risk concerns with a new chemical, TSCA Section 5(e) authorizes EPA to issue consent orders allowing the manufacturer to market the chemical only in conformance with certain enforceable conditions [5]. EPA has discretion to limit the manufacture, processing, distribution, use, or disposal of the chemical to address the concerns EPA's review has revealed. Once the chemical is commercialized subject to a consent order, the notifier is legally required to observe the terms and conditions in the consent order.

The moment the chemical has been placed on the TSCA Inventory, it is no longer considered “new” and other manufacturers of the same chemical may manufacture the chemical without submitting a PMN. TSCA Section 5(a)(2) authorizes EPA to require notifications on “significant new uses” of existing chemicals. In promulgating a Significant New Use Rule (SNUR), EPA is required to consider “all relevant factors,” including, for example, the projected volume and the extent to which a new use increases the magnitude or changes the type of exposure.

To avoid the competitive imbalance that would otherwise ensue if follow-on manufacturers were free to manufacture and use the chemical without the commercial restrictions imposed on the original PMN submitter under the TSCA Section 5(e) consent order, EPA can issue a SNUR imposing the consent order's requirements on subsequent chemical manufacturers. These are known as “Section 5(e) SNURs.” For other substances, EPA may determine that although the manufacture, processing, and/or use of the chemical substance as described in a PMN does not present health and/or environmental risks requiring EPA action, there are other potential uses not described by the PMN submitter that EPA determines represent “significant new uses” such that a SNUR is needed. EPA can use its SNUR authority to regulate such potential uses, and these are referred to as “non-5(e) SNURs” to reflect that no Section 5(e) consent order was issued to the original PMN submitter.

POINTS TO CONSIDER IN COMMERCIALIZING BIOBASED NEW CHEMICALS

Whether a biobased chemical is new or existing is a question that needs to be known well in advance of any plans for commercial activities. If an Inventory listing for the chemical(s) can be established, the PMN hurdle as a new chemical can be avoided. If one or

CONTINUED ON NEXT PAGE

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*The name of the company was incorrect in the April 2013 issue and Annual Meeting's Expo Guide. AOCS regrets the error.

Thank you Exhibitors!

INFORMATION

- *U.S. Biobased Products Market Potential and Projections Through 2025*, M.A. Williamson (ed.), Nova Science Publishers, 2010, p. 1.
- Lux Research, Inc., *Global Bio-based Chemical Capacity Springs to Scale* (December 2011), available at https://portal.luxresearchinc.com/research/report_excerpt/9418.
- 15 U.S.C. §§ 2601-2692.
- TSCA § 3(2), 15 U.S.C. § 2602(2).
- See TSCA § 5(e)(1)(A), 15 U.S.C. § 2604(e)(1)(A).
- *National Bioeconomy Blueprint* (April 2012), available at <http://www.whitehouse.gov/blog/2012/04/26/national-bioeconomy-blueprint-released>.

more of the chemicals is subject to TSCA new chemical notification, this point needs to be recognized and addressed early. When EPA targets a chemical for regulation, this will result in unplanned delays, potentially lasting for months to years, resulting in a barrier to commercialization.

Given the origins of the Inventory with its prevalence of petroleum-based substances, a number of anomalous situations arise. Whereas EPA is generally supportive of new chemistries that can replace older, petroleum-based chemistries, biobased chemicals will continue to be the subject of regulatory scrutiny by EPA as

“new” chemicals. This can lead to a disproportionate amount of regulatory scrutiny at the point of commercial introduction when these new, presumptively greener chemicals are attempting to break into the market and compete with established nonrenewable chemicals that, as Inventory-listed substances, escape such regulatory scrutiny under TSCA.

Emphasizing the benefits of a biobased new chemical is important. The PMN form includes a section entitled “Optional Pollution Prevention Information.” This section should be used to discuss the benefits of a biobased new chemical. In developing the points to include, it may be helpful to think of the task as one of essentially “making the case” for a new biobased chemical introduction and including points establishing: renewable sourcing; pollution prevention or risk reduction benefits (these could include reduced pollution, reduced agricultural waste, use of safer processes or products, avoidance of toxic intermediates, reduced or less toxic waste generation, energy efficiency, relatively safer or less polluting than competing existing chemicals, and related considerations); and cost or performance benefits (these could include improved product performance; lower costs; more energy efficient production, processing, or use; and related factors).

HOW TO APPROACH YOUR BIOBASED PMN CHEMICAL TO HELP ENSURE SUCCESS

Ensure TSCA Compliance Is a Core Element of the Business Plan. Know the TSCA requirements, understand the regulatory responsibilities, and be prepared to meet both the requirements and the responsibilities as a part of a business development plan for the biobased chemical.

Understand the Relevance of Chemical Nomenclature and Naming Conventions. Recognize and understand the importance of how a chemical is named and identified and how that can affect new chemical responsibilities. It is important to understand the relevance of chemical nomenclature and naming conventions to the manufacturing process.

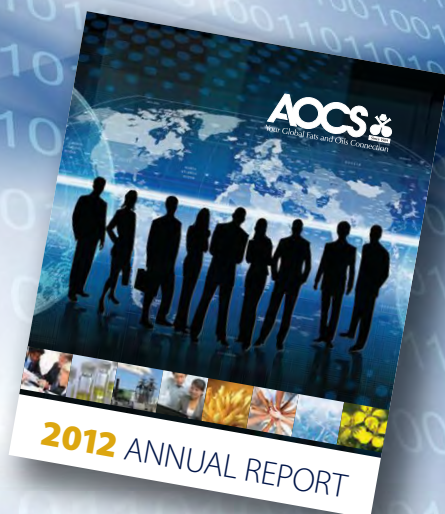
Know the TSCA Review Process. A basic understanding of EPA’s review process and regulatory approach is essential. Although EPA works from the information included in the PMN, it also considers information on other “related” cases, applies structural activity relationship analysis when hazard test data are not available, and will use assumptions about likely exposures and releases if information is not provided in the PMN.

Consider Testing in Advance of PMN Notification. If EPA is likely to impose testing requirements on a biobased new chemical, consider the benefits of either doing the testing in advance of the notification or, if future commercialization plans involve additional structurally similar new chemicals, whether it might make sense to develop a testing strategy that would encompass and account for the range of new chemicals likely to be introduced. If other firms are known to be active in this area of new chemical development, there might be significant cost saving and advocacy opportunities for organizing consortia to share the costs and responsibility of testing.

Work with EPA. Regardless of the approach taken, it is always wise to consult with EPA before embarking on chemical-specific testing or developing and implementing a testing strategy to ensure an understanding of EPA’s views on and obtain its receptivity to the approach proposed.

CONTINUED ON PAGE 480

The 2012 AOCs Annual Report is now available on www.aocs.org.





Farmed fish: a major provider or a major consumer of omega-3 oils?

Jogeir Toppe

A recent FAO/WHO expert consultation [Joint FAO/WHO Expert Consultation on the Risks and Benefits of Fish Consumption (2011), available at www.fao.org/docrep/014/ba0136e/ba0136e00.pdf] concluded that fish in the diet of women giving birth to children lowers the risk of suboptimal development of the brain and neural system compared to children of women not eating fish. Strong evidence also underlines how consumption of fish, and in particular oily fish, lowers the risk of death (36%% reduction) caused by coronary heart diseases (CHD)—a particularly growing health problem in developing countries. A daily intake of only 250 mg EPA + DHA per adult gives optimal protection against CHD.

For optimal brain development in children, the daily requirement is only 150 mg. Evidence on the role DHA has in preventing mental illnesses is now becoming more and more

- Fish and other seafood products are getting more and more attention among consumers due to their health benefits. Such benefits are linked to the valuable long-chain omega-3 fatty acids—eicosapentaenoic (EPA) and docosahexaenoic acid (DHA)—which are almost exclusively found in foods from the aquatic environment.
- As farmed fish, particularly marine fish, must get EPA and DHA through their feed, they are consumers as well as providers of omega-3 oils.
- The following article looks at total EPA and DHA inputs and outputs in an attempt to assess the net gain and sustainability of the farmed fish industry.

convincing. This is particularly important as brain disorders are dramatically increasing all over the world; and in the developed nations, the cost related to mental disorders is now greater than the cost related to CHD and cancer combined.

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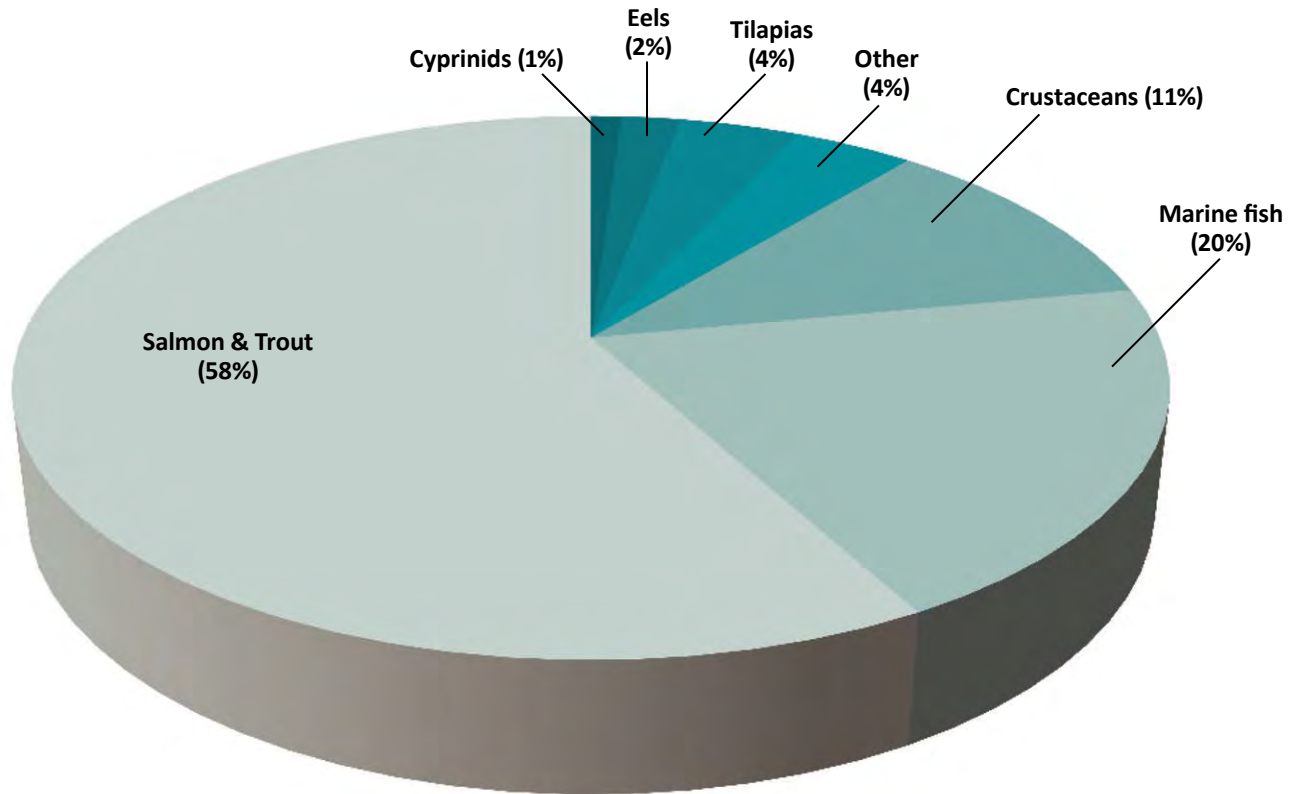


FIG. 1. The pie chart shows the relative usage of fish oil by major groups of farmed species. Carps consume only about 1% of the total EPA + DHA, all contributed through fishmeal. Fishmeal accounts for about 25% of the 210,000 metric tons EPA + DHA used annually in aquaculture feeds.

As with humans, most fish need to get EPA and DHA through their diets. This is particularly true for fish from the marine environment where marine algae are the main producers of these valuable fatty acids ending up in our food chain. Freshwater fish seem to be better able to elongate short-chain omega-3 fatty acids into EPA and DHA.

Farmed fish, and particularly marine fish, need to be provided the beneficial EPA and DHA through their feed. This will secure a final product comparable to and as healthy as their wild counterparts. Fish oil is in practice the only economically viable source of these essential fats for feed purposes, and around 80% of all fish oil is consumed by the aquaculture sector. However, this amount seems to be going down despite the growing aquaculture production, as the demand for fish oil for direct human consumption is rapidly increasing.

Let's take a closer look at the total consumption of these essential omega-3 fats (EPA + DHA) by the aquaculture sector. The global production of fish oil is around 1 million metric tons (MMT)/yr and is not expected to increase. Every year roughly 800 000 metric ton (MT) of pure fish oil are used for aquaculture feed. The level of EPA + DHA in fish oil is usually between 15% and 25%, so with an average content of 20% we would expect 160,000 MT of EPA + DHA from fish oil to fish feed purposes. Additionally, fishmeal provides 50,000 MT of EPA + DHA for fish feed (based on 3.1 MMT fish meal containing 8% oil). At present, the aquaculture sector therefore consumes

an estimated total of 210,000 MT of EPA + DHA, all originating from the marine environment. One can see in Figure 1 how the total amount of EPA + DHA is consumed by the different groups of farmed species.

Salmon and trout (salmonids) farming alone uses 122,000 MT of the 210,000 MT EPA + DHA provided annually. In 2010, production of salmonids was 2.4 MMT: 1.6 MMT salmon and 0.8 MMT trout. Based on recent nutrient composition data for Atlantic salmon and rainbow trout, which represent about 90% of all farmed salmonids, the EPA + DHA content in salmon and trout is estimated at an average 22 g/kg fish, providing 53,000 MT of EPA + DHA. This estimate shows that 43% of the essential EPA + DHA fats from feed is retained in the fish.

This is in line with commercial feed producers claiming 50% of fish oil is retained, and scientific studies show retention of EPA + DHA in salmon from 30% to 75% depending on the level of fish oil in feed; lower levels of fish oil give higher retention rates.

Since salmonids consume a major part of fish oil in aquaculture, the EPA + DHA retention rate of 43% is used for calculating the contribution of these essential fatty acids for other species consuming fish oil, although one would expect better retention in fish having a diet with lower levels of fish oil. Cyprinids do not get fish oil in their diets, but some fishmeal adds some limited amount of EPA + DHA to their feed (Fig. 2).

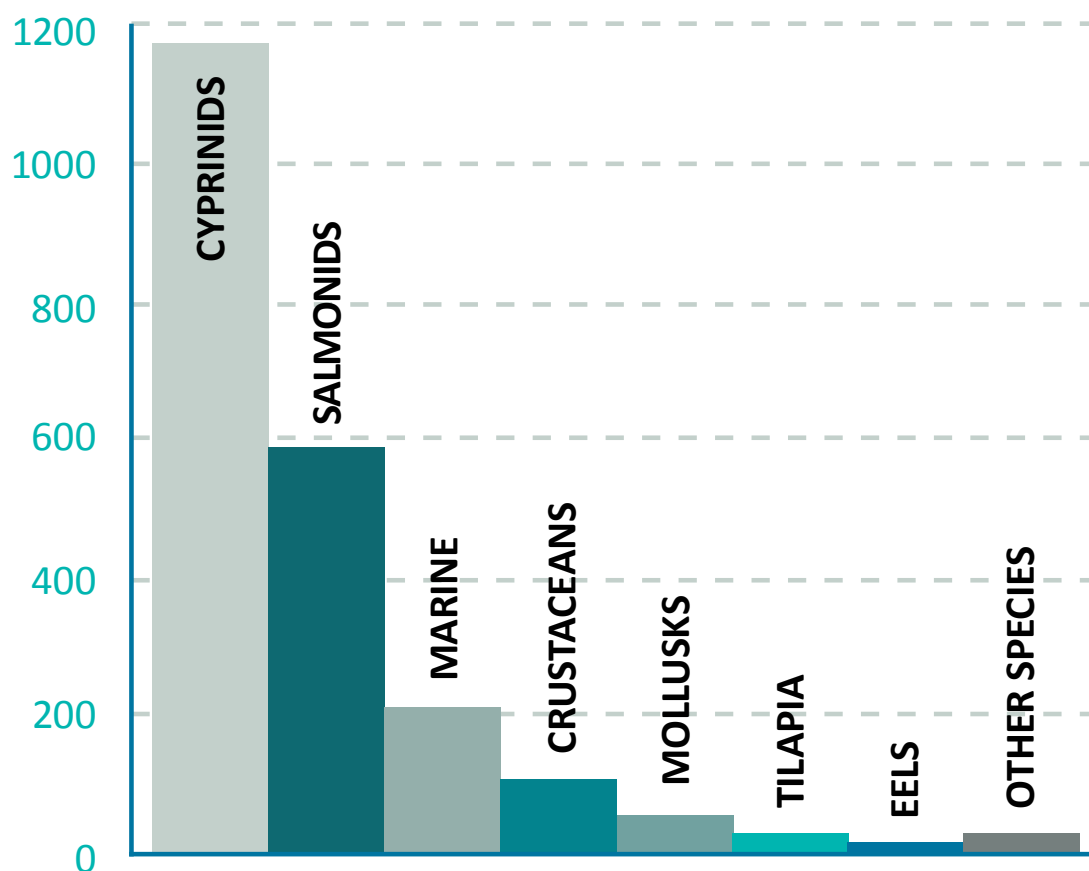


FIG. 2. Farmed fish provides enough omega-3 fatty acids (EPA + DHA) to cover the yearly need of more than 2 billion people. This figure shows the estimated contribution of essential omega-3 oils, by groups of species and per million people. Estimates are based on live weight equivalents.

However, with an annual production of 24 MMT of carp, these fish contribute around 108,000 MT of EPA + DHA, assuming a level of EPA + DHA of 4.5 g/kg of fish (calculation based on literature values for common carp, silver carp, catla, and crucian carp). Mollusks are not consumers of feed but are net providers of EPA + DHA with an estimated contribution of 6,000 MT.

Based on the assumptions above, the aquaculture sector as a whole provides 206,000 MT of EPA + DHA, but at the same time consumes a total of 210,000 MT; that is, in practice providing the same amount as it consumes. Figure 2 shows the major farmed species providing long-chain omega-3 fatty acids to our diets. At present the aquaculture sector provides enough EPA + DHA to cover the need of more than two billion people. All carps combined consume less than 1% of all EPA + DHA provided by fish oil and fishmeal but contribute more than 50% of all the EPA and DHA coming from aquaculture products.

Alternatives such as EPA and DHA production based on microalgae are too costly, and from an economic point of view not a viable alternative. Researchers have reported that plant-based oils from genetically modified plant seed oil can have a 15% DHA content. However, ingredients based on genetically modified plants are not yet widely accepted as feed ingredients. Despite this, with the increasing focus on reducing levels of fish oil and fish meal in diets for aquaculture, the sector is

soon to be a net provider of these valuable and essential fatty acids to our diets.

Jogeir Toppe works for the Products, Trade and Marketing Service, Food and Agriculture Organization (FAO) of the United Nations, Rome, Italy. He can be reached at Jogeir.Toppe@fao.org.

This article is reprinted from the website of Globefish, a unit in the FAO Fisheries Department responsible for information on international fish trade. See <http://tinyurl.com/GlobefishEPA-DHA>.

ERRATUM

The April 2013 issue of *Inform* included a list of companies with exhibits at the 104th AOCS Annual Meeting & Expo in Montréal, Canada. The name of one company was incorrect. The correct name is ÖHMI AG, not ÖHMI Engineering. AOCS regrets the error.

Advocate, Advocate, Advocate. As a final thought, advocate the benefits of a biobased new chemical. This should involve careful preparation of the points that can be made on the optional Pollution Prevention section of the PMN notice. Beyond that, there may be value in recognizing and advocating the bigger-picture policy benefits of biobased chemicals to ensure that the EPA new chemical reviewers are aware of and appropriately consider and value those aspects. While EPA at the higher management levels is likely aware of US government policy drivers (such as the recently announced National Bioeconomy Blueprint [6]), this awareness may or may not have reached the scientists and other career EPA staff levels actually reviewing PMN notifications. As with testing, while individual companies can and should emphasize relevant policy drivers in their interactions with EPA's new chemical reviewers, there may also be considerable value in and a role for consortia to press these points with EPA.

Lynn L. Bergeson is the managing partner of Bergeson & Campbell, P.C., a Washington, DC law firm focusing on conventional, nano, and biobased chemical, pesticide, and other specialty chemical product approval and regulation, environmental, health, and safety law, chemical product litigation, and associated business issues. She is also president of The Acta Group, with offices in the United States, United Kingdom, and China. She can be contacted at lbergeson@lawbc.com.

Charles M. Auer is the president of Charles Auer & Associates, LLC and is an affiliate with Bergeson & Campbell, P.C. Mr. Auer retired in January 2009 as the director of the EPA Office of

Pollution Prevention and Toxics where he was responsible for chemical assessment and management issues under TSCA, pollution prevention and Design for the Environment under the Pollution Prevention Act, and a broad portfolio of international responsibilities (with, for example, the European Union under REACH [Registration, Evaluation, Authorization and registration of Chemical substances], Canada under the Canadian Environmental Protection Act [CEPA], and intergovernmental organizations [Stockholm and Rotterdam Conventions, Strategic Approach to International Chemicals Management, Organisation for Economic Co-operation and Development, etc.]). Over his 32 year career at EPA, he gained broad and deep experience in chemical notification, assessment, and management issues as a senior executive, mid-level manager, and technical assessor. He can be contacted at auer.charlesm@gmail.com.

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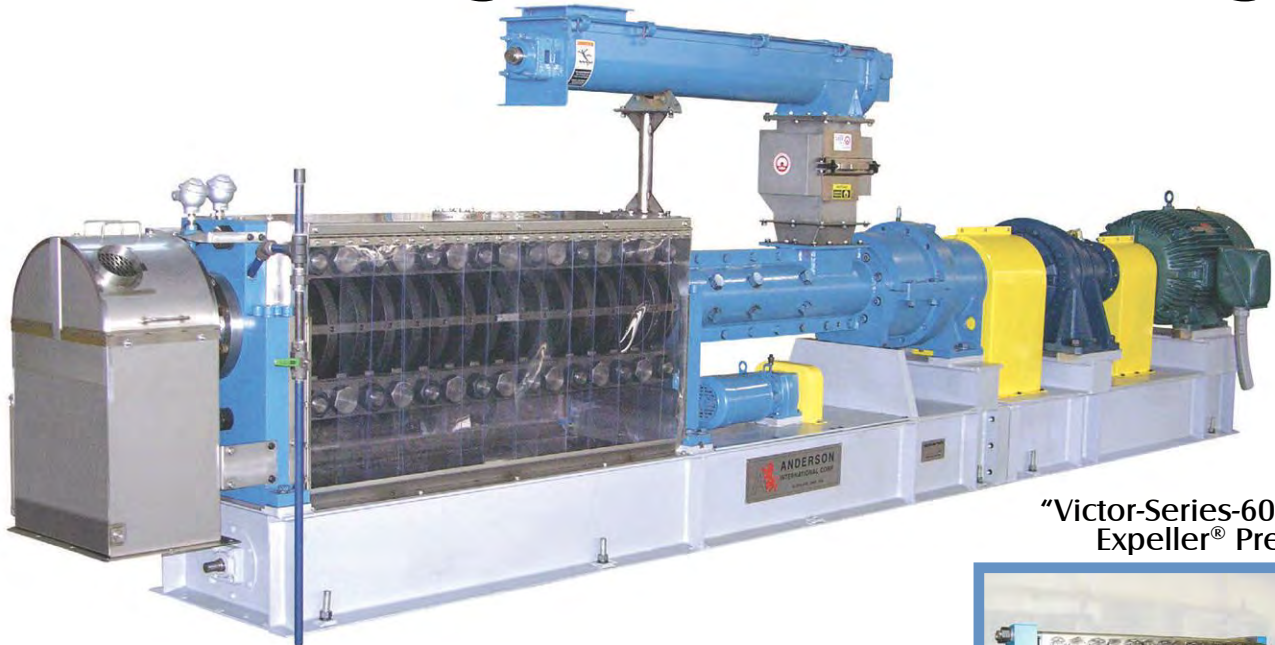
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SUPPLEMENT



2013 AOCS
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Structure: the ultimate expression of nature's complexity

Supplemental figures for Alejandro G. Marangoni's article,
based on his 2013 Stephen S. Chang Award presentation.

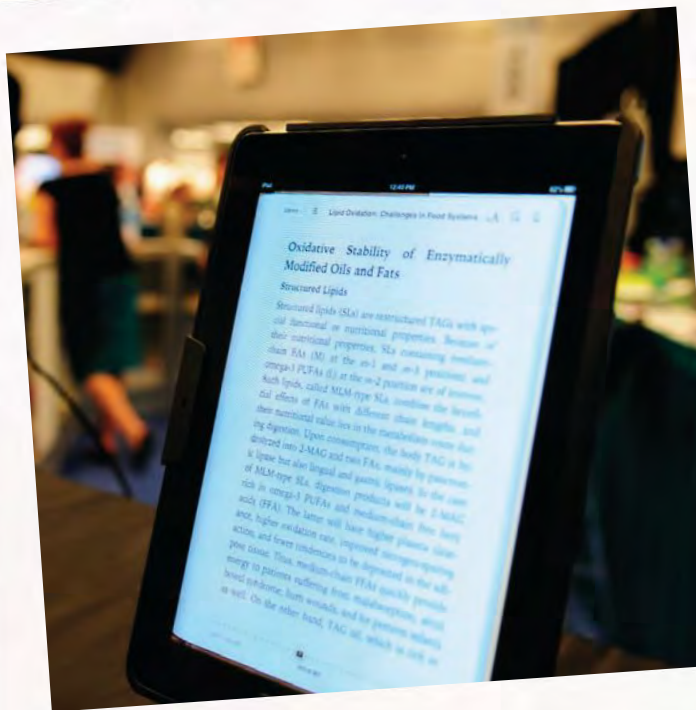
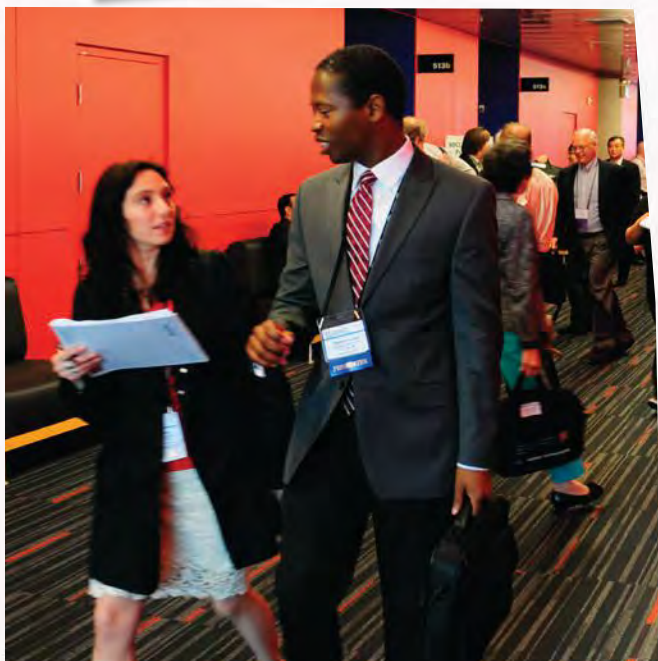
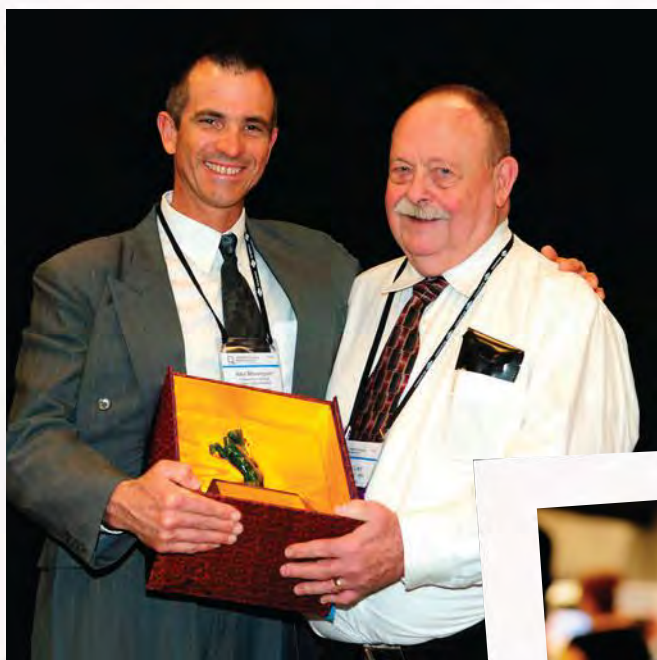
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2013 AOCS Annual Meeting & Expo







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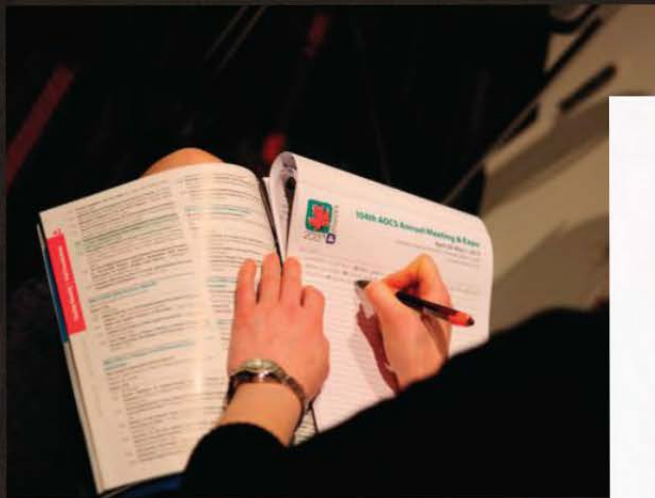
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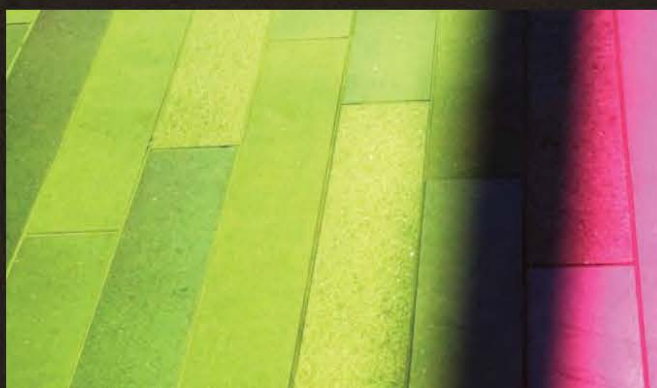
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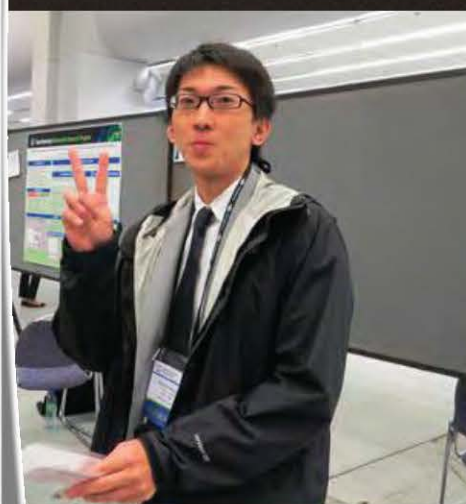


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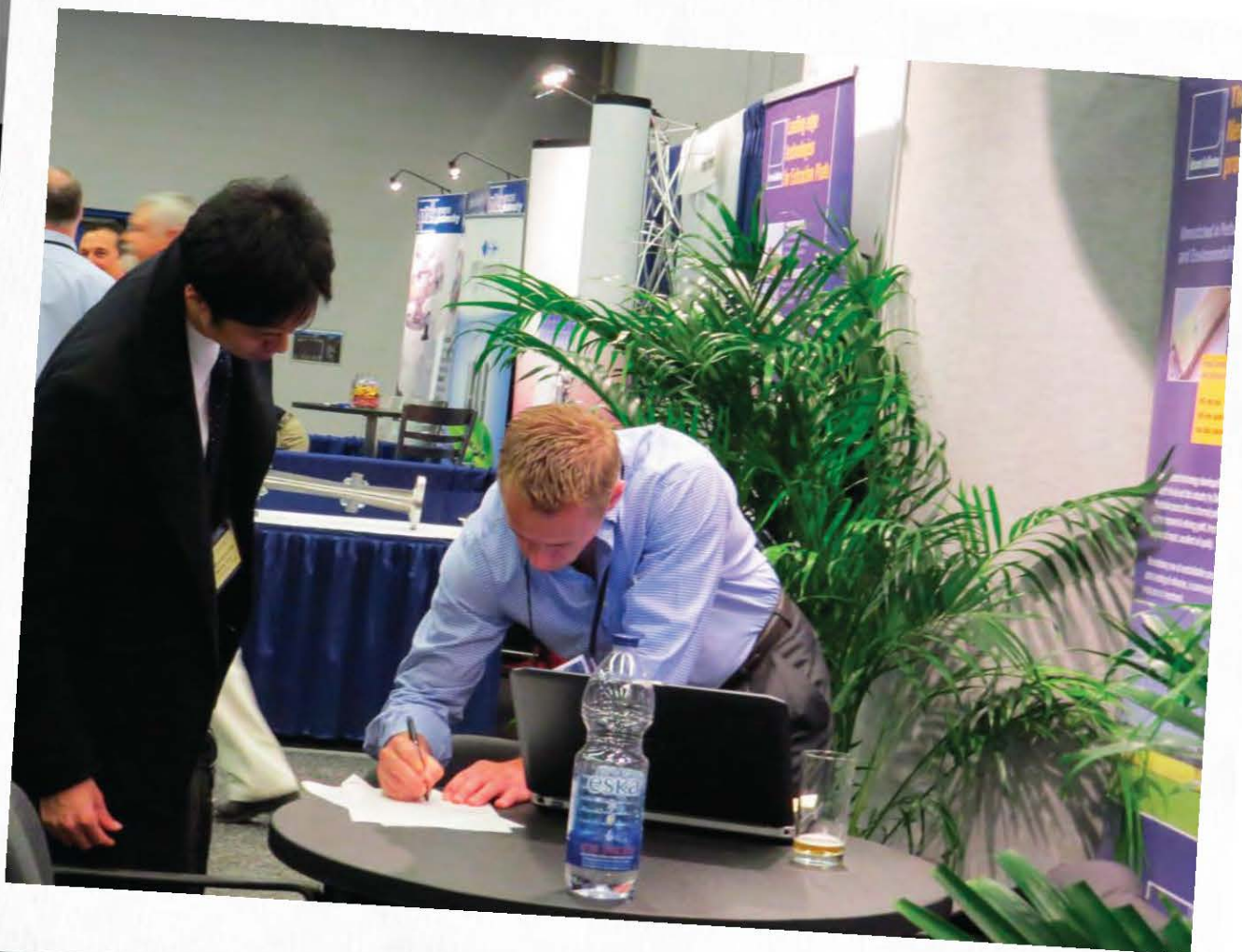
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July/August 2013

S15

Structure: the ultimate expression of nature's complexity

These images supplement the article, "Structure: the ultimate expression of nature's complexity," on page 454.

FIG. 3. (RIGHT)

Confocal laser scanning microscopy micrograph of Nile red-stained milkfat. The width and length of the figure are each about 62 μm .

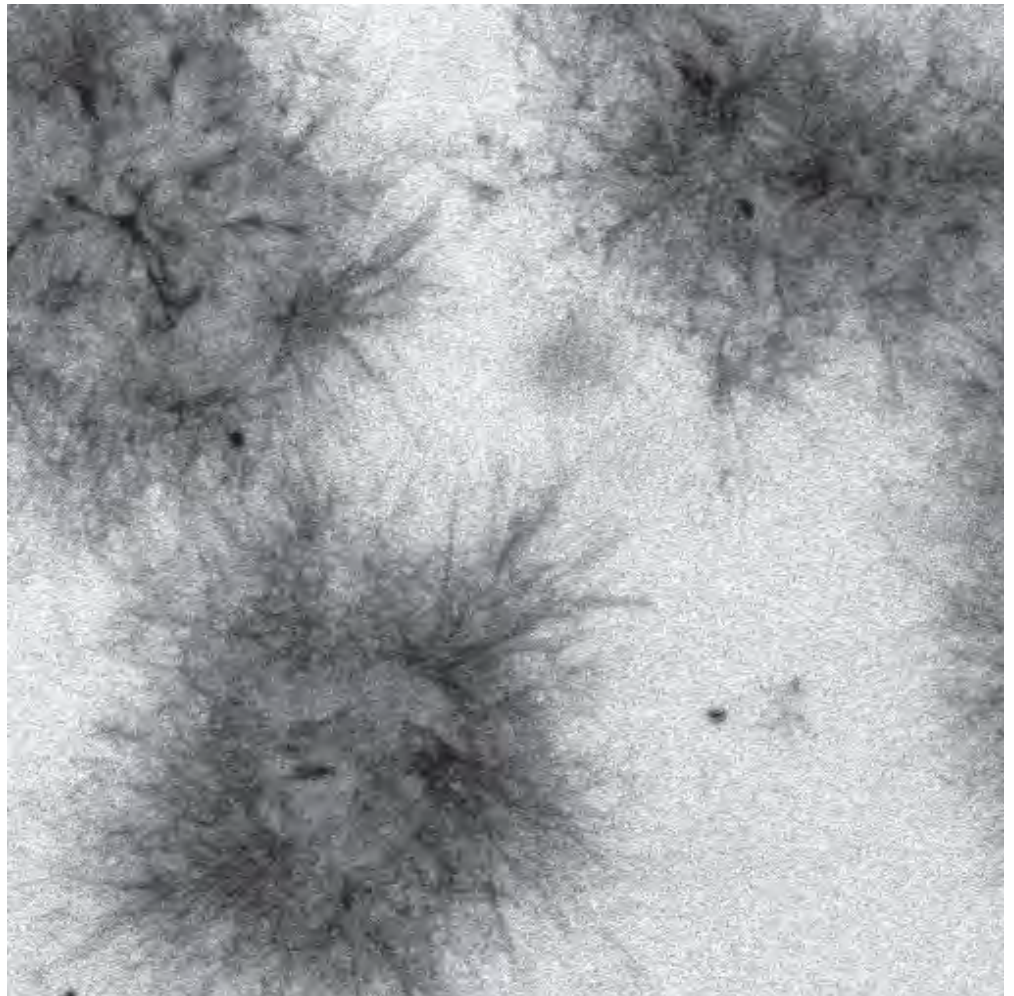
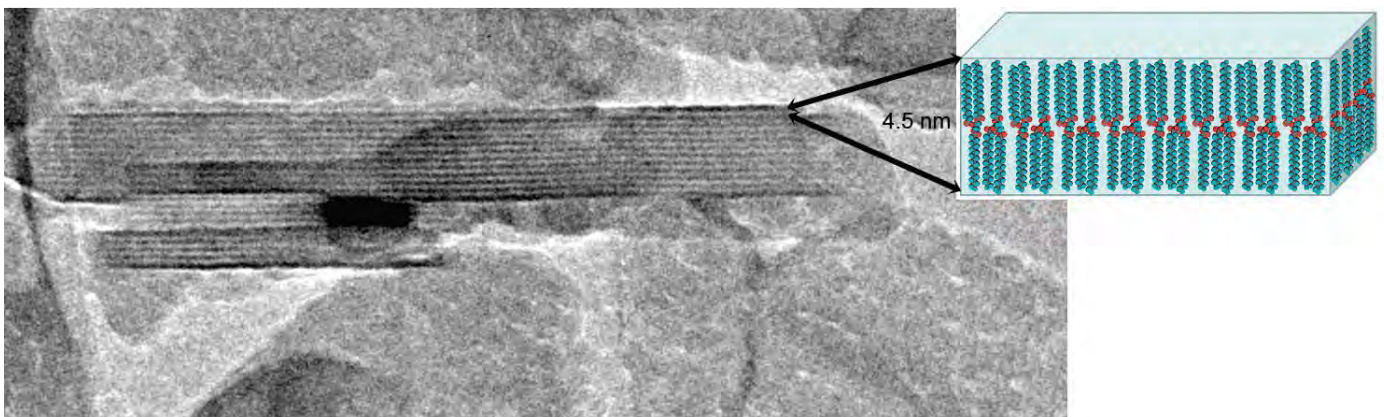


FIG. 4. (BOTTOM)

Cryogenic transmission electron microscopy micrograph of a solvent-extracted nano-platelet from fully hydrogenated soybean oil.



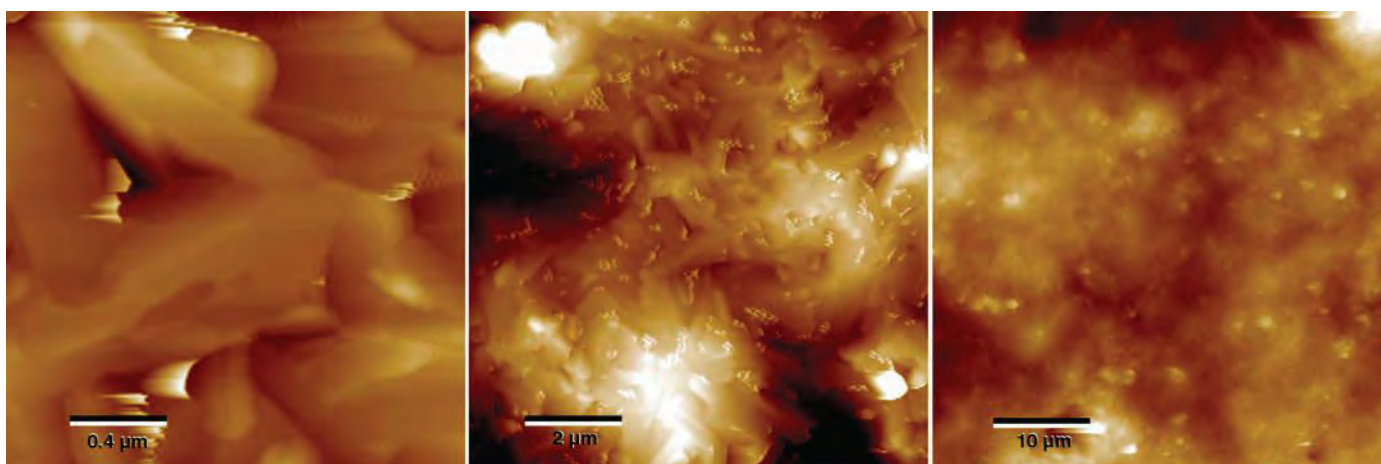


FIG. 5. Atomic force micrograph of cocoa butter showing different levels of structure from nanoplatelets (left), to primary clusters (center), to clusters of clusters (right).

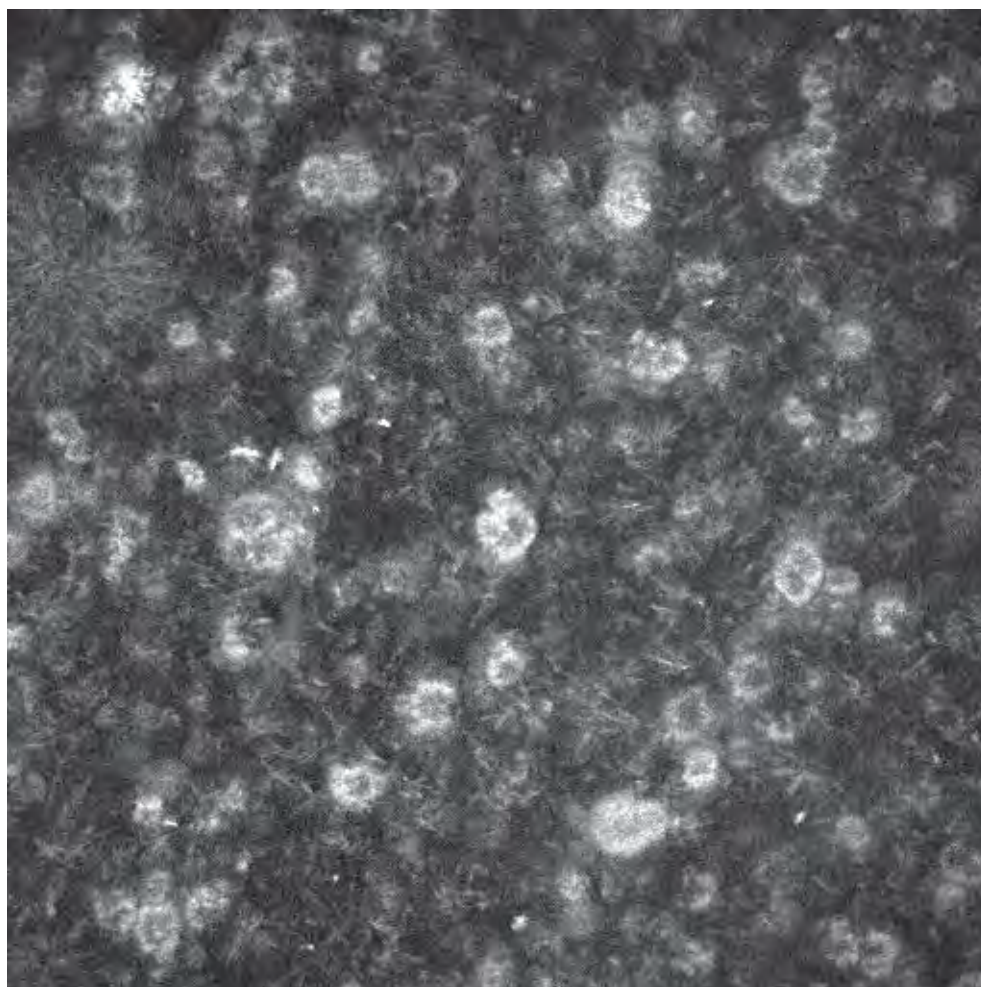


FIG. 6. Multiple photon excitation autofluorescence micrograph of native milk-fat. The width and length of the figure are each about 62 μm .

FIG. 7.

*Confocal laser scanning
microscopy micrograph
of the Nile red
(oil) and coumarin
(water) stained
structured emulsion,
Coasun.*

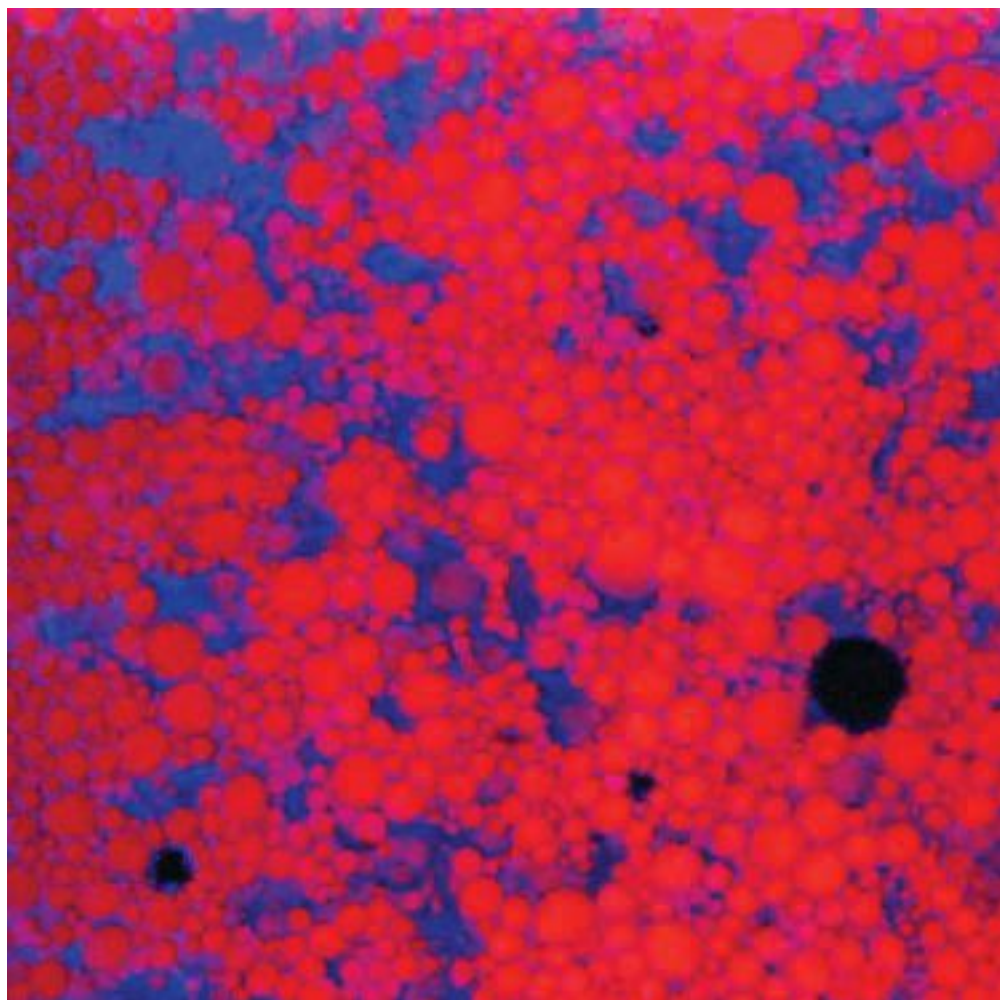
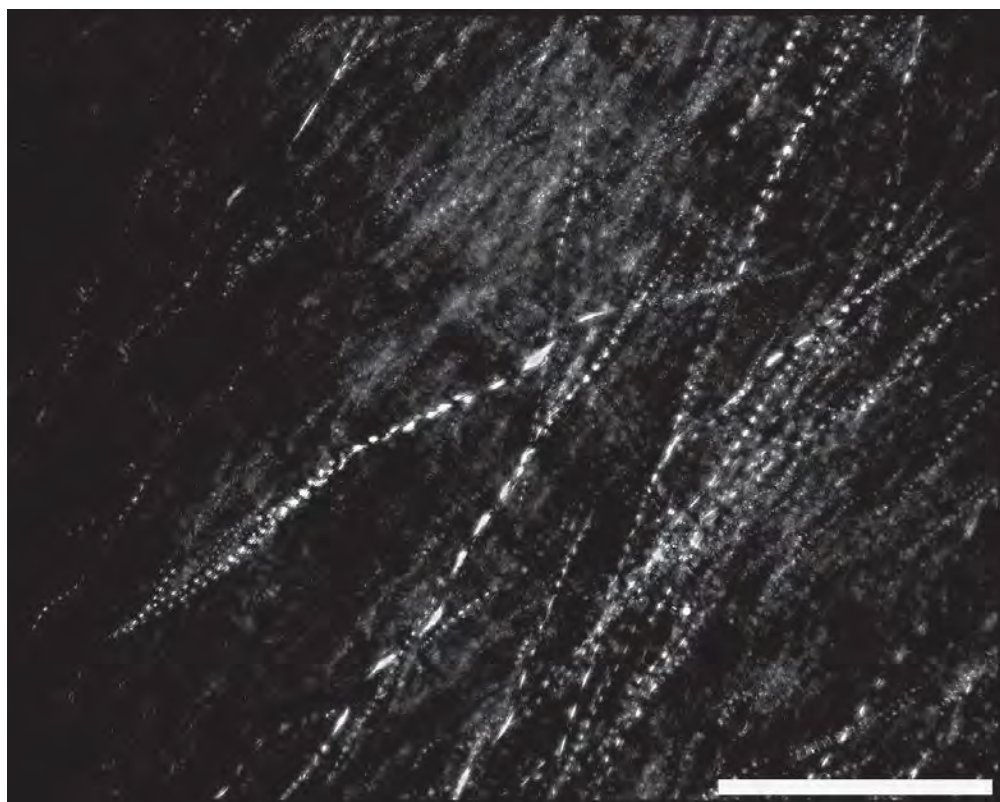


FIG. 8.

*Polarized light
micrograph of
12-hydroxystearic
acid-canola oil oleogel.
The magnification bar
corresponds to 100 μm .*



EXTRACTS & DISTILLATES

Synthesis of structured lipid enriched with omega fatty acids and *sn*-2 palmitic acid by enzymatic esterification and its incorporation in powdered infant formula

Nagachinta, S., and C.C. Akoh, *J. Agric. Food Chem.* 61:4455–4463, 2013.

Structured lipid (SL) enriched with arachidonic (ARA) and docosahexaenoic (DHA) acids was produced from tripalmitin using Lipozyme TL IM. The effects of acyl donors, that is, free fatty acids vs. fatty acid ethyl esters, on the reactions were compared. The highest total incorporation of ARA and DHA was obtained when the reaction continued for 24 hours, at a substrate mole ratio of 9, using free fatty acids as acyl donors (acidolysis). The SL prepared by a large-scale acidolysis reaction contained $17.69 \pm 0.09\%$ total ARA, $10.75 \pm 0.15\%$ total DHA, and $48.53 \pm 1.40\%$ *sn*-2 palmitic acid. SL thermograms exhibited multiple peaks indicating complexity of the triacylglycerol (TAG) distribution. Reversed phase-high pressure liquid chromatography analysis of SL revealed nine of 26 TAG molecular species that were similar to those of human milk fat. Powdered infant formulas containing the SL were prepared by wet-mixing/spray-drying and dry-blending methods. Formula prepared with microencapsulated SL and the dry-blending method had better oxidative stability and color quality.

Effect of nutrient-based fertilisers of olive trees on olive oil quality

Tekaya, M., et al., *J. Sci. Food Agric.* 93:2045–2052, 2013.

This work was conducted to determine the effects of two nutrient-based fertilizers on the general physicochemical characteristics (including free fatty acid content, peroxide value and ultraviolet spectrophotometric characteristics), fatty acid profile, total phenols, *o*-diphenols, and phytosterol composition of olive oil. Foliar applications were carried out in two successive years and included four treatments: TC (control, without foliar nutrition), T1 (rich in nitrogen, applied at the start of vegetation, 10 days later, and 20 days later), T2 (rich in boron, magnesium, sulfur, and manganese, applied at the beginning of flowering and 10 days later), and T3 (T1 + T2). At the end of the experiment (after 2 years), oils were extracted and analyzed. No effect was found on either general physicochemical characteristics or fatty acid composition.

Foliar fertilization caused a significant decrease in both polyphenol and *o*-diphenol contents. Total sterol content was unaffected by foliar fertilization. However, the phytosterol composition of the oil, particularly its β -sitosterol level, was markedly improved after foliar nutrient application. Principal component analysis of the phytosterol composition showed discrimination between the control oil and the oils from T1, T2, and T3 treatments. The results of this study extend the current knowledge of such cross-talk between plant nutrition and quality of oil.

Olive leaves (*Olea europaea* L.) versus α -tocopheryl acetate as dietary supplements for enhancing the oxidative stability of eggs enriched with very-long-chain *n*-3 fatty acids

Botsoglou, E.N., et al., *J. Sci. Food Agric.* 93:2053–2060, 2013.

Ninety-six brown Lohmann laying hens were equally assigned into four groups with six replicates. Hens within the control group were given a corn/soybean-based diet supplemented with 30 g kg^{-1} fish oil. Two other groups were given the same diet further supplemented with olive leaves at 5 (OL5) and 10 (OL10) g kg^{-1} , respectively, while the diet of the fourth group was supplemented with α -tocopheryl acetate (TOC) at 200 mg kg^{-1} . Eggs were analyzed for lipid hydroperoxide and malondialdehyde (MDA) contents, fatty acid profile, α -tocopherol content, and susceptibility to iron-induced lipid oxidation. Neither OL nor TOC supplementation affected ($P > 0.05$) the fatty acid composition. Dietary supplementation with OL10 or TOC reduced ($P \leq 0.05$) the lipid hydroperoxide content but exerted no ($P > 0.05$) effect on the MDA content of fresh eggs compared with controls. Eggs submitted to iron-induced lipid oxidation from the OL5 group presented higher ($P \leq 0.05$) MDA levels than the control but lower ($P \leq 0.05$) than the OL10 group. Eggs from the TOC group presented lower ($P \leq 0.05$) MDA levels compared with all groups at all incubation time points. The results of this study suggested that dietary supplementation with both OL10 and TOC could protect *n*-3 fatty acids in eggs from deterioration.

A rapid method to determine sterol, erythrodiol, and uvaol concentrations in olive oil

Mathison, B., and D. Holstege, *J. Agric. Food Chem.* 61:4506–4513, 2013.

A rapid, accurate, and efficient method for determining the sterol, uvaol, and erythrodiol concentrations was developed to meet International Olive Council (IOC) certification criteria for extra virgin olive oil (EVOO). The unsaponifiable fraction

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of the sample (0.2 g) was separated with a diatomaceous earth column, and the sterol and triterpenic dialcohols were isolated with a novel base-activated silica solid-phase extraction (SPE) cartridge cleanup protocol. The improved method and the IOC method provided identical pass/fail results ($n = 34$) for each of the six sterol and erythrodiol/uvaol IOC criteria used to assess olive oil. This method was validated, and recoveries of stigmasterol (88%) and β -sitosterol (84%) were greater than previously published values obtained using the IOC method. This method requires approximately one-third the time required to complete the IOC method and has great utility for the rapid screening of EVOO to detect adulteration, false labeling, and an inferior product.

Plasma carotenoid concentrations of infants are increased by feeding a milk-based infant formula supplemented with carotenoids

Mackey, A.D., *et al.*, *J. Sci. Food Agric.* 93:1945–1952, 2013.

Human milk is the gold standard of infant nutrition and is a source of important substances, including carotenoids. Infant formulas are designed to mimic the composition and/or performance of human milk, although currently carotenoids are not routinely added to US infant formulas. The aim of this study was to assess plasma concentrations of β -carotene, lutein, and lycopene 56 days after feeding infants milk-based infant formula without (Control) or with different concentrations of added carotenoids (L1 and L2). Plasma carotenoid concentrations increased in infants fed carotenoid-supplemented formulas as compared with the control formula with no added carotenoids. At study day 56, infants fed the supplemented formulas (L1 and L2) had mean plasma lutein, β -carotene, and lycopene concentrations that were within the range of a concurrent group of human milk-fed infants (HM). Anthropometric measurements were comparable among all study groups. Plasma carotenoid concentrations of infants fed the supplemented formulas were within the range of the HM group and are consistent with reported plasma carotenoid ranges in HM. The experimental formulas were well tolerated and anthropometric measurements were comparable among all study groups.

Effect of cocoa and theobromine consumption on serum HDL-cholesterol concentrations: a randomized controlled trial

Neufingerl, N., *et al.*, *Am. J. Clin. Nutr.* 97:1201–1209, 2013.

Evidence from clinical studies has suggested that cocoa may increase high-density lipoprotein (HDL) cholesterol concentrations. However, it is unclear whether this effect is attributable to flavonoids or theobromine, both of which are major cocoa components. We investigated whether pure theobromine increases serum HDL cholesterol and whether there is

an interaction effect between theobromine and cocoa. The study had a two-center, double-blind, randomized, placebo-controlled, full factorial parallel design. After a 2-wk run-in period, 152 healthy men and women (aged 40–70 yr) were randomly allocated to consume one 200-mL drink/day for 4 weeks that contained (i) cocoa, which naturally provided 150 mg theobromine and 325 mg flavonoids [cocoa intervention (CC)], (ii) 850 mg pure theobromine [theobromine intervention (TB)], (iii) cocoa and added theobromine, which provided 1000 mg theobromine and 325 mg flavonoids [theobromine and cocoa intervention (TB+CC)], or (iv) neither cocoa nor theobromine (placebo). Blood lipids and apolipoproteins were measured at the start and end of interventions.

Results: In a two-factor analysis, there was a significant main effect of the TB ($P < 0.0001$) but not CC ($P = 0.1288$) on HDL cholesterol but no significant interaction ($P = 0.3735$). The TB increased HDL cholesterol concentrations by 0.16 mmol/L ($P < 0.0001$). Furthermore, there was a significant main effect of the TB on increasing apolipoprotein A-I ($P < 0.0001$) and decreasing apolipoprotein B and low density lipoprotein cholesterol concentrations ($P < 0.02$). Theobromine independently increased serum HDL cholesterol concentrations by 0.16 mmol/L. The lack of significant cocoa and interaction effects suggested that theobromine may be the main ingredient responsible for the HDL cholesterol-raising effect. This trial was registered at www.clinicaltrials.gov as NCT01481389.

Analysis of processing contaminants in edible oils. Part 1. Liquid chromatography–tandem mass spectrometry method for the direct detection of 3-monochloropropanediol monoesters and glycidyl esters

MacMahon, S., *et al.*, *J. Agric. Food Chem.* 61:4737–474, 2013.

A new analytical method has been developed and validated for the detection of glycidyl esters (GE) and 3-monochloropropanediol (3-MCPD) monoesters in edible oils. The target compounds represent two classes of potentially carcinogenic chemical contaminants formed during the processing of edible oils. Target analytes are separated from edible oil matrices using a two-step solid-phase extraction (SPE) procedure. The extracts are then analyzed using liquid chromatography–tandem mass spectrometry (LC–MS/MS) with electrospray ionization (ESI). Chromatographic conditions that separate *sn*-1 and *sn*-2 monoesters of 3-MCPD have been developed for the first time. The method has been validated for GE; *sn*-1 3-MCPD monoesters of lauric, myristic, linolenic, linoleic, oleic, and stearic acids; and *sn*-2 3-MCPD monoesters of oleic and palmitic acids in coconut, olive, and palm oils using an external calibration curve. The range of average recoveries and relative standard deviations (RSD) across the three oil matrices at three spiking concentrations are 84–115% (3–16% RSD) for the GE, 95–113% (1–10% RSD) for the *sn*-1 3-MCPD

monoesters, and 76.8–103% (5.1–11.2% RSD) for the *sn*-2 3-MCPD monoesters, with limits of quantitation at or below 30 ng/g for the GE, 60 ng/g for *sn*-1 3-MCPD monoesters, and 180 ng/g for *sn*-2 3-MCPD monoesters.

Application of novel extraction technologies for bioactives from marine algae

Kadam, S.U., *et al.*, *J. Agric. Food Chem.* 61:4667–4675, 2013.

Marine algae are a rich source of bioactive compounds. This paper outlines the main bioactive compounds in marine algae and recent advances in novel technologies for extracting them. Novel extraction technologies reviewed include enzyme-assisted extraction, microwave-assisted extraction, ultrasound-assisted extraction, supercritical fluid extraction, and pressurized liquid extraction. These technologies are reviewed with respect to principles, benefits, and potential applications for marine algal bioactives. Advantages of novel technologies include higher yield, reduced treatment time, and lower cost compared to traditional solvent extraction techniques. Moreover, different combinations of novel techniques used for extraction and technologies suitable for thermolabile compounds are identified. The limitations of and challenges to employing these novel extraction technologies in industry are also highlighted.

Novel bioactive glycerol-based lysophospholipids: new data—new insight into their function

Grzelczyk, A., and E. Gendaszewska-Darmach, *Biochimie* 95:667–679, 2013.

Based on the results of research conducted over the last two decades, lysophospholipids (LPL) were observed to be not only structural components of cellular membranes but also biologically active molecules influencing a broad variety of processes such as carcinogenesis, neurogenesis, immunity, vascular development, or regulation of metabolic diseases. With a growing interest in the involvement of extracellular LPL in both normal physiology and pathology, it has become evident that those small molecules may have therapeutic potential. While lysophosphatidic acid (LPA) and sphingosine-1-phosphate (S1P) have been studied in detail, other LPL such as lysophosphatidylglycerol (LPG), lysophosphatidylserine (LPS), lysophosphatidylinositol (LPI), lysophosphatidylethanolamine (LPE), or even lysophosphatidylcholine (LPC) have not been elucidated to such a high degree. Although information concerning the latter LPL is sparse as compared to LPA and SIP, within the last couple of years much progress has been made. Recently published data suggest that these compounds may regulate fundamental cellular activities by modulating multiple molecular targets, for example, by binding to specific receptors and/or altering the structure and fluidity of lipid rafts. Therefore, the present review is devoted to novel bioactive glycerol-based LPL and recent findings concerning their functions and possible signaling pathways regulating physiological and pathological processes.

Cholesterol photosensitized oxidation in food and biological systems

Cardenia, V., *et al.*, *Biochimie* 95:473–481, 2013.

Lipid oxidation is one of the main chemical degradations occurring in biological systems and leads to the formation of compounds that are related to aging and various chronic and degenerative diseases. The extent of oxidation will depend on the presence of antioxidants/pro-oxidants, the unsaturation degree of fatty acids, and environmental conditions. Lipid oxidation can also affect other molecules that have double bonds in their chemical structures, such as cholesterol. Cholesterol oxidation products (COP) have been studied in depth because of their negative and controversial biological effects. The formation of COP can be particularly favored in the presence of light and photosensitizers, since they generate excited singlet oxygen that rapidly reacts with the double bond by a nonradical mechanism and without any induction period. The present review intends to provide an overall and critical picture of cholesterol photosensitized oxidation in food and biological systems, and its possible impact on human health and well-being.

Epigenetic regulation of oxysterol formation

Meaney, S., *Biochimie* 95:531–537, 2013.

Oxysterols are oxygenated derivatives of cholesterol that may be formed by either enzymatic or nonenzymatic mechanisms. Expression of the genes responsible for oxysterol synthesis (GROS) is known to be restricted across different tissues and cell types. Regulation of the transcription of GROS and the activity of their enzyme transcripts has been the subject of intense activity for many years. Recent studies have sought to decipher the mechanism(s) that underpin the restricted expression of the GROS. Available data indicates that epigenetic mechanisms have an important role to play in the control of the expression of GROS. In the current review we summarize the available evidence for the epigenetic regulation of these genes.

Fate of dietary phytosteryl/-stanyl esters: analysis of individual intact esters in human feces

Lubinus, T., *et al.*, *Eur. J. Nutr.* 52:997–1013, 2013.

The objective was to investigate the metabolic fate of phytosteryl/-stanyl fatty acid and ferulic acid esters on consumption by healthy humans. A capillary gas chromatographic methodology was employed to follow a randomized, single-blind three group crossover clinical trial and to quantify simultaneously individual intact esters, liberated phytosterols/-stanols, and their metabolites in feces. Skimmed milk drinking yogurts enriched with complex mixtures of phytosteryl/-stanyl fatty acid esters and ferulates, respectively, were employed as food

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carriers. On average, 73% of total plant stanyl fatty acid esters and 80% of total plant steryl fatty acid esters were hydrolyzed. Among the individuals, the hydrolysis rates ranged from 40 to 96%. In addition, there were subject-dependent discrepancies between the amounts of phytosterols/-stanols actually determined in the feces and the calculated hydrolysis rates. On average, 69% of the amounts of sterols/stanols expected from the amounts of remaining intact esters were found. The study revealed large interindividual variability regarding the recoveries of dietary phytosteryl/-stanyl esters upon gastrointestinal passage in healthy humans. Nevertheless, there was a significant impact of the acid moiety (oleate = linoleate = linolenate > eicosanoate > palmitate > ferulate) on the hydrolysis rates; the influence of the phytosterol/-stanol moiety was less pronounced.

Flash thermal conditioning of olive pastes during the olive oil mechanical extraction process: impact on the structural modifications of pastes and oil quality

Esposito, S., *et al.*, *J. Agric. Food Chem.* 61:4953–4960, 2013.

The quality of virgin olive oil (VOO) is strictly related to the concentrations of phenolic and volatile compounds, which are strongly affected by the operative conditions of the VOO mechanical extraction process. The aim of this work is to study the impact of a new technology such as flash thermal conditioning (FTC) on olive paste structural modification and on VOO quality. The evaluation of olive paste structure modification by cryo-scanning electron microscopy (cryo-SEM) showed that

the application of FTC after crushing produces significant differences in terms of the breaking of the parenchyma cells and aggregation of oil droplets in comparison to the crushed pastes. The virgin olive oil flash thermal conditioning (VOO-FTC) featured a higher concentration of volatile compounds compared to that in the control, particularly of all saturated and unsaturated aldehydes and esters, whereas the phenolic concentration was higher in VOO obtained from the traditional process (VOO-C).

Solid-phase extraction of long-chain fatty acids from aqueous solution

Yuan, W., *et al.*, *Sep. Pur. Technol.* 106:1–7, 2013.

Microbially derived long-chain free fatty acids are useful precursors for biofuel production. However, effective and biocompatible methods for their separation from aqueous solutions do not presently exist. The overall and relative efficacy of several commercially available hydrophobic, anion exchange, and mixed-mode adsorbents for the recovery of laurate, a model 12-carbon saturated fatty acid, was compared according to both equilibrium and kinetic studies. Mixed-mode adsorbents exhibited the greatest adsorption capacity and affinity, with Amberlite IRA-402 able to adsorb up to 430 g laurate/kg. Meanwhile, the anion exchange resin Amberlite IRA-67 adsorbed up to 426 g laurate/kg, while the hydrophobic resin Dowex Optipore L-493 adsorbed a maximum of only 106 g laurate/kg. Polymer gel adsorbents, which display the greatest aqueous swelling, achieved the fastest rates of laurate recovery. Adsorption kinetics were well represented by a pore-diffusion model for all adsorbents. Estimated pore diffusion coefficients were as high as $7.2 \times 10^{-10} \text{ m}^2/\text{s}$ for Amberlite IRA-402. ■