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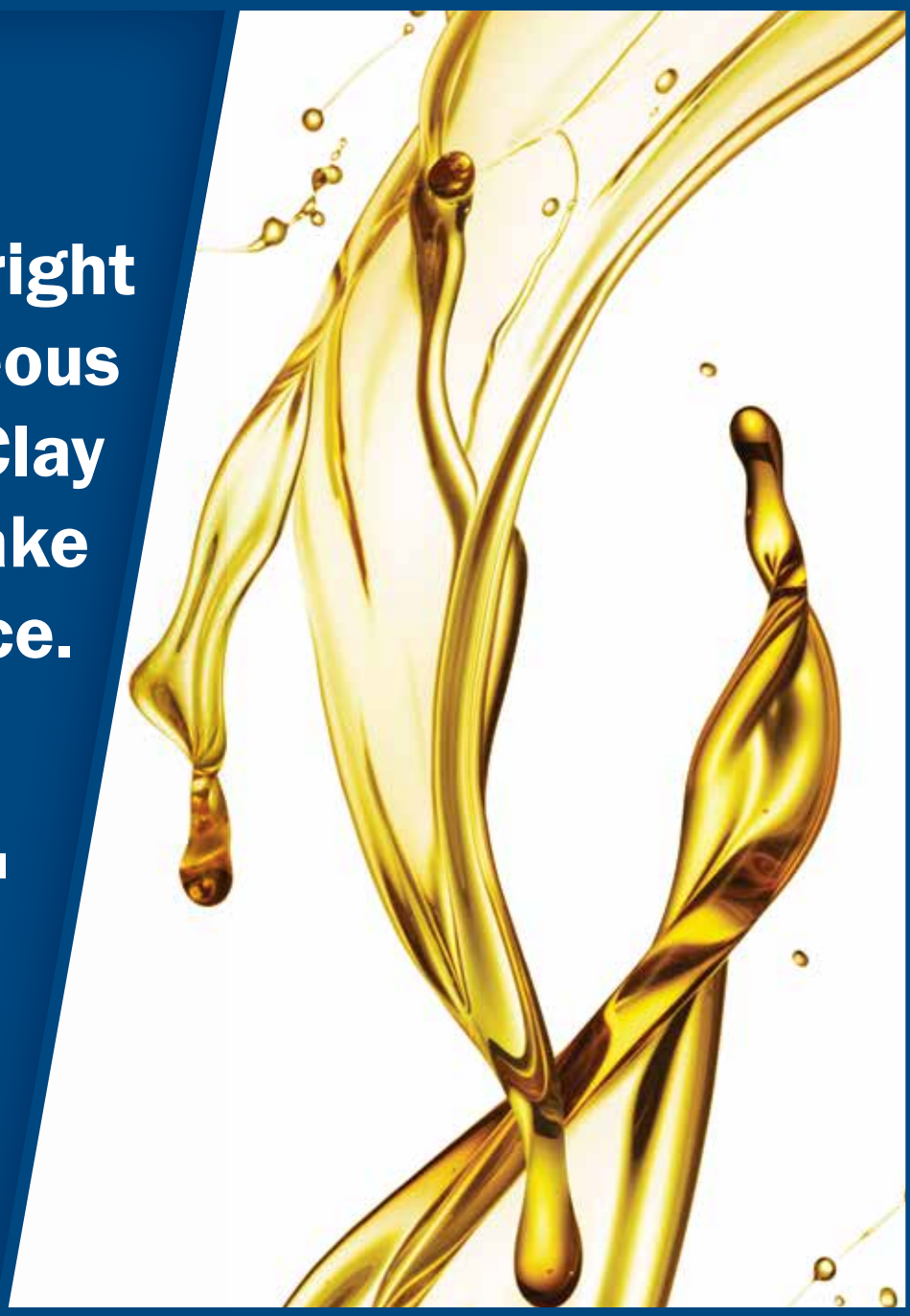

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Fermentation, the new protein supply chain

Rebecca Guenard

High-protein foods are not just for body builders and extreme athletes; today's consumers consider the ingredient an integral part of their diet. According to a recent market analysis (https://tinyurl.com/y2evtyz2), by 2025, protein ingredient sales will reach $48 billion globally. In 2016, animals supplied 72 percent of the global protein ingredient industry. Meeting future demand will require a protein supply chain that does not rely solely on animals. Plant-based protein sources are available, but for many applications they do not exhibit the same sensory or functional properties as animal proteins do.

- **Living cells metabolize nutrients to produce a wide range of products through fermentation. In the past five years, more and more companies have been using this technology to make proteins for food and cosmetic ingredients (Fig. 1).**
- **The new protein products are attractive to vegans, because animals are not involved in their production. Using cells instead of animals to produce protein also offers environmental advantages, since cellular fermentation produces fewer emissions and requires fewer resources than raising animals.**
- **The technology used to optimize the microorganisms for protein production enables scientists to expand synthetic capabilities and develop new molecules based on the biodiversity that exists in nature.**

Instead of adjusting to make a plant-based protein formulation more like an animal one, advancements in biotechnology have sparked start-ups that supply proteins made-to-order. Companies can identify the ideal protein for a given application and, working backwards, determine the genetics necessary to produce it. They then encode the genetic information into the nucleus of a host organism, such as bacteria or fungi. When these microorganisms feed on sugar or other nutrients in fermentation tanks, the cells follow the encoded instructions and produce an abundance of the specified protein. After separating the proteins from the host cells, the final step in the process is purification.

Using fermentation, companies are tapping a microorganism's natural metabolic process and optimizing proteins for a variety of market applications, from anti-aging cosmetics to vegan substitutes for dairy products. With multimillion-dollar investments in protein companies now a routine, the dream of cellular agriculture is quickly becoming reality. The success of biotech-enhanced fermentation is evident in the rapid growth of companies like Geltor (https://www.geltor.com) and Perfect Day (https://www.perfectdayfoods.com).

"So many start-ups and other early-stage companies are thinking about fermentation to build biomaterials that had historically been sourced from animals or other sources that were non-sustainable or challenging for other reasons," says Alex Lorestani, co-founder and CEO of Geltor, a cosmetic ingredient company, based in San Leandro, California, that specializes in collagen.

"Once you create a new protein that comes from a more efficient, cleaner source and can be tailored to individual applications like foods, there is a lot of opportunity there," says Tim Geistlinger, chief technology officer at Perfect Day, a company in San Francisco, California, that makes vegan dairy substitutes. "This is the beginning of a way to create a new protein supply chain."

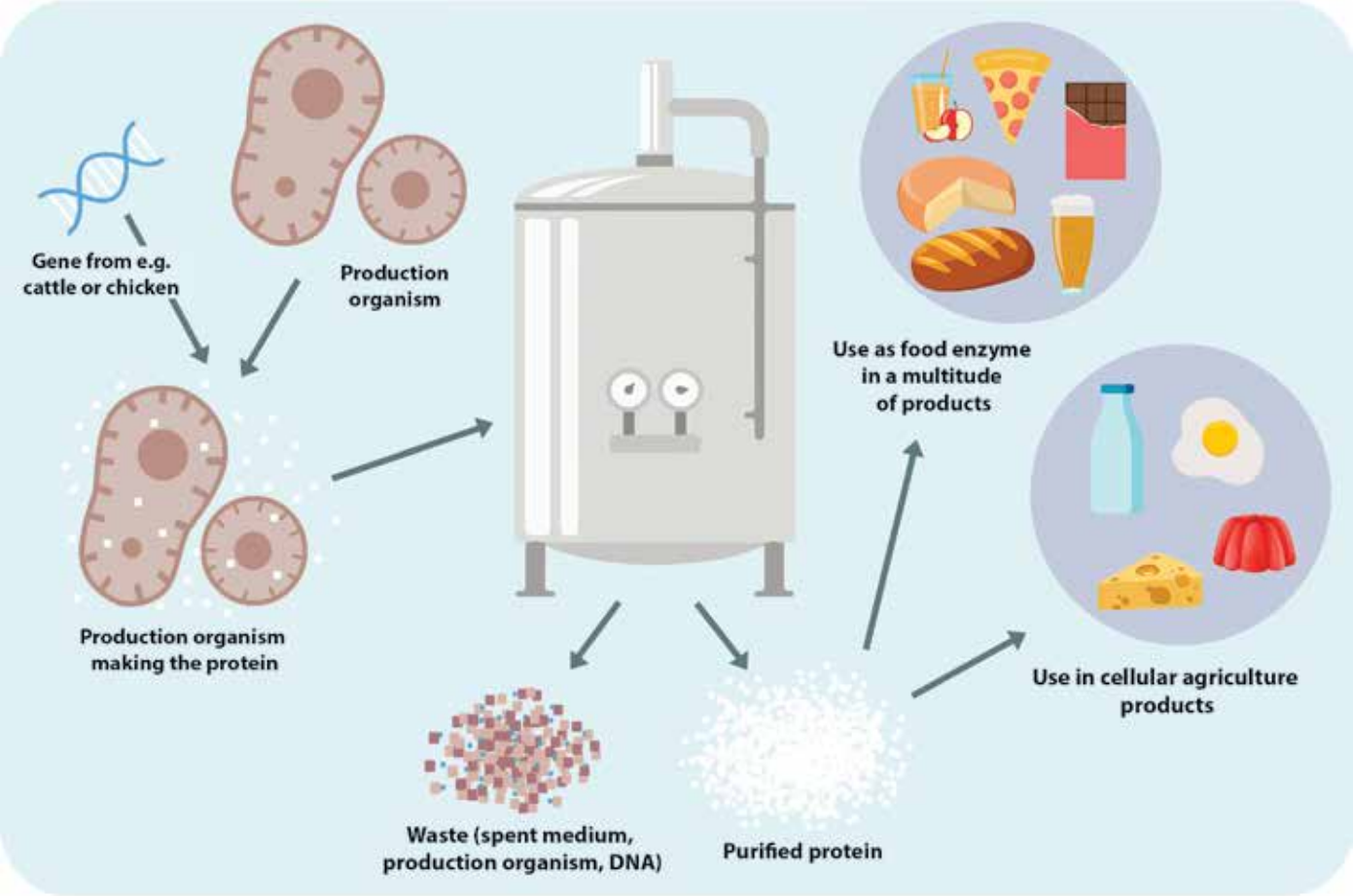

FIG. 1. Cellular agriculture, a method of making animal proteins without using animals. This figure has been republished from "Cellular Agriculture: An extension of common production methods for food" with permission from The Good Food Institute.

BEAUTY FROM MICROBES

Geltor began in 2015, with a bench-scale proof of concept for a collagen Lorestani and his co-founder, Nick Ouzounov, developed. In April 2018, they launched their first commercial scale product, N-Collage™, and six months later they received $18.2 million from investors to expand their product offerings (https://tinyurl.com/y3ffqr47).

Lorestani says that he observed the challenges associated with using cellular agriculture to produce proteins for a large consumer market, like replacing beef in the food industry. Instead, his company chose to focus on higher-value ingredients produced in smaller quantities. After seeing synthetic biology used so successfully for drug development, he and Ouzounov wanted to apply it the consumer products industry.

"What we have been able to do is take a protein science approach to improving the ingredients in cosmetics and personal care products," he says. For example, to produce a collagen that feels silky on the skin, they find natural collagens that exhibit such a quality. Using computational biology, they develop an amino acid sequence for the desired protein and engineer microorganisms to make it.

"By this means we produce a pure protein product that is identical to one found in nature," says Lorestani. He adds that most natural proteins are not yet manufactured on an industrial scale. For example, collagen is one of the most abundant proteins in the animal kingdom, but only two types are currently harvested from animals.

Fermentation allows scientists access to the diversity of nature through the myriad ways a microorganism's DNA can be altered. It provides a brand-new tool kit for scientists to create any molecule they can imagine. For Lorestani, and many others launching products in this arena, the more important thing is that cellular agriculture enables his company to make a protein product without the inefficiency of raising and slaughtering an animal.

"DAIRY" WITHOUT COWS

Like Geltor, Perfect Day, set out to mimic the drug industry's biotechnology success in the consumer goods industry, and quickly brought a protein product to market. Perfect Day was established in 2014, raised $40 million from investors in the first few years, and by the end of 2018, had entered into a joint development agreement with Archer Daniels Midland (https://tinyurl.com/y38fyg9d). One difference between the two companies is the co-founders of Perfect Day are vegan.

Perfect Day makes dairy proteins without the cow. "To make the proteins that make dairy special requires a lot of different proteins," Geistlinger says. "They are commonly referred to as the whey proteins and the curd proteins. They

fall into those two different classes of proteins. We are making a large majority of the major proteins that are in dairy."

The company founders wanted to provide a product with the benefit of milk's nutritional and sensory characteristics, but without harming animals or demanding the land and water use of raising an animal. And they wanted to produce a vegan product that appealed to everyone.

Geistlinger says their dairy proteins are not yet used to make milk, since milk is so complicated. They use microflora to make proteins, such as caseinate proteins, that are well-known to food formulators. "We are using a couple of different organisms that have been used in the food industry to make proteins and enzymes and probiotics," he says. The company uses fungi, yeast, and bacteria to produce a range of proteins. By using a variety of cells, they can manufacture a variety of products. "We can make multiple proteins from a single host, or we can make an individual one. We can control those ratios so we can recombine them later, or we can start with a mixture," says Geistlinger. Perfect Day is currently focusing on making individual proteins to meet consumer demands for a self-tailored, high-nutritional profile, he says.

UNBOUND VERSATILITY

According to Geistlinger, Perfect Day is replacing ingredients for a wide variety of applications across a broad range of items in the grocery store, but he points out that the technology they are using goes beyond proteins. "This technology has applications in biomaterials and medicine and all kinds of things," he says. "This is really a fascinating market place."

"The ability to engineer cells and design them very purposefully has become orders of magnitude better than it was in the past, and the science continues to grow at a rapid pace," says Christophe Schilling, CEO and co-founder of Genomatica, a San Diego, California-based company that uses fermentation for a different product arena. Genomatica creates compounds to replace those that were once only available through petrochemical processing, such as nylon and butylene glycol.

Fermentation is not just more efficient for making proteins as compared to industrial farming; according to Schilling, it is more efficient in general. Manufacturing with biology reduces the intermediates and side reactions that are common in chemical processing. For example, chemically manufactured butylene glycol results in a 50-50 racemic mixture that is difficult to separate. "We can make whichever form we want at almost 100 percent purity at the same cost that it takes to produce the racemic mixture," says Schilling. "If there are applications that need one form or another form of that molecule, biology will deliver easily over chemistry. That is a huge advantage."

The scientific advantages that fermentation brings is attracting new start-ups almost weekly (https://tinyurl.com/y7ydzk33). Eagerness to get into the market has also launched supporting industries. The latest, Cultural Biosciences, specializes in running proof-of-concept experiments for companies planning to enter this space (https://tinyurl.com/y5tkwe5o). The latest companies would be smart to take the time to learn from those who have proceeded them.

"The companies that are succeeding now are actually making products substantially better than anything that you can get from petroleum, or a pig, or a plant, for that matter," says Lorestani. "Making things that are better is what allows you to succeed in this industry." In the upcoming months, consumers will get the chance to judge for themselves as products from Geltor and Perfect Day begin competing against traditionally sourced products in the market place.

Rebecca Guenard is the associate editor of Inform *at AOCS. She can be contacted at rebecca.guenard@aocs.org.*

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October 8–11, 2019. 18th AOCS Latin American Congress and Exhibition on Fats, Oils and Lipids, Bourbon Cataratas Convention & Spa Resort, Foz do Iguaçu, Brazil.

November 5–7, 2019. AOCS Pulse Science and Technology Forum. Courtyard by Marriott, Toronto, Canada.

November 8–10, 2019. 2nd AOCS China Section Conference: Health, Advanced Processing, and Value-Added Utilization, Zhujiang (Pearl River) Hotel, Guangzhou (Canton), China.

April 26–29, 2020. AOCS Annual Meeting & Expo, Palais des congrès de Montréal, Montréal, Québec, Canada.

May 2–5, 2021. AOCS Annual Meeting & Expo, Oregon Convention Center, Portland, Oregon, USA.

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Esters of linear monounsaturated dicarboxylic acids for lubricants

S. Joseph Asadauskas and Jean-Luc Dubois

Dibasic esters constitute a viable segment of oleochemical- and petrochemical-based lipid products, such as adipates, phthalates, succinates, sebacates, and "dimer acids," used in plasticizers, cosmetics, lubricants, paint thinners, colorant diluents, and other industrial oil products.

- **Esters of linear alpha,omega-dicarboxylic acids are used in high-performance hydraulic fluids.**
- **Despite poorer oxidative stability, monounsaturation provides many benefits.**
- **Mono-unsaturated diacids can be produced by metathesis or biocatalytically.**

Among larger-volume products, saturated dibasic esters of higher molecular weight are sometimes employed in high-performance hydraulic fluids, which require specified viscosities, good fluidity at low temperatures, resistance to aging, lubricity, and other more specialized properties. Currently, high-performance hydraulic fluids are dominated by sebacates and azelates, esters of C10:0 1,10-di-OOH and C9:0 1,9-di-OOH alpha,omega-dicarboxylic acids, respectively. Usually 2-ethyl hexanol or longer-chain petrochemical alcohols are used for esterification, producing viscosity grades of ISO VG22 and VG12 for niche applications. Sebacic acid is generally manufactured from castor oil, and its price is typically higher than that of commodity diacids such as adipic acid. In spite of this price disadvantage, petrochemical esters are widely used as basestocks for high-performance hydraulic fluids. Basestock is by far the dominant component in lubricant formulations; for hydraulic fluids it usually comprises over 95% wt.

Despite numerous efforts, biodegradable basestocks have not been incorporated into conventional internal combustion or diesel engine oils to any significant extent. In addition, current attempts to develop motor

lubricants must consider the implications of electrical vehicles, which do not need traditional engine oils at all. Therefore, lubricant-oriented valorization of innovative basestocks is shifting toward hydraulic fluids, whose global market exceeds 10 million metric tons and includes products of quite diverse technical requirements.

Current advancements in green chemistry and bio-based technologies have given rise to new players among dibasic esters. High-temperature reactions over montmorillonite clay can produce a mix of methyl-branched C22 alpha,omega-dicarboxylic acids, which can be turned into dibasic esters [1]. For feedstock, 11-undecenoic acid is used, yielding trans double bonds. Unconventional raw materials and a complex purification procedure make this process difficult to scale up. Another pathway is presented by metathesis, which can also yield dibasic esters from oleate, erucate, and other unsaturated fatty acid (FA) esters, leading to a mixture of cis and trans isomers [2]. For this process, conventional monounsaturated FA or their esters can be used as feedstock. Biocatalytical pathways are also available to afford longer chain alpha,omega-dicarboxylic acids from these raw materials [3], yielding mostly cis isomers (Fig. 1).

The scenarios in Fig. 1 initially lead to unsaturated dibasic esters dominated by monounsaturation, which can be hydrogenated into saturated ones, if necessary. The lubricant industry is cautious about using unsaturated basestocks because of the higher probability of oxidative degradation. Nevertheless, many commercially successful hydraulic fluids use rapeseed, canola, and other vegetable oils as their basestocks, which comprise more than 20% mol. methylene-interrupted polyunsaturated FA. A well-formulated antioxidant package can inhibit oxidative degradation effectively in hydraulic fluids based on such vegetable oils, assuring excellent performance. Consequently, while medium iodine values in basestocks raise some concerns, highly monounsaturated dibasic esters remain strong candidates for high-performance hydraulic fluids.

Compared to mineral oil and petrochemical basestocks, dibasic esters offer several benefits for hydraulic fluids. They can be produced from renewable resources and appear to be easily biodegradable. They demonstrate high thermal conductivity, which results in lower operating temperatures and subsequent advantages in hydraulic systems. The volatility and flash points of dibasic esters are lower than those of petrochemical basestocks from the same viscosity grade. Their heat-thinning is not as rapid, and their inherent lubricity is considered to be better. Such advantages depend both on ester functionalities and monounsaturation, and it must be noted that they are often based on user experience, without much substantiation from research findings. Therefore, to better understand the impact of molecular factors on the properties of dibasic esters, each parameter must be assessed more thoroughly.

HEAT-THINNING OF UNSATURATED ESTERS

Operational viscosity is very important in hydraulic systems. Viscosity grades of hydraulic fluids are determined at 40°C, which is a very approximate average temperature in a hydraulic system. When designing pumps and other components, viscosity's dependence on temperature is always accounted for,

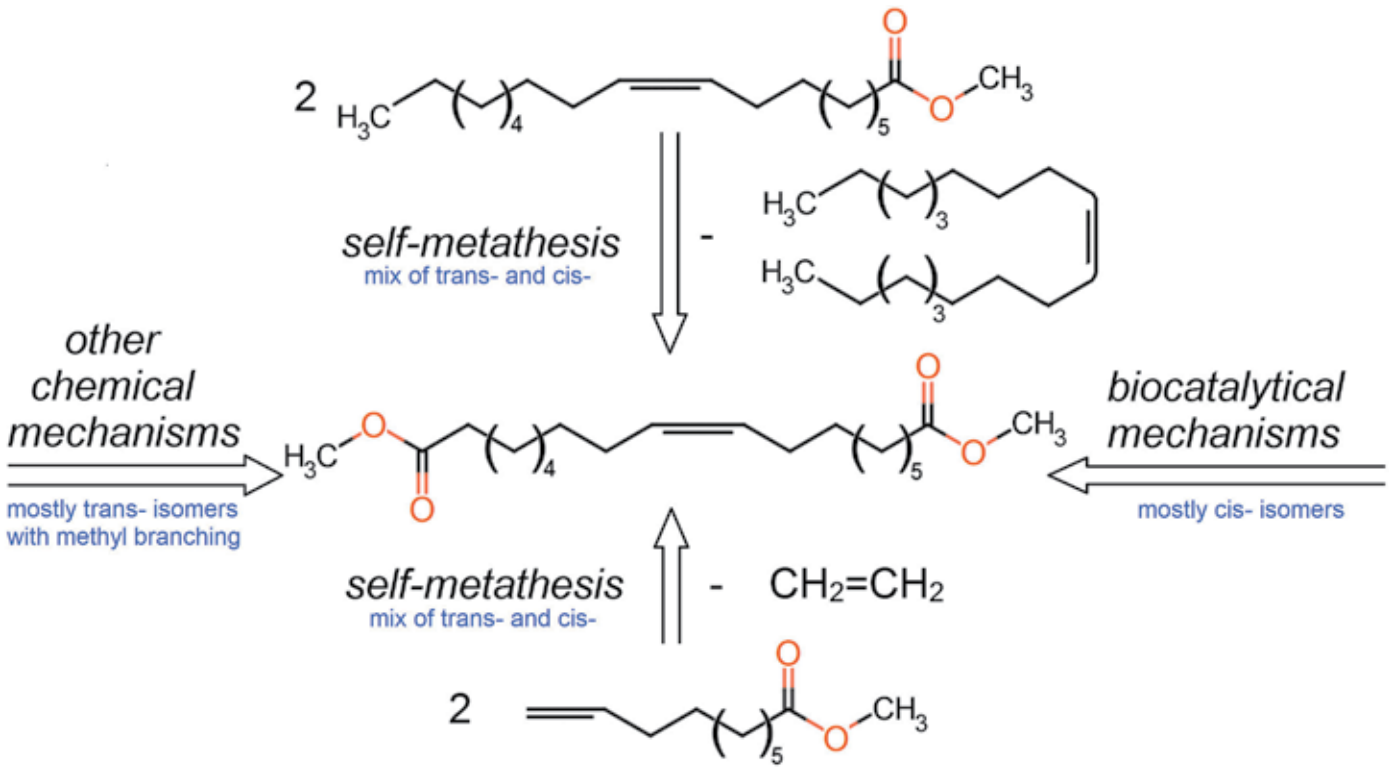

FIG. 1. Synthetic pathways to obtain monounsaturated linear alpha,omega-dibasic esters with the dominant isomers listed in parenthesis for each process

but performance can still be strongly affected by viscosity variations. Multiple studies report that the best energy efficiency and overall performance are achieved when heat-thinning is as low as possible. For example, in winter, hydraulic equipment must be turned on when the weather is very cold. In summer, when the equipment operates continuously, hydraulic fluid often reaches 90°C or higher. In lubricant technology, heat-thinning is assessed by the Viscosity Index (VI), which is determined by measuring kinematic viscosities at 40°C and 100°C or two similar temperatures. For example, squalane, which is often compared to a typical molecule of conventional lubricants, has kinematic viscosities of 20.9 and 4.2 mm²/s at 40°C and 100°C, respectively, producing a VI of 103.

Most mineral oil basestocks have a VI below 100, while poly alpha olefins, a dominant synthetic basestock, have a VI of about 130. Fluids with high VI undergo less heat-thinning. Polymer additives are used to improve the VI of many lubricants, because in the friction zone temperatures are much higher than in bulk lubricants, and oil remains more viscous in the asperity contact. Consequently, surfaces are better separated, less metal-to-metal contact takes place, and wear is reduced. However, in hydraulic fluids, VI-improver polymers are exposed to extensive mechanical shear, which frequently reduces their VI to the vicinity of the basestock values.

Dibasic esters have significant advantages when it comes to VI, especially if they approach linear molecular structure. Di 2-ethylhexyl ("di-2EH") ester of azelaic acid shows just a medium VI = 97 because of its two ethyl branches. However, di-2EH ester of C18:0 saturated dibasic acid approaches VI 190 due to its more linear molecular architecture (Table 1). Unsaturation is another molecular factor that boosts VI, especially cis-double bonds. This is very obvious when comparing vegetable oils; rapeseed oil has a VI of 222, while soybean oil, which is less saturated, hits VI = 246. Dibasic esters show similar effects, with di-2EH ester of C18:1 dibasic acid (mostly trans-) achieving VI = 197.

Monounsaturated esters of linear long-chain dibasic acids approach VI of rapeseed oil. For hydraulic equipment, which operates at higher temperatures, rapeseed oil viscosity might be higher than that of a VG46 fluid of VI=100, which records 6.8 mm²/s at 100°C. Dibasic esters can provide a closer alternative to design specifications with a number of other benefits.

LOW TEMPERATURE FLUIDITY

In hydraulic fluids, good performance at low temperatures is often required, depending on climatic conditions. The first measure used to describe cold fluidity is usually the pour point, the point when fluid chilled at a prescribed rate of 0.3 to 3°C/min stops pouring out of a test tube when periodically inverted. As seen in Table 1, dibasic esters of C12:0 or shorter chains perform very well at low temperatures. Monounsaturation is very helpful for C18 dibasic esters, even despite predominant trans isomerization. In aviation, forestry, and some other fields, cold performance might be among the top criteria for hydraulic fluids.

THERMAL CONDUCTIVITY OF ESTERS

The higher thermal conductivity of esters relative to hydrocarbons can help reduce the temperature of a hydraulic system. Thermal conductivities of vegetable oils, which are about 167 mW/(m·K) at 20°C are nearly a quarter higher than those of mineral oils, which are about 133 mW/(m·K). Other esters have been recorded to have similar thermal conductivities, while those of dibasic esters are not very well established. Some data shows that unsaturation might also be beneficial towards thermal conductivity, but more tests are needed to correlate it to the number of double bonds.

WEAR-REDUCTION BY UNSATURATED DIBASIC ESTERS

Hydraulic fluids prevent pumps from wearing too much under normal operating conditions by forming protective tribofilms on friction zone surfaces. These protective films must be constantly replenished by hydraulic fluid components to prevent metal from wear. Ideally, basestocks should contribute to tribofilm formation. In saturated basestocks, friction zone temperatures must be quite high to ensure that effective tribofilms are formed. Anti-wear additives must be formulated carefully. Since double bonds are considered to be at least 10 times more reactive chemically, their contribution to tribofilm formation should be much higher. In addition, ester monolayers can saponify to form soaps on metal surfaces, which can enhance the protective effects of tribofilms. More studies are needed, but it seems that unsaturated dibasic esters might provide better wear-reduction

TABLE 1. Viscosity and Viscosity Index (VI) of commercial basestocks and reported di-(2-ethylhexyl) esters of di-OOH alpha,omega-dicarboxylic acids; e.g., alpha-omega 9:0; i.e., azelaic a.

Basestock	mm²/s 40°C	mm²/s 100°C	VI	pour pt °C
Paraffinic mineral oil	46	6.8	100	-12
Poly alpha olefin	50.5	8.2	135	<-66
Rapeseed oil	46.8	10.7	222	-24
di-2EH of azelaic a.	10.5	2.7	97	-57
di-2EH of α-ω 12:0	14.7	3.7	145	-48
di-2EH of α-ω 18:0	23.9	5.7	194	-9
di-2EH of α-ω 18:1	22.4	5.5	197	-57
di-2EH of α-ω 20:0	29.0	6.5	190	-3

with lower concentrations of anti-wear additives. This is especially beneficial to hydraulic fluids, which have a long service life in which additive depletion is a major issue.

Our research indicates that monounsaturated dibasic esters of linear alpha,omega-dicarboxylic acids have very good potential as basestocks for high-performance hydraulic fluids. Their heat-thinning is much slower, which is very beneficial for hydraulic systems. Thermal conductivity is significantly higher, resulting in energy savings and much lower operating temperatures. Oxidative stability can be balanced with antioxidants, while wear can be reduced more easily than in saturated basestocks. Other properties, including low temperature fluidity, should also meet high-performance requirements. Therefore, synthesis and testing efforts in this direction can result in new industrial oil products of significant potential volumes.

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Both authors report to the European project COSMOS on valorization of camelina and crambe oils.

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The project COSMOS has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 645405.

Prospective solutions for a trans-fat-free world: enzymatic glycerolysis

Reed A. Nicholson and Alejandro G. Marangoni

- **Enzymatic glycerolysis could be used as an alternative to hydrogenation and interesterification in the production of edible fats such as shortenings.**
- **Mono- and diacylglycerols produced through glycerolysis increased the crystallization temperature of various oils without affecting the fatty acid composition.**
- **Increases in solid fat contents to upwards of 20% at 5°C were achieved for several edible oils as a result of glycerolysis.**

Partially hydrogenated oils (PHOs) were used in shortenings for many years because of the functional characteristics provided by the trans fats. These included plasticity (ability to be shaped and molded), along with a high oil-binding capacity; and a melting point that is at or below body temperature (which prevented the material from being too waxy). Such characteristics resulted in baked goods and pastries with desirable textural and sensory properties. However, due to the negative effects that trans fats have been shown to have on cholesterol levels, PHOs were removed from all food products in the United States and Canada last year. Removing PHOs left a void in the functional properties of shortenings. This void is currently being filled with either palm oil, or oils which have undergone hydrogenation, interesterification, and fractionation to improve their functional properties.

While palm oil has many desirable properties for various food applications, it is high in saturated fat (particularly palmitic acid), and the production of oil palm plantations has led to extensive destruction of rainforests in Malaysia and Indonesia. The production of hardstock fats by full hydrogenation converts the unsaturated fatty acids of an oil into saturated fatty acids, producing a hardstock fat. However, the food industry should be wary of the use of this process, as it is currently recommended that consumers keep their saturated fat caloric intake to less than 10% of their overall daily caloric intake. Additionally, the word "hydrogenation" is not favored by consumers. As a result, such hydrogenated oils are frequently avoided.

Interesterification is a method of redistributing the fatty acids along the glycerol backbone, and can be achieved through chemical or enzymatic methods. This redistribution is typically performed between a liquid oil and a hardstock fat. This hardstock fat is often either palm oil or a fully hydrogenated vegetable oil (again, bringing the hydrogenation process along). This greatly improves the physical properties and usefulness of the oil, but it does so through the addition of saturated fat.

Finally, fractionation processes separate the high and low melting components, producing a highly saturated fraction and a more unsaturated-rich fraction. These can be used directly as food ingredients, or the high melting fraction may be interesterified with liquid oil (often the case with this fraction from palm oil). Furthermore, over the past two decades many alternative oil structuring agents have been investigated for their use in food systems. These include waxes, fatty acids and fatty alcohols, phytosterols, ceramides, and ethylcellulose. While many of these components have been shown to effectively structure oil, inadequate plasticity and textural properties, melting profile, and oil binding were all commonalities.

We are currently investigating enzymatic glycerolysis as a prospective solution to the issues associated with current shortening production technologies. This technique is showing promise as an alternative oil structuring method for shortening applications and would allow for shortenings to be produced without hydrogenation or interesterification. Enzymatic glycerolysis is a well-researched technology typically used to produce monoacylglycerols (MAGs) and diacylglycerols (DAGs) for their use in foods as emulsifiers. During this process, the ester bonds linking the fatty acids and glycerol of the triacylglycerol (TAG) molecules are cleaved. The fatty acids are then available to be attached to glycerol that has been added to the system, producing MAGs and DAGs, while having no effect on the fatty acid composition of the oil. A schematic diagram depicting this reaction is shown in Figure 1. Although these molecules would generally then be isolated from the mixture and used as food ingredients, they can in fact directly structure the oil used to produce them. Not only does this process have no effect on the oil's saturated fat content, but previous research on the anti-obesity effects and reduction in blood-TAG levels due to the consumption of DAG oil has been well-documented [1], meaning that this shortening alternative stands to provide added health benefits when used in place of a highly saturated shortening.

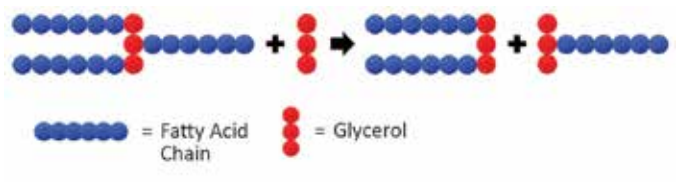

FIG. 1. A schematic diagram depicting the production of monoacylglycerol (MAG) and diacylglycerol (DAG) from triacylglycerol (TAG) and glycerol through a glycerolysis reaction

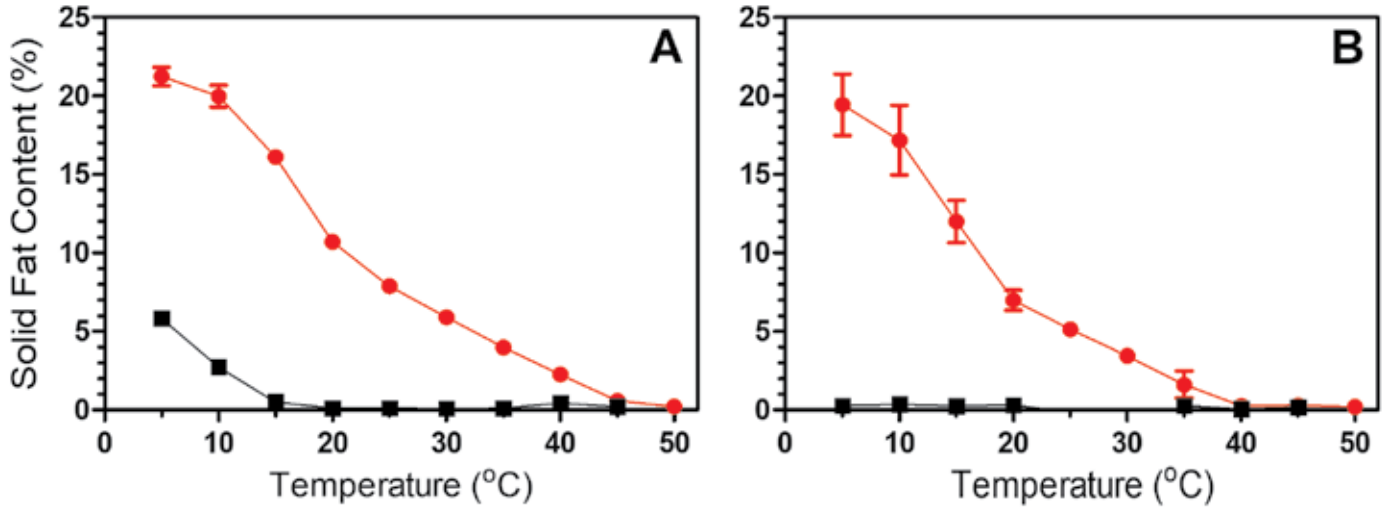

FIG. 2. Solid fat content (SFC) melting profiles for (A) cottonseed oil and (B) rice bran oil before (represented by black line) and after (represented by red line) glycerolysis. Samples were crystallized at 5°C for 1 week prior to measuring the SFC using nuclear magnetic resonance (NMR).

DAGs are known to crystallize in a different manner compared to TAGs. As a result, DAGs (specifically the 1,3-isomer) have a melting point that is higher than that of TAGs containing the same fatty acids [2]. In addition, MAGs have been known to crystallize at higher temperatures than their TAG counterparts, and can thus act as a template for TAG crystallization[3]. In our research, using the enzyme *Candida antarctica* lipase B, glycerolysis reactions were run for a variety of time lengths with different glycerol:TAG ratios in order to optimize the process to achieve the highest increases in the solid fat content (SFC) of the system.

Both cottonseed and rice bran oils have shown promise as potential shortening products, as both these oils demonstrated appreciable SFC increases. The SFC melting profiles of cottonseed and rice bran oil before and after glycerolysis are depicted in Figure 2. Cottonseed oil underwent an increase in SFC from 6% to 21% at 5°C after the glycerolysis process. Even after the temperature of the oil was increased to 20°C, nearly 11% solids remained. Similarly, the SFC of rice bran oil increased from <1% to nearly 20% when measured at 5°C, with close to 7% solid fat remaining at 20°C.

Optimizing the glycerolysis process to achieve the greatest increases in SFC produced a cottonseed oil sample with 49% DAGs and 33% MAGs. Furthermore, the onset of crystallization of this oil was increased by over 20°C, increasing from -5°C to 20°C after the glycerolysis reaction. Similarly, rice bran oil previously had a crystallization onset of -5°C. The glycerolysis reaction increased this to 18°C. Figure 3 shows the crystallization curves of cottonseed and rice bran oil before and after glycerolysis. In addition to potentially using these oils for shortening applications, the emulsification properties of the MAGs and DAGs make them an excellent choice for the oil phase of

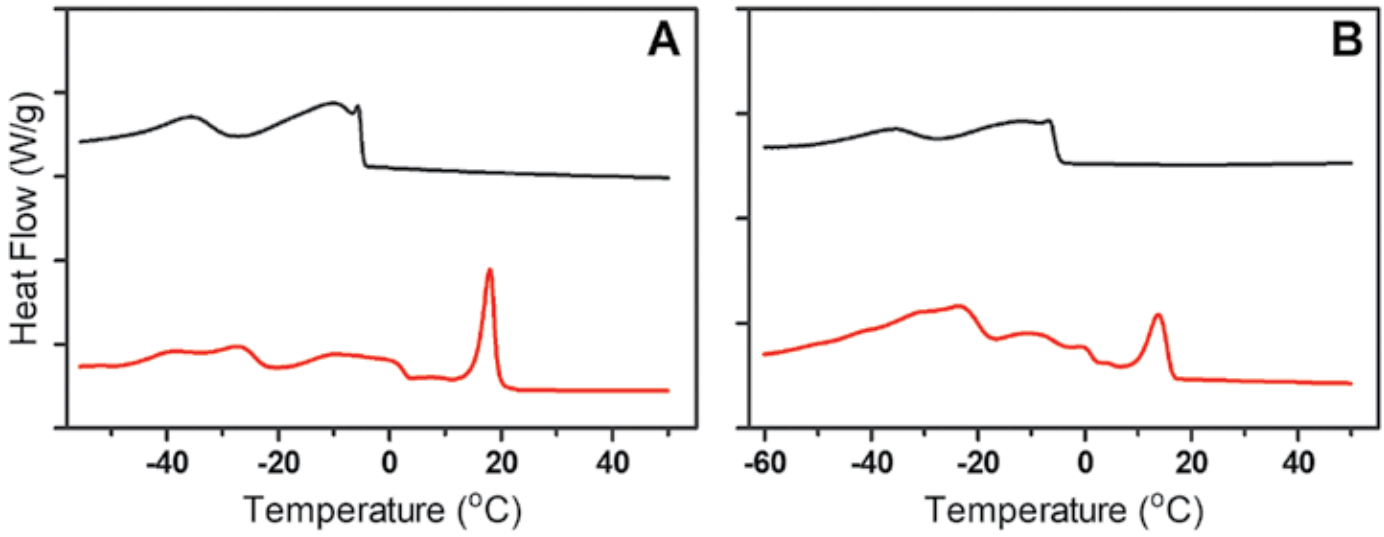

FIG. 3. Differential scanning calorimetry (DSC) crystallization curves for (A) cottonseed oil and (B) rice bran oil before (represented by black line) and after (represented by red line) glycerolysis

margarines and spreads, eliminating the need to incorporate more emulsifier into the formulation.

Should the new genetically modified gossypol-free cottonseeds be approved for human and animal consumption, there is likely to be an increase in both the supply of these oilseeds and the number of products produced from cottonseed flour. This should lead to a large increase in the supply of cottonseed oil. Improving the functionality of this oil through glycerolysis would be a great way to increase the cottonseed oil utilization in a variety of food applications.

While more research is still required to test the applicability of these structured oils in both margarine and shortening applications, the MAGs and DAGs formed during enzymatic glycerolysis greatly improved the functional properties of the oils. Without changing the fatty acid composition, these components increased the crystallization temperature to produce a much higher SFC at a wide range of temperatures. These promising changes may provide the plasticity and oil binding capacity effects necessary for this technology to be used as an alternative to hydrogenation and interesterification in shortenings and other food applications.

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Cyclopropane fatty acids in foods

Veronica Lolli, Daniele Del Rio, and Augusta Caligiani

In recent years, the study of fatty acids, together with their involvement in the occurrence of human diseases, is of notable interest. For example, numerous investigations have attributed functional properties to omega-3 and omega-6 long-chain polyunsaturated fatty acids (PUFA), conjugated isomers of linoleic (CLA), and alpha-linolenic (CLNA) acids (Zárate, R., *et al.*, https://doi.org/10.1186/s40169-017-0153-6, 2017).

- **Cyclopropane fatty acids (CPFA), such as dihydrosterculic and lactobacillic acids, are carboalicyclic fatty acids that are widely distributed among microorganisms and plants. Such carboalicyclic fatty acids were recently discovered in foods of animal origin, especially in dairy products and bovine meat (Fig. 1).**
- **In the dairy sector, CPFA represent authenticity markers for Protected Designation of Origin (PDO) cheeses. Their determination has been included in the Disciplinary of Production of Parmigiano Reggiano cheese, among the official quality-control procedures.**
- **CPFA bioavailability in humans was assessed by their detection in human plasma after the consumption of CPFA-rich food sources.**

Fatty acids containing a carbocyclic unit (Fig. 2) naturally occur in specific genera of bacteria and in certain eukaryotes, including protozoa, fungi, and plants (Moore, B.S., and Floss, H.G., *Reference Module in Chemistry, Molecular Sciences, and Chemical Engineering, from Comprehensive Natural Products Chemistry*, 1999).

Bacteria (e.g., lactic acid bacteria) synthetize cyclopropane fatty acids, such as dihydrosterculic acid (9,10-methylene octadecanoic acid) and lactobacillic acid (11,12 methylene octadecanoic acid), to strengthen their membranes, improving their resistance to environmental stress. (Montanari, C., *et al.*, https://doi.org/10.1016/j.fm.2009.12.003, 2010).

In plants, cyclopropene fatty acids, such as sterculic acid (*cis*-9,10-methylene-9- octadecenoic acid) and malvalic acid (*cis*-8,9-methylene-heptadecenoic acid), are distributed across several families, mainly in Sterculiaceae, Malvaceae, Bombacaceae, Tiliaceae, and Sapindaceae.

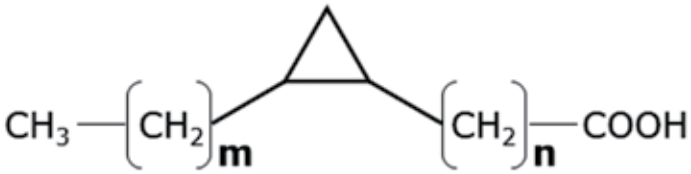
Sterculia foetida seed oil contains 65–78% of cyclopropene fatty acids, principally sterculic acid (Bao, X., *et al.*, https://doi.org/10.1073/pnas.092152999, 2002).

Many seed oils containing cyclopropene fatty acids are extensively consumed by humans, especially in tropical areas. Some studies have suggested that, in mammals, sterculic acid (Fig. 3) inhibits enzymes involved in lipid metabolism (E. Bichi, E., *et al.*, https://doi.org/10.3168/jds.2012-5349, 2012; Kadegowda, A.K., *et al.*, https://doi.org/10.1007/s11745-013-3823-1, 2013). Fatty acids with a cyclopropane in the structure, especially cyclopropaneoctanoic acid 2-hexyl (CPA2H), have been indicated as markers of metabolic disorders and increased cardiovascular risk (Mika, A., *et al.*, https://doi.org/10.1007/s11745-016-4141-1, 2016).

A NEW MARKER FOR PARMIGIANO REGGIANO AUTHENTICATION

CPFA, especially dihydrosterculic and lactobacillic acids, have been identified in ensiled feeds, such as maize silage, and dairy products from cows fed silages. This has led to the hypothesis that these CPFA might be derived from the bacterial fermentation that occurs during the ensiling process. Consequently, their presence has been proved to be a marker

FIG. 1. Cyclopropane fatty acids, such as dihydrosterculic and lactobacillic acids, were discovered as secondary compounds of the lipid profile of milk and dairy foods and beef meat products, but also in some species of fish and mushrooms (Lolli V., *et al.*, https://doi.org/10.1080/09637486.2018.1540556, 2018).



m,n	Common name
9,5	lactobacillic acid
6,7	dihydromalvalic acid
7,7	dihydrosterculic acid

FIG. 2. Structure of cyclopropane fatty acids (CPFA) most commonly detected in bacteria (Caligiani, A. and Lolli, V., https://doi.org/10.5772/intechopen.80500, 2018)

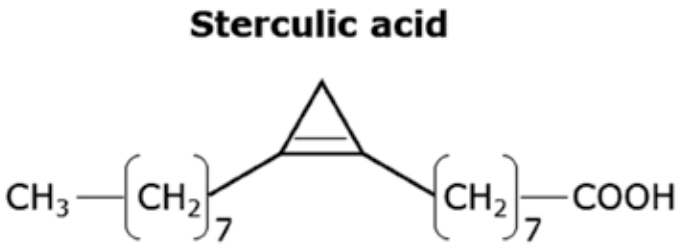


FIG. 3. Chemical structure of sterculic acid, a major component in *Sterculia foetida* seed oil

for the authentication of Protected Designation of Origin (PDO) cheeses, like Parmigiano Reggiano, for which the use of silages is strictly forbidden during production (Caligiani, A., *et al.*, https://doi.org/10.1021/acs.jafc.6b00913, 2016). Their determination has been included in the Disciplinary of Production of Parmigiano Reggiano, among the official quality-controls (UNI11650).

CPFA IN FOODS: MAIN SOURCES AND CONTENTS

CPFA content in foods has been investigated in previous studies (Caligiani, A., *et al.*, https://doi.org/10.1021/jf4057204, 2014; Lolli, V., *et al.*, https://doi.org/10.1155/2018/8034042,

2018; Lolli V., *et al*., https://doi.org/10.1080/09637486.2018.1540556, 2018).

As shown in Table 1, the most relevant food source of CPFA (mainly dihydrosterculic acid) is Grana Padano cheese (hard, slow-ripened, semi-fat, cow's-milk cheese from Italy) with concentrations ranging between 9.0 and 30.0 mg/100 g of food.

CPFA were found in several commercial bovine meat samples (0.7–4 mg/100 g of food) and two species of fish (eel and mullet) with concentrations between 3.7–41.3 mg/100 g of food. Low amounts of CPFA were also detected in probiotic products (0.0–0.3 mg/100 g of food) and in mushrooms, especially in *Boletus edulis* (0.3–1.9 mg/100 g of food), whereas they are generally absent in vegetable products (edible vegetable oils and soy-derived foods), eggs, pork, horse, and chicken meat.

Globally, experimental results suggest the bacterial and fungal origin of CPFA, indicating a strong correlation between their presence in foods with the use of silages in animal feeding. On the contrary, plant organisms generally do not produce CPFA.

It has also been demonstrated that food processing, manufacturing, seasoning steps, cooking, and fermentation only slightly affect CPFA content in food matrices.

Daily CPFA intake from these food items in the Italian population resulted 12.0±6.0 mg/day, not negligible in view of a possible physiological effect.

TABLE 1. CPFA content (mg/100g of food) as the sum of total isomers (dihydrosterculic and lactobacillic acids) in different food categories (Lolli V., *et al*., https://doi.org/10.1080/09637486.2018.1540556, 2018)

Food categories	No. of positive samples to CPFA/tot	Mean ± Standard Deviation	Range
Meat and meat products			
Beef meat	20/26	2.0±1.0	0.7–4.0
Others[1]	0/36	-	-
Dairy products			
Cow milk	49/50	0.8±0.6	0.2–2.2
Yogurt and fermented milk	4/4	0.5±0.1	0.4–0.6
Milk-based desserts	3/3	3.0±1.5	2.6–3.6
Cow cheeses			
Grana Padano	72/72	16.2±3.3	9.0–30.0
Parmigiano Reggiano	0/100	-	-
Others	30/79	10.8±5.4	5.4–30.0
Other cheeses			
Sheep cheese	0/17	-	-
Goat cheese	0/5	-	-
Probiotic food supplements[2]	2/2	0.1±0.1	0.0–0.3
Fish			
Eel	18/18	35.0±17.5	28.0–41.3
Mullet	4/4	4.3±0.6	3.7–5.0
Others	0/12	-	-
Mushrooms			
Boletus edulis	11/11	1.0±0.1	0.3–1.9
Cantarellus cibarius	4/6	0.1±0.1	0.0–0.2
Amanita cesarea	1/1	0.4±0.0	-
Others	0/10	-	-
Oils and fats			
Vegetable oils[3] and cocoa butter	0/100	-	-
Butter and creams	6/10	16.0±8.0	7.2–26.8
Soy-derived products	0/2	-	-
Eggs	0/2	-	-

Notes: [1]Fresh commercial meat (horse, chicken, lamb, goose, turkey, rabbit, pork, and cured meat); [2]*Bifidobacterium lactis*, *Lactobacillus spp*., *Streptococcus thermophilus*; [3]Extra virgin olive, corn, soy, and peanuts oils.

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CPFA BIOAVAILABILITY IN HUMANS

Triglycerides (TG) are the major components of dietary fats. Once ingested, they are submitted to an enzymatic hydrolytic process catalyzed by lipases acting at gastric and, mainly, at duodenal levels.

As previously mentioned, fatty acids containing a cyclopropane ring in their structure, like dihydrosterculic acid (DHSA), were detected in foods of animal origin, especially in dairy products and bovine meat.

In a recent study (Lolli, V., *et al*., https://doi.org/10.1016/j.jfoodeng.2018.05.034, 2018), CPFA digestibility (as the rate of hydrolysis of DHSA from triglycerides of Grana Padano cheese) was evaluated through an *in vitro*- simulated human gastrointestinal (GI) digestion experiment, proving their potential bioaccessibility and bioavailability in humans.

In vivo CPFA bioavailability is currently under investigation (https://clinicaltrials.gov, ID: NCT03612700).

Veronica Lolli is a post-doctoral researcher in the Department of Food and Drug at the University of Parma (Italy). Her research topic mainly focused on cyclic fatty acids in foods, and their origin, bioactivity, and use as molecular markers of quality. She can be contacted at veronica.lolli@unipr.it.

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A better **biodiesel?**

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

Rebecca Guenard

For as long as the Diesel motor has been in use, agricultural oils have been a probable fuel source. After a century of relying on abundant petroleum fuel, researchers are turning to these oils once again. Oil companies have dedicated years of research to establish a sustainable fuel with less environmental impact than petroleum. They quickly determined that prioritizing land for fuel instead of food was not sustainable in light of the challenges associated with feeding a burgeoning population. So, many scientists have shifted away from edible oils and are experimenting with ways to turn spent cooking oil into the automotive and aviation fuel known as biodiesel.

The most common method for repurposing waste cooking oil (WCO) into biodiesel is transesterification. The vegetable oil's fatty acids are converted into esters through a reaction with methanol in the presence of a catalyst, hence they are often called Fatty Acid Methyl Esters (FAME). Though this technique has shown promise, the properties of the resulting fuel do not match those of petroleum diesel (https://tinyurl.com/y7mfmwcj). Many of the performance issues are due to the esterification process. The resulting fuel is an oxygen-containing compound that can encourage microbial growth. In addition, partially converted fats form waxy coatings that seize engines in cold weather, while impurities leave deposits in fuel injectors. Good quality feedstocks help eliminate these problems; however, quality cannot be assured with waste oils. Besides, even when the quality is favorable the resulting fuel often has higher NO_x emissions than other types of diesel (https://doi.org/10.1007/978-1-4419-7145-6_15).

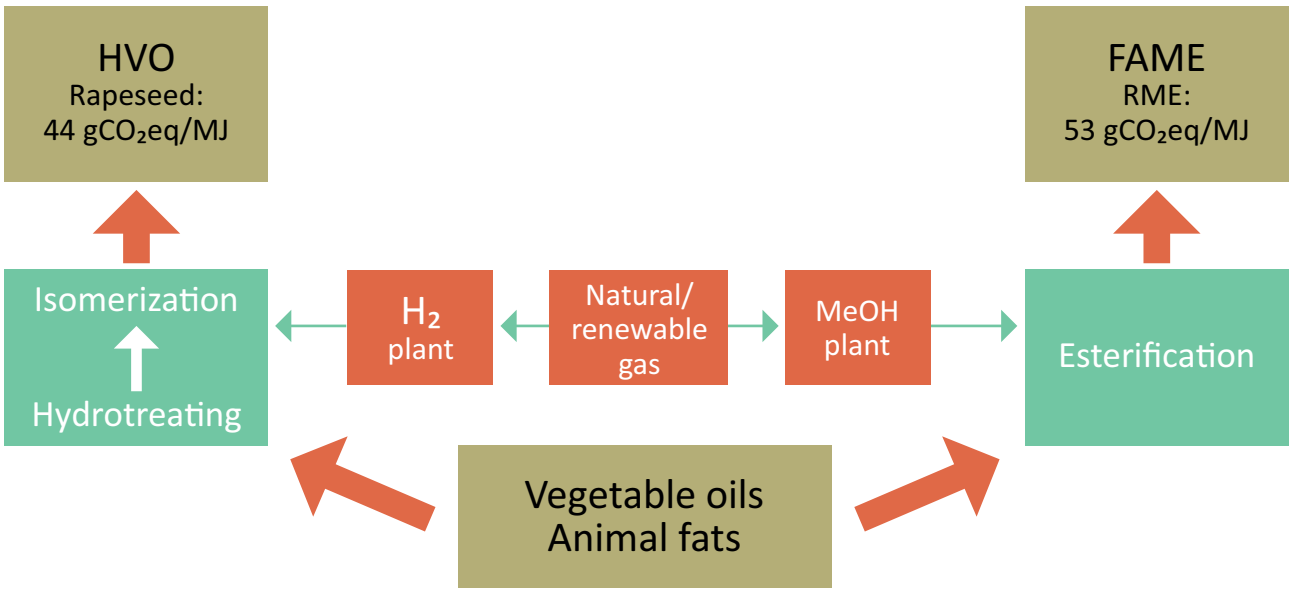
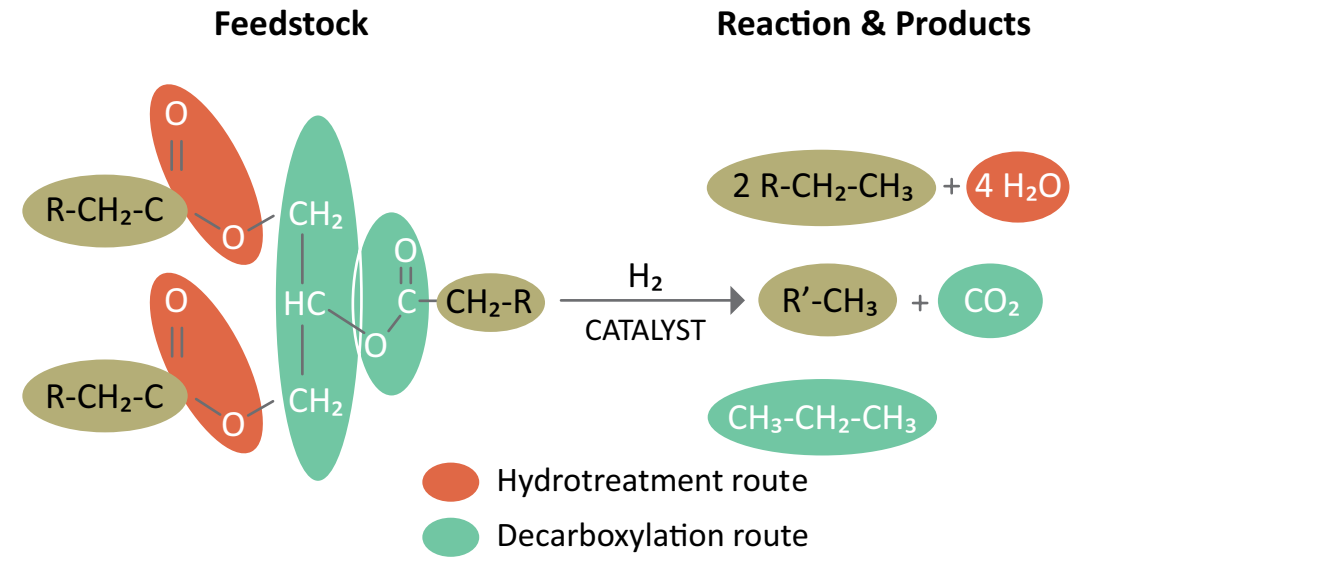


FIG. 1. Simplified scheme showing inputs and outputs of esterification and hydrotreating processes for biofuel production



Triglyseride
$R = C_xH_y$
- Straight hc chain, R typically $C_{12}...C_{20}$
- number of double bonds depends on feedstock type

HVO diesel fuel
C_nH_{2n+2}
- fully saturated paraffinic hydrocarbon

FIG. 2. HVO synthesis

Over the past decade a company in Finland has been optimizing a new method of biodiesel production. The product is a cleaner burning, more stable fuel, but is it likely to have an impact on the global biodiesel industry?

The fuel is known as hydrotreated vegetable oil (HVO), it results when triglyceride vegetable oil molecules react with hydrogen over a metal catalyst and remove oxygen. The reaction breaks down the triglycerides into a mixture of three hydrocarbon chains. The resulting fuel is simple, straight-chain and branched hydrocarbons that accomplish a cleaner combustion (Fig 1, page 23).

"The term, HVO is not correct, because it implies only vegetable oil," says Zissis Samaras, professor of mechanical engineering at Aristotle University of Thessaloniki in Thessaloniki, Greece. "This is how it started, but you can use any kind of oil or fats as a feedstock. The term is kept because of tradition," he says. Samaras studies the performance of fuels in different types of engines. Most recently he has worked with Neste, headquartered in Espoo, Finland, to test their fuels in passenger cars, an application where FAMEs have a tainted reputation due to possible engine damage (https://tinyurl.com/y8nhytul).

In 2007, Neste was the first company to produce HVO, which they call renewable diesel, and it is now the world's largest producer, reaching €1 billion profit in 2018. In addition to Finland, the company has production sites in Singapore and The Netherlands (https://www.neste.us/).

"Renewable diesel is a similar hydrocarbon diesel to what you make from a crude oil," says Markku Honkanen, head of Neste's technical services. "You have the same C15 to C18 length carbon chains and no oxygen. It is a diesel fuel of the same standard as a crude oil diesel fuel." See Figure 2.

According to Honkanen, the simplicity of the transesterification process means a company can start biodiesel production on little capital investment. "With biodiesel you don't necessarily need to use any pressure, you only mildly heat the oil, you use sodium hydroxide as a catalyst, and you end up with fatty acid methyl esters," he says. The process his company uses to make renewable diesel is more complicated. The fuel is made using high temperature, high pressure, and a metal catalyst like in a crude oil refinery. To prevent poisoning, the metal catalyst the oils use to make renewable diesel must be pretreated to remove any nitrogen or metals. Though these steps require more specialized equipment compared to traditional biodiesel, Honkanen says they result in a better product. "Renewable diesel has a higher cetane number and burns cleaner than crude oil diesel while also having the advantage of being better for an engine than biodiesel," he says.

The experiments Samaras performed in collaboration with Neste confirm this claim (https://doi.org/10.3389/fmech.2018.00007). When compared to diesel fuel currently on the market, renewable diesel emissions contain less soot, HC, and CO. In addition, NO_x emissions are on par with current

TABLE 1. Properties of HVO compared to market diesel (Dimitriadis, A., *et al.* 2018)

Property	Unit	Market diesel	HVO
FAME content	% v/v	7	0
Density at 60° C	kg/m^3	832.4	778.7
Kinematic viscosity	mm^2/s	3.24	2.82
Flash Point	°C	59	83
Cloud Point	°C	-5	-22
Sulfur content	ppwt	9.1	<5.0
Cetane number		56.5	76.3
Ash content	% m/m	0.002	<0.001
Water content	mg/kg	160	20
Polyaromatic hydrocarbons	% m/m	2.2	0
CFPP	°C	-5	-21
Heating value	MJ/kg	43	44
Oxidation stability	hr	>6	>22
Distillation	°C	191–357	189–301
A/Fs		14.2	15.2
Oxygen content	% wt	0.77	0
C/H ratio		7.26	5.49
Hydrogen content	% wt	12	15.4
Carbon content	% wt	87.2	84.6

market diesel. Samaras points out that renewable diesel also has a similar viscosity to crude oil diesel with the advantage of a significantly higher cetane number. "These are basic characteristics, that differentiate it very strongly from biodiesel," he says.

The transportation industry has taken notice (https://tinyurl.com/yxquffrg). Five years ago, Air BP partnered with Neste to reduce greenhouse gas emissions in the aviation industry (https://tinyurl.com/yb98z7yb). Neste Renewable Jet Fuel is being sold through BP Biojet to supply green aviation fuel to airports in Bergen and Olso, Norway, as well as, Halmstad, Sweden. The fuel was also used at Chicago O'Hare, one of the busiest airports in the world, for a single day in late 2017, as a proof of concept (https://tinyurl.com/ya7wxeoa). Renewable diesel is added to existing crude oil jet fuel without the need for adaptation to the jet engine. The new fuel could help the industry reach its 2050 goal of reducing carbon emissions by 50 percent.

Neste is also selling their renewable diesel product to the auto industry. It is available across the Baltic Sea region and in parts of North America. "We sell about one third in North America and the rest in Europe," says Honkanen. "California is our main market there, but we have been selling to the other West Coast states and Canada." Neste is also experiencing competition in HVO production. After being the only producer for a long time there is now HVO diesel produced in Italy, France, and the United States.

Some are still concerned about the viability of a fuel made from waste oil feedstock. "I think this applies not just to HVO, but to biodiesel as well," say Samaras. "The question is, do we have sufficient quantities of WCO to have a sustainable production of fuels? I would say, no." One media outlet even claims that Neste opened a second production plant in Singapore to be closer to palm oil sources that were used to produce their fuel (https://tinyurl.com/ybvon64u). Neste refutes that claim (https://tinyurl.com/y9xd9dlx).

According to their website, Neste does use some palm oil to make their product, but it is not a major component. The company states that 80 percent of their feedstock is from waste and residue, an amount they are working to increase (https://www.neste.us/). Honkanen says that one of the key things about their product is that the feedstock quality does not impact the product quality. "Due to the pretreatments we developed, we can use lower quality feedstocks than biodiesel," he says. "And even from the low-quality feedstock we get the high-quality fuel."

Rudolf Diesel introduced the design of his high-efficiency engine in 1886. As he saw it manufactured, he insightfully questioned how it would be sustainably fueled. In 1912, in an introduction to the book *Diesel Engines for Land and Marine Work* he wrote, "If at present, the applicability of vegetable and animal to Diesel motors seems insignificant, it may develop in the course of time to reach an importance equal to that of natural liquid fuels and tar." He goes on to write, "We cannot predict at present the role which these oils will have to play in the colonies in days to come. However, they give the certainty that motive power can be produced by the agricultural transformation of the heat of the sun, even when our total natural store of solid and liquid fuel will be exhausted."

Olio is produced by Inform*'s associate editor, Rebecca Guenard. She can be contacted at rebecca.guenard@aocs.org.*

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Has **Beijing's** new draft regulation introduced **China-REACH?**

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

Heng Li

China has introduced a groundbreaking draft law covering all existing and new chemical substances, a big change from the past decade when regulators focused on new substances, especially under the ambit of the Ministry of Ecology and Environment (MEE).

The MEE published the draft Regulation on the Environmental Risk Assessment and Control of Chemical Substances in January, with public comments accepted until February 20.

The wide-ranging draft will affect companies manufacturing, processing and using, importing, and exporting chemicals in and from China. It covers the environmental risk assessment and control of chemical substances, and offers a preview of changes that may be incorporated into China's new substances management regime.

When the text of the draft law was unveiled, some in China referred to it as the "real" China-REACH. This article examines the draft in detail to determine whether that description is accurate and what companies need to know about the changes.

CHINA'S CHANGING LAWS

A single chemical is now regulated by a variety of laws and Chinese authorities depending on its legal status as, for example, a new, existing, or hazardous chemical.

The MEE has promulgated MEP Order 7, which has been in effect since October 15, 2010, and is now being revised. It introduces REACH-like requirements for the registration of new chemical substances but has a different scope from EU-REACH, which covers existing and new chemical substances.

The ministry has been laying the groundwork for the regulation of existing chemical substances since 2016. China drafted the technical guidelines for screening chemicals subject to prioritized assessment and it issued the first batch of priority control chemicals in 2017. The changes indicate that the MEE does not intend to regulate all types of existing substances, focusing instead on those that are prioritized.

The draft Regulation is expected to become the overarching legislation governing existing and new chemical substances, but with an emphasis on the control of environmental risk. This is defined as "the degree and probability that a chemical substance with environmental or health hazard properties will enter into the environment and cause harmful effects on the ecological environment and human health."

Since the draft Regulation is likely to be promulgated by the State Council pursuant to China's Legislative Law, its legal effect is expected to be superior to the departmental rules promulgated by the relevant ministries (including the revised MEP Order 7), reflecting the MEE's intention to intensify the regulation of chemicals.

IMPORTANT POINTS FOR COMPANIES

There are several key features that companies may want to consider.

THE DRAFT REGULATION INTRODUCES THE POSSIBILITY OF SEVERE PENALTIES FOR COMPANIES MANUFACTURING, PROCESSING AND USING, AND IMPORTING AND EXPORTING CHEMICALS IN AND FROM CHINA. FOR EXAMPLE, A COMPANY FAILING TO COMPLETE THE REQUIRED NEW SUBSTANCE REGISTRATION COULD FACE AN ADMINISTRATIVE FINE OF UP TO RMB2,000,000 ($295,000), COMPARED WITH A FINE OF UP TO RMB30,000 UNDER MEP ORDER 7.

The draft Regulation governs both existing substances and new substances that are not included in the Inventory of Chemical Substances of China (ICSC**)**. The MEE will establish and update the ICSC, which is newly introduced in the draft. It is likely to be based on the current Inventory of Existing Chemical Substances of China (IECSC). It is not clear if the ICSC will include all of the existing substances in the IECSC, however.

The draft will not apply to substances "used for laboratory-scale research or reference standards," but there is an exception for new chemical substances manufactured or imported in quantities at or above 100kg/year. While the phrase "used for laboratory scale research or as reference standards" is not defined, this may be clarified in the implementation rules or MEE guidelines.

DRAFT HIGHLIGHT

The draft Regulation highlight involves the provisions on environmental risk assessment and control, which apply to any "chemical substance," not distinguishing between existing and new substances.

In essence, the draft requires the MEE to organize the environmental risk assessment of chemical substances subject to prioritized assessment, based on information acquired through industry reporting and specific activities carried out by the MEE, including environmental risk screening.

Any company manufacturing, processing and using, and importing a chemical substance would need to provide the MEE with an annual report including basic information about the substance, including its name, quantities, and uses.

As part of the environmental risk screening, the MEE is to establish a plan for the risk assessment of chemical substances subject to prioritized assessment. Companies manufacturing, processing and using, and importing a substance in the plan would need to provide information, including data on emissions, physico-chemical properties, toxicology, and eco-toxicology.

Once the risk assessment is complete, the MEE will promulgate the relevant risk control measures, along with other ministries, to establish:

- a catalogue of chemical substances subject to prioritized control (the Prioritized Control Catalogue, or PCC), including substances that must abide by additional laws such as the Prevention of Atmospheric Pollution, of Water Pollution and of Soil Pollution Laws;
- a catalogue of restricted chemical substances (the Restriction Catalogue), including substances selected from the PCC subject to restrictions on uses and relevant import/export licensing;
- a catalogue of prohibited chemical substances (the Prohibition Catalogue), including substances selected from the PCC that would be strictly prohibited from being manufactured, processed and used, imported and exported in and from China; and
- an Information Publication Platform for Chemical Substances Subject to Prioritized Control requiring companies to disclose information annually.

KEY CHANGES FOR NEW SUBSTANCES

The draft Regulation reveals key changes that are likely to become part of China's substance management regime. These are:

- new substances would be subject to registration or filing. The current requirement of simplified registration provided by MEP Order 7 appears to be replaced by the filing process;
- registration would apply to the new substances that are manufactured or imported at or above one ton/year;
- filing would apply to the new substances below one ton/year (except for the new substances which are "used for laboratory scale research or as reference standards" and are below 100 kg/year) and the other specified substances (for example, low-concern polymers);
- the application for the registration of persistent bioaccumulative toxic chemicals (PBTs) and "the substances possessing the same hazards" would be rejected, and they would be included in the Prohibition Catalogue; and
- registration would be subject to a fee payable to the MEE.

The draft Regulation maintains the statutory timeframe for inclusion of a registered new substance into the ICSC, which is five years after completion of the registration. In addition, the draft empowers the MEE to provide, in the ICSC, the restrictive conditions on the uses of certain substances where necessary.

ENFORCEMENT

The draft Regulation introduces the possibility of severe penalties for companies manufacturing, processing and using, and importing and exporting chemicals in and from China.

For example, a company failing to complete the required new substance registration could face an administrative fine of up to RMB2,000,000 ($295,000), compared with a fine of up to RMB30,000 under MEP Order 7. In the most severe cases, they may be ordered to cease business.

Rapid promulgation of the legislation is not expected, given China's legislative priorities and the need to align the interests of the various affected ministries before the State Council can take action.

The draft may also be revised and subject to additional consultations leading up to its promulgation, so companies should submit comments if they want to propose changes or introduce new provisions.

It is vital that companies actively monitor the enactment of the implementation rules of the draft. While the draft Regulation introduced general requirements, many detailed requirements must be specified by the relevant departmental rules and official guidelines to be promulgated by the MEE and other ministries.

These include:

- the definition of technical terms such as PBTs and "substances possessing the same hazards";
- the detailed procedure of environmental risk assessment and control, specifically whether the industry would be provided with opportunities to defend their products;
- the protection of CBI; and
- detailed requirements on new substance management to be provided in revised MEP Order 7 and the associated official guidelines.

Companies are also encouraged to assess the draft Regulation's impact on their products, supply chain organization, and global compliance strategy from a legal and regulatory standpoint at the earliest possible stage.

THE "REAL" CHINA-REACH?

There are certainly REACH-like elements in the draft Regulation. Like EU-REACH, it governs existing and new substances.

The environmental risk assessment process also appears to be similar to substance evaluation under EU-REACH, where the MEE will play a dominant role and could ask industry to submit additional data.

Furthermore, the process for including a substance in the Restriction Catalogue is similar to the restriction process under the European law. Both are risk-based and are initiated by the authorities.

But the draft Regulation differs in other respects.

While the draft covers only environmental risk, EU-REACH covers all types of risks, including those caused by the physical and health hazards of a chemical substance.

The draft requires the registration or filing of new substances only, irrespective of the tonnage. EU-REACH, however, requires the registration of existing and new substances at or above one ton/year.

China's draft Regulation introduces the inclusion of a substance in the Prohibition Catalogue but it doesn't provide an authorization process. Listing in the catalogue would result in a ban on its manufacturing, use, import and export in and from China. Under EU-REACH, however, even if an SVHC is included in Annex XIV the industry can apply for an authorization to continue its use(s) in the EU.

In summary, the draft Regulation has REACH-like elements but it cannot be considered "China-REACH."

The differences between this legislation and EU-REACH, and its relationship with the other laws in China, reflect the unique nature of the country's legal and administrative systems. Chinese legislators take this into consideration when drafting legislation.

Heng Li is a senior associate at Mayer Brown law firm in Beijing, China.

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Pulses in Argentina

Leslie Kleiner

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

As I was reading the local Argentinean newspaper, *La Nación*, I came across an interesting article written by Josefina Pagani (https://www.lanacion.com.ar/2216620-las-legumbres-quieren-destronar-carne). The article describes consumption and production of different pulses in Argentina, and the possibility of these crops impacting the meat industry. Pulses are crops of global relevance, and they have an important role in nutrition and global food security. To increase awareness of these crops, the United Nations declared February 10th as "World Pulses Day." Coupled with this effort, and to further emphasize the role of plants in nutrition and health, the year 2020 was declared as "The International Year of Plant Health." The objective is to foster increased production of healthy plants and to reduce global economic losses due to plant diseases (http://www.fao.org/news/story/en/item/1175295/icode/). In this context, I have adapted the content of Pagani's work into a Q&A format.

Q: Which type of pulses grow in Argentina? What were the approximate volumes for 2018 production?

Argentina produces a variety of pulses, including peas, garbanzo beans, lentils, and a variety of beans (white, black, red, cranberry, and mung). These pulses grow in different regions of the country. For example, the provinces of Santa Fé and Buenos Aires are the major producers of peas and lentils, while garbanzo beans grow mostly in the northwest of the country and north of Córdoba province. All told, the "Cámara de Legumbres de la República Argentina (Argentine Chamber of Pulses)" reported a 750, 000 metric ton production of pulses for the 2018 year. Most of this production (~560,000 metric tons) was exported.

Q: What was the lentils, peas, garbanzo beans, and black beans production for 2018?

Lentils are consumed domestically. They are not destined for exports, as profit margins are higher within Argentina than they are abroad. Pea production has been steady for several years, somewhere between 70 and 100,000 metric tons. Most of the peas are exported to Brazil and Europe. Garbanzo bean production and exports had a large growth in 2018. During the last ten years, garbanzo bean production rose from 30 to 160,000 metric tons. Finally, black bean production was between 130 and 140,000 metric tons. This crop was primarily exported, mainly to Brazil (85%), Cuba, and Venezuela.

Q: What is the consumption of pulses in Argentina?

Nicolás Karnoubi, the vice president of the Argentine Chamber of Pulses, reported that "the internal consumption per capita is quite low: 800 grams of pulses, per person, per year. In contrast, India consumes 20.8 kg per capita, which represents ~26 times the consumption in Argentina." Karnoubi contrasted the local consumption of pulses to that of beef, which is 56 kg per capita per year, and beef, chicken, pork, and fish, which is 100 kg per year. Therefore, the annual per capita consumption of meat and fish in Argentina is ~125 times that of pulses.

Q: What is the distribution of pulses consumed in Argentina?

Lentils account for half of the total per capita consumption (800 grams), this is followed by 200/250 grams of canned peas, 100 grams of beans, and negligible amounts of remaining types of beans. Karnoubi emphasized that "in Argentina, people are used to animal protein and not plant-based protein." Therefore, the Chamber of Pulses promotes these crops as a way to improve nutrition and health for children, and to families as a lower-cost alternative protein.

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

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A finger on the pulse of AOCS

Member Spotlight is a regular column that features members who play critical roles in AOCS.

One look at the Fast Facts entry for "other involvement" sums up why Janitha Wanasundara is known among AOCS staff as a "go-to" AOCS member who is always ready and willing to help whenever and wherever she can.

"With the increased attention to the science and technology surrounding plant-based proteins at the 2018 Annual Meeting, it wasn't surprising that Janitha jumped right in and volunteered to co-chair the processing-related session at the inaugural AOCS Pulse Science and Technology Forum in November 2019 (www.aocs.org/pulseforum)," explains Jeffry L. Newman, AOCS senior director, programs.

Given her background, Wanasundara's focus on helping AOCS broaden its scope by providing information and programming on pulses (high-protein, nitrogen-fixing crops that are a part of the legume family) makes perfect sense. "We saw inquiries about plant protein increase in early 2010 and knew it was time to expand the offerings of the Protein and Co-Products Division," she says. "After all, AOCS is a natural home for pulse-related research, given the expertise and technology represented by the soy protein industry." (See https://www.aocs.org/stay-informed/hottopic/pulse-crops-for-a-sustainable-future.)

Wanasundara's own research on pulses goes back to the early 2000s. Then, when she joined Agriculture and Agri-Food Canada in 2004, she was part of the national research team for bioproducts and clean technology. "Most of my research is related to the chemistry and technology of utilizing the proteins of Canadian crops for bioproducts, understanding the nature of proteins in oilseeds and pulses, and developing different compounds and molecules," she notes.

Her volunteer work for AOCS, which she estimates generally takes no more than several hours per month, complements her responsibilities on the job by allowing for interaction with academic, government, and industry leaders in plant proteins and oilseed processing, as well as biofuels and biofuel co-products. She also was involved with a special issue of the *Journal of the American Oil Chemists' Society* on plant and alternative protein sources (https://aocs.onlinelibrary.wiley.com/toc/15589331/2018/95/8?utm_source=Pulse_page). That effort in particular has advanced her "scientific involvement in relation to editorial work," she says, adding that all of her volunteer work has allowed her to get to know many fellow peers from other countries as well as the next generation of science leaders—graduate students.

"AOCS is a great place to meet new people," she says.

Fast facts

Name	Janitha Wanasundara
Joined AOCS	2004
Education	Ph.D. in food science, Memorial University, Newfoundland, Canada (1996)
Job title	Research Scientist
Employer	Agriculture and Agri-Food Canada (Saskatoon, Saskatchewan, Canada)
Role in AOCS	Member, Pulse Initiative Steering Committee
High-fat Indulgence	Poutine (Poutine is a Canadian dish consisting of french fries [chips] and cheese curds topped with a brown gravy.)
Favorite Social Media	LinkedIn
Most memorable AOCS experience	As a grad student, I made a presentation at the 1995 Annual Meeting & Expo (AM&E) in San Antonio, and found that the scientific content of the program, the professionalism of the AOCS staff and members, and the balanced representation of industry, government, and academia was exceptional.
Other involvement	AM&E session chair and Administration Committee; Books and Special Publications Committee; Division Council; Protein and Co-Products Division Executive Steering Committee and Student Poster Award Committee

PATENTS

Fermented vegetable oils and methods of preparing the same

Kim, K.-N., *et al.*, Damy Chemical Co., Ltd. and Korea Research Institute of Bioscience and Biotechnology, US10188594, January 29, 2019

The present invention relates to a fermented vegetable oil, to a method for preparing the oil, and to a composition including the oil. More particularly, the present invention relates to a technique for providing a fermented vegetable oil having the effects of enhancing emulsion stability due to water retention ability, improving texture and flavor, and enhancing moisturization.

Method for polyol synthesis from triacylglyceride oils

Curtis, J.M., *et al.*, The University of Alberta, US10189761, January 29, 2019

A method for preparation of polyols from an unsaturated TAG oil that involves first epoxidizing the unsaturated TAG oil; then subjecting the epoxidized TAG oil to transesterification using a diol and/or triol in the presence of a catalyst to produce hydroxyalkyl esters of fatty acid epoxides; and finally hydroxylating the transesterification product using a diol and/or triol and a solid acid catalyst to obtain a polyol with relatively high hydroxyl value and low viscosity.

Hydrophobic additive for use with fabric, fiber, and film

Mor, E., Techmer PM, LLC, US10189959, January 29, 2019

The present invention relates to a hydrophobic additive for use with fabric, fiber, and film. One aspect of the present invention comprises a master batch composition for use in preparing a non-woven fabric in order to increase its hydrophobicity. In one embodiment, the master batch composition includes a polymer and a lipid ester. The lipid ester comprises 10 wt. % to 40 wt. % of the master batch. The fabric, when including the master batch composition, has a contact angle ranging from 100.degree. to 125.degree. when measured according to test method ASTM D2578.

High-performance environmentally acceptable hydraulic fluid

Gunawidjaja; R, *et al.*, Washington State University, January 29, 2019

A novel hydraulic (e.g., a biohydraulic) fluid which has high-performance attributes is disclosed herein. Such a novel hydraulic fluid includes a contribution of a range of 10% up to about 85% by weight of at least one of: natural esters, synthetic esters, polyols, a vegetable oil, 1% up to about 40% by weight of polyalphaolefin (PAO), 1% up to about 40% by weight of polyalkylene glycol (PAG), and mixtures thereof, and wherein up to about 10% by weight quantity of one or more additives are introduced to provide desired properties that include at least one of: a high viscosity index, a low pour point, a hydrolytic stability, and an oxidative stability, as part of the hydraulic fluid contribution.

High-yield production of fuels and petro- and oleo-chemical precursors from vegetable oils and other liquid feedstocks in a continuous-flow pyrolysis reactor with or without catalysts

Shirazi, Y., *et al.*, The University of Toledo, US10190058, January 29, 2019

Systems, methods, and materials for pyrolyzing vegetable oil feedstocks to obtain high yields of various products are described.

Lipid comprising long-chain polyunsaturated fatty acids

Petrie, J.R., *et al.*, Commonwealth Scientific and Industrial Research Organisation, Nuseed Pty Ltd., and Grains Research and Development Corporation, US10190073, January 29, 2019

The present invention relates to extracted plant lipid or microbial lipid comprising docosahexaenoic acid, and/or docosapentaenoic acid, and processes for producing the extracted lipid.

Enrichment of palmitoleic acid and palmitoleic acid derivatives by dry and solvent-aided winterization

Byelashov; O.A., *et al.*, Omega Protein Corp., US10190075, January 29, 2019

The present invention provides a fatty acid mixture enriched with palmitoleic acid and palmitoleic acid derivatives relative to the starting lipid mixture; fractionations procedure described herein are winterization methods. The invention provides methods of dry winterization and solvent-aided winterization alone and in combination. In some embodiments, the palmitoleic acid and palmitoleic acid derivative enriched mixture described herein contains less than 1% of palmitic acid and palmitic acid derivative. The invention also provides palmitoleic derivatives of use as dietary supplements.

Crumb process

Wehrle, K., *et al.*, Mars, Inc., US10194676, February 5, 2019

A process for the production of crumb is disclosed in which a wet crumb feedstock comprising bulk sweetener, protein, and water is formed and then simultaneously dried and comminuted in

a thin layer rotary paddle dryer (20). The wet crumb feedstock is preferably formed into discrete, free-flowing granules prior to the simultaneous drying and comminuting. Apparatus for the production of crumb is also disclosed.

Plant powder-containing white chocolate-impregnated food and method for producing same

Saijo, A., *et al*., Meiji Co., Ltd., US10194677, February 5, 2019

The present invention provides a white chocolate-impregnated food that is a porous food into which a white chocolate that contains a plant powder is impregnated. A median diameter of the plant powder is 5 to 20 .mu.m. In the white chocolate-impregnated food, the white chocolate that contains the plant powder is impregnated into inside of the porous food.

Emulsifiers having water-in-oil-stabilizing properties and compositions, uses and methods relating to same

Thibodeau, A., Innovacos Corp., US10195123, February 5, 2019

Emulsifiers are provided that are able to stabilize water-in-oil emulsions. The emulsifiers are homogenous and have a relatively low melting point (e.g., soft pastes, gels, or liquids at room temperature), enabling their use in cold-process methods/formulations which reduce energy consumption, manufacturing costs, as well as allow the use thermolabile-active ingredients. The water-in-oil emulsifiers may comprise: (a) polyglycerol fatty acid esters consisting of saturated and unsaturated fatty acid esters of polyglycerol; (b) polyhydroxystearic acid copolymers consisting of copolymers of hydroxystearic acid with saturated and unsaturated fatty acids; and (c) hydroxystearic acid. Methods and uses relating to the emulsifiers are also described, for example in cosmetic and pharmaceutical compositions.

Compounds and compositions for intracellular delivery of agents

Benenato, K.E., *et al*., ModernaTX, Inc., US10195156, February 5, 2019

The disclosure features amino lipids and compositions involving the same. Nanoparticle compositions include an amino lipid as well as additional lipids such as phospholipids, structural lipids, PEG lipids, or a combination thereof. Nanoparticle compositions further including therapeutic and/or prophylactic agents such as RNA are useful in the delivery of therapeutic and/or prophylactic agents to mammalian cells or organs to, for example, regulate polypeptide, protein, or gene expression.

Dustless powder materials

Morrison, D.M., *et al*., US10196524, February 5, 2019

This invention relates to a coated powder material containing a powder material having a surface layer that has been chemically immobilized with one or more surface-active agents and coated with an oil. The surface-active agents are present in an amount of at least about 0.1% by weight, based on the powder material; the oil is present in an amount ranging from about 0.1 to 180% by weight, based on the powder material; and the combined weight percentage of the surface-active agents and oil is at least about 4.0% by weight, based on the powder material. The oil-absorption rate of the powder material ranges from about 0.01 to about 0.70 gram of oil per gram of dry powder. The coated powder material is useful as a cosmetic.

Production method of highly unsaturated fatty acid with high purity/high yield

Tabata, H., *et al*., Bizen Chemical Co., Ltd., US10196584, February 5, 2019

A production method of highly unsaturated fatty acids with a high purity/high yield that compensates for shortcomings of conventional techniques is provided. A purification method of highly unsaturated fatty acids and/or derivatives thereof comprising (a) contacting and stirring first raw materials comprising the substances with a first silver salt aqueous solution to collect a first oil layer and a first aqueous layer; (b) separating the first aqueous layer into a second silver salt aqueous solution and the substances; and (c) contacting and stirring the first oil layer with the second silver salt aqueous solution for separation into an oil layer and an aqueous layer to obtain a second aqueous layer comprising the substances.

Hair cosmetic composition which comprises a plant lecithin

Behler, A., *et al*., BASF SE, US10201487, February 12, 2019

Described is a hair cosmetic composition which comprises at least one plant lecithin, at least one anionic surfactant, and at least one fatty alcohol.

Nanoparticle formulation

Bell, J., *et al*., United Kingdom Research and Innovation, US10201499, February 12, 2019

The present invention concerns nanoparticle formulations suitable for the delivery of one or more therapeutic agents, the formulations comprising: a cationic cholesterol derivative; a neutral phospholipid; cholesterol or a neutral cholesterol derivative; and a saturated fatty acid, PEGylated neutral derivative of phosphatidylethanolamine or phosphatidylcholine.

Positively charged liposomes as lipophilic molecule carriers

e Sousa Martins, D., Kemin Industries, Inc., US10201508, February 12, 2019

A method of producing positively charged liposome vesicles for use as carriers of lipophilic molecules. A mixture of hydrogenated phospholipids, a cationic excipient, and a lipophilic molecule are dissolved in a solvent to form a composition. The composition is dried to remove the solvent. The dried composition is hydrated to form liposome vesicles, and optionally the liposome vesicles are homogenized to form smaller vesicles. The vesicles are useful for delivery lipophilic molecules, such as, but limited to, lutein and zeaxanthin to ocular tissues using iontophoresis.

Methods and compositions for improving cognitive function

French, S., *et al.*, Mars, Inc., US10201522, February 12, 2019

This invention relates to compositions, and methods of use thereof, for (i) enhancing executive cognitive function(s) (for example, decision making, planning, working memory, multitasking, judgment, numerical problem-solving, reading comprehension), and/or (ii) increasing blood flow in brain vasculature, comprising administering to a subject in need thereof, certain polyphenols such as flavanols, procyanidins, or pharmaceutically acceptable salts or derivatives thereof.

Controlled-release fertilizer employing epoxidized fatty acid triglyceride oil as a coating additive

Xing, B., *et al.*, Agrium, Inc., US10202314, February 12, 2019

Controlled-release fertilizer employing epoxidized fatty acid triglyceride oil as a coating additive.

Viscoelastic foams having high dissipation energy

Binti Hanzah, N., *et al.*, Malaysian Palm Oil Board, US10202482, February 12, 2019

A viscoelastic polyurethane foam formed from a polyisocyanate and a polyol composition comprising palm olein-based polyol in an amount of 10% to 35% by weight of the total polyol composition and petroleum-based polyol in an amount of 65% to 90% by weight of the total polyol composition. The dissipation energy of the viscoelastic polyurethane foam is between 0.01 J to 0.30 J as calculated based on a hysteresis loop normalized a density of 40.80 kg/m.sup.3. This shows that the viscoelastic foam produced has an improved dampening property. The introduction of palm olein-based polyol into the production of viscoelastic foam does not affect the support factors and mechanical properties of the foam produced. The viscoelastic foams can be produced using an amount of up to 35% of palm olein-based polyol derived from palm olein or up to 25% of palm olein-based polyol derived from a mixture of palm olein and soybean oil by weight of total composition without any adjustment in the catalyst package.

Graffiti removal compositions and the use thereof

Leenan, A., *et al.*, Guard It Solutions Pty Ltd., US10202514, February 12, 2019

The present invention relates to graffiti removal compositions and the use thereof for the removal of graffiti from surfaces. The compositions comprise (i) alkyl esters of one or more soybean oil fatty acids; (ii) one or more aliphatic diesters of dicarboxylic acids; (iii) one or more compounds of the formula R.sub.2C(0)OR.sub.3, wherein R.sub.2 is a C.sub.1-C.sub.20 alkyl and R.sub.3 is C.sub.1-C.sub.20 alkyl; and (iv) a surfactant.

Biodiesel emulsion comprising a lecithin-based emulsifier for cleaning bituminous-coated equipment

Reinke, G., *et al.*, ALM Holding Company and Ergon Asphalt & Emulsions, Inc., US10202564, February 12, 2019

Methods of cleaning equipment such as hand tools dirtied by bituminous mixture. A biodiesel emulsion comprising biodiesel, water, and emulsifier(s) is applied to the surface of the equipment for a period of time (e.g., at least about 15 minutes) and optionally agitated. The biodiesel emulsion produces cleaning properties comparable to straight biodiesel, at a cost reduction, due to the replacement of biodiesel with water.

Patent information was compiled by Scott Bloomer, a registered US patent agent and Director, Technical Services at AOCS. Contact him at scott.bloomer@aocs.org.

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How peer reviewing has helped my career

Douglas G. Hayes

My first encounter with peer review was in graduate school, when I received a harsh but fair review of my first paper. I was livid after receiving it, but then a senior student in my department took the time to explain to me that the reviewer had invested a great deal of time and effort looking at my manuscript, with the sole purpose being to improve it, in terms of its scientific and technical writing quality. I learned a lot from that experience. As a senior grad student, I helped the younger students in our department with their writing and presentations, and later I provided similar help to people in my research group, especially by providing them with opportunities to serve as peer reviewers.

While I was working as a postdoc at the US Department of Agriculture, Agricultural Research Service, colleagues encouraged me to join the AOCS community. As a new AOCS member, I was given several opportunities to serve as reviewer for the *Journal of the American Oil Chemists' Society* (*JAOCS*). When I went into academia in 1994, I continued my involvement as a peer reviewer for *JAOCS*. Five years later, I was asked to serve as an Associate Editor, and in 2010, I became an Associate Editor for the *Journal of Surfactants and Detergents* (*JSD*). In 2013, I was promoted to Senior Associate Editor for *JAOCS*. I thank mentors such as Bob Kleiman, Ken Carlson, Mike Haas, Rich Hartel, and Jean-Louis Salager for their assistance in these roles. I am now in my 25th year as a faculty member, and I have continued serving as a peer reviewer of manuscripts for several different journals (~20 per year) and of research proposals within the United States and internationally.

Serving as a peer reviewer of manuscripts has helped me: 1) improve my own technical writing (a lifelong journey!); 2) build my critical thinking skills; 3) deepen expertise in my main research area while expanding my knowledge far beyond the narrow window of my PhD project; and 4) communicate and assess other scientists' work in a manner that is fair, diplomatic, beneficial, and not condescending nor hurtful—a skill that falls under "*collegiality*" (an area where I still need improvement).

The technical writing and critical thinking skills I have honed as a reviewer have had several specific impacts on my career, as these skills are essential for success in academia, industry, and government laboratories. Such skills are used every day on the job, and can be helpful in one's personal life as well. I have shaped my own technical writing style by incorporating best practices I have observed from reviewing well-written papers and by avoiding the mistakes I have seen while reviewing poorly written manuscripts.

Reviewing forces me to engage more deeply in the research topic at hand, often requiring me to review the relevant scientific literature. As a result, I improve my capabilities as a scientist. Research priorities of government funding agencies change from year-to-year. Therefore, I have had to adapt my research program to fit an ever-changing list of funding opportunities. Exposure to new research areas has helped me develop new research projects and has enabled me to collaborate with others in interdisciplinary research, including the opportunity to serve in leadership roles. I believe the grand challenges awaiting our society, such as supply of fuels, chemicals, and materials from renewable resources; climate change; and combatting disease from antibiotic-resistant microorganisms, will require an interdisciplinary approach to solve. Also, peer reviewing has helped me generate new approaches and made me aware of new instrumentation that can improve experimental research.

My teaching has also benefitted from peer reviewing. I have applied fundamental science that I have learned in reviewing papers to my engineering courses, and in some cases the papers (after publication) have served as examples in my lectures, homework assignments, or exams. Likewise, re-learning science and engineering principles for classroom preparation is often synergistic with the relearning of principles—material and energy balances, momentum, heat and mass transfer, and so on—that are refreshed during the assessment of manuscripts. Peer review has particularly made me better when it comes to mentoring students and communicating with others. Receiving criticism is never easy, and teachers, professors, and colleagues have a duty to deliver critiques in a constructive manner—a skill that remains a work in progress for me! I believe that the thoughtful and constructive peer reviews I received led me to being invited as an editor for AOCS journals. Perhaps the most important benefit of peer reviewing has been the privilege of helping colleagues and students improve their papers. Others have poured time and effort into helping me, and it is an honor to be able to return the favor.

I encourage any graduate students, postdocs, or scientists to serve as reviewers for AOCS journals. Effective peer reviews are the key step in insuring quality journal publications. *JAOCS*, *JSD* and *Lipids* are continually in need of dedicated reviewers. Please strongly consider this invitation.

Douglas G. Hayes, Senior Associate Editor for JAOCS *and Associate Editor for* JSD*, is a professor in the Department of Biosystems Engineering and Soil Science, University of Tennessee, Knoxville, Tennessee, USA. He can be contacted at +1 (865)-974-7991; dhayes1@utk.edu.*

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In vitro gastrointestinal digestibility of crystalline oil-in-water emulsions: influence of fat crystal structure

Jiao, W., *et al., J. Agric. Food Chem. 67*: 927–934, 2019, https://doi.org/10.1021/acs.jafc.8b04287.

To investigate how the fat crystal structure affects lipid *in vitro* digestibility, 30% palm stearin-in-water emulsions consisting of different polymorphic forms, sizes, and quantities of fat crystals were prepared after storage at different temperatures (4, 25, and 37 °C) for 1 h. The variation of particle size (d4,3), zeta potential, and microstructure during the gastrointestinal digestion and the free fatty acid (FFA) released in small intestine phase were investigated. After oral and gastric digestion, all of the emulsions underwent partial or complete coalescence and flocculation. During intestinal digestion, the d4,3 and zeta potentials did not notably affect lipid digestion. The FFA-released assay results indicated that the lipid digestion extent decreased as the fat crystal size and content of the beta polymorph increased, and there was no obvious relationship between FFA release and fat crystal quantity or solid fat content (SFC). This study highlighted the crucial roles of fat crystal size and polymorphic form in regulating the digestion behavior of lipid-based O/W emulsions.

Directed coevolution of beta-carotene ketolase and hydroxylase and its application in temperature-regulated biosynthesis of astaxanthin

Zhou, P., *et al., J. Agric. Food Chem. 67*: 1072–1080, 2019, https://doi.org/10.1021/acs.jafc.8b05003.

Because it is an outstanding antioxidant with wide applications, biotechnological production of astaxanthin has attracted increasing research interest. However, the astaxanthin titer achieved to date is still rather low, attributed to the poor efficiency of beta-carotene ketolation and hydroxylation, as well as the adverse effect of astaxanthin accumulation on cell growth. To address these problems, we constructed an efficient astaxanthin-producing *Saccharomyces cerevisiae* strain by combining protein engineering and dynamic metabolic regulation. First, superior mutants of beta-carotene ketolase and beta-carotene hydroxylase were obtained by directed coevolution to accelerate the conversion of beta-carotene to astaxanthin. Subsequently, the Gal4M9-based temperature-responsive regulation system was introduced to separate astaxanthin production from cell growth. Finally, 235 mg/L of (3S,3′S)-astaxanthin was produced by two-stage, high-density fermentation. This study demonstrates the power of combining directed coevolution and temperature-responsive regulation in astaxanthin biosynthesis and may provide methodological reference for biotechnological production of other value-added chemicals.

Unraveling of the fishy off-flavor in steam-treated rapeseed oil using the sensomics concept

Matheis, K. and M. Granvogl, *J. Agric. Food Chem. 67*: 1484–1494, 2019, https://doi.org/10.1021/acs.jafc.8b05723.

The sensomics concept was applied to two steam-treated rapeseed oils, one eliciting a fishy off-flavor (OF) and the other the desired aroma attributes (PC = positive control). After screening the most important odorants via comparative aroma extract dilution analysis, identification experiments and quantitation via stable isotope dilution analysis (SIDA) using gas chromatography–mass spectrometry (GC-MS) were performed. Only five compounds differed in their concentrations by a factor ≥5. In addition, trimethylamine with an intense fishy odor quality and first overlooked by gas chromatography-olfactometry, was only present in OF and finally characterized via ion exchange chromatography and solid phase microextraction GC-MS. For data validation, recombination experiments were performed using all odorants with OAVs ≥ 1, and excellent accordance between GS and OF and their corresponding recombinates was achieved, confirming a correct characterization of all key odorants with trimethylamine as the only odorant responsible for the fishy off-flavor.

Vitamin E encapsulation within oil-in-water emulsions: impact of emulsifier type on physicochemical stability and bioaccessibility

Lv, S., *et al., J. Agric. Food Chem. 67*: 1521–1529, 2019, https://doi.org/ 10.1021/acs.jafc.8b06347.

The influence of plant-based (gum arabic and quillaja saponin) and animal-based (whey protein isolate, WPI) emulsifiers on the production and stability of vitamin E-fortified emulsions was investigated. Their impact on lipid digestibility and vitamin bioaccessibility was also studied utilizing an *in vitro* gastrointestinal tract. WPI and saponin produced smaller emulsions than gum arabic. All emulsions had good storage stability at room temperature (4 weeks, pH 7). Saponin- and gum arabic-emulsions were resistant to droplet aggregation from pH 2 to 8 because these emulsifiers generated strong electrosteric repulsion. WPI-coated droplets

flocculated around pH 5 due to a reduction in charge near their isoelectric point. Lipid digestion was slower in saponin-emulsions, presumably because the high surface activity of saponins inhibited their removal by bile acids and lipase. Vitamin bioaccessibility was higher in WPI- than in saponin- or gum arabic-emulsions. This information may facilitate the design of more efficacious vitamin-fortified delivery systems.

Dietary lycopene powder improves meat oxidative stability in Hu lambs

Xu, C., *et al.*, *J. Sci. Food Ag. 99*: 1145–1152, 2019, https://doi.org/10.1002/jsfa.9282.

The aim of this study was to evaluate the effect of dietary lycopene powder on meat quality and the oxidative stability of lipid and protein of longissimus thoracis (LT) in lamb. A total of 30 male lambs were randomly sampled from three feeding groups (control without lycopene supplement, 200 and 400 mg kg–1 lycopene powder respectively) after 3 months of feeding. The muscle samples were taken after slaughter and stored at 4°C for 7 days. Compared with the control, the results showed that supplementation with lycopene powder gave a higher a* value (redness), and increased the levels of vitamin A and vitamin E. Increasing dietary lycopene powder resulted in a lower degree of lipid and protein oxidation, as evidenced by lower contents of thiobarbituric acid-reactive substance and carbonyl compounds, and higher levels of sulfhydryl groups. Dietary lycopene powder is an effective antioxidant that blocks the oxidation of meat proteins and lipids, and has a positive effect on increasing lamb meat quality during storage.

The effects of different frying oils on the formation of heterocyclic aromatic amines in meatballs and the changes in fatty acid compositions of meatballs and frying oils

Ekiz, E. and F. Oz, *J. Sci. Food Ag. 99*: 1509–1518, 2019, https://doi.org/10.1002/jsfa.9325.

The effects of different frying oils (sunflower, hazelnut, canola, commercially mixed, corn, riviera olive, and natural extra virgin olive) on the formation of heterocyclic aromatic amines (HCAs) in meatballs, and the changes in fatty acid composition of meatballs and frying oils before and after deep-fat frying, were determined. Frying oils had a very significant effect ($P < 0.01$) on fatty acid composition and the total HCA content of meatballs. It was determined, in meat, intermuscular fat, meatballs, and all of the different frying oils, that the most common saturated fatty acids (SFAs) were palmitic acid and stearic acid, the most common monounsaturated fatty acid (MUFA) was oleic acid, and the most common polyunsaturated fatty acid (PUFA) was linoleic acid. Only 2-amino-3,8-dimethylimidazo[4,5-f]quinoxaline (MeIQx) was detected in deep-fat fried meatballs, whereas other HCAs (2-amino-3-methylimidazo[4,5-f]quinoxaline (IQx), 2-amino-3-methylimidazo[4,5-f]quinoline (IQ), 2-amino-3,4-dimethylimidazo[4,5-f]quinoline (MeIQ), 2-amino-3,7,8-trimethylimidazo[4,5-f]quinoxaline (7,8-DiMeIQx), 2-amino-3,4,8-trimethylimidazo[4,5-f]quinoxaline (4,8-DiMeIQx), 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP), 2-amino-9H-pyrido[2,3-b]indole (AαC) and 2-amino-3-methyl-9H-pyrido[2,3-b]indole (MeAαC)) could not be detected. The total amount of HCAs in the meatballs ranged between 30.43 and 43.71 ng g–1. The results of the present study showed that MeIQx could be formed in deep-fat fried meatballs with different frying oils. The lowest MeIQx content was found in meatballs fried in hazelnut oil and the highest MeIQx content was found in meatballs fried in commercially mixed oil.

Molecular species determination of oligosaccharides and glycoconjugates in soybean lecithin powders

Kang, J., *et al.*, *J. Sci. Food Ag. 99*: 1525–1532, 2019, https://doi.org/10.1002/jsfa.9328.

Oligosaccharides and glycoconjugates in soybean lecithin powder are very important for the properties and functions of the materials that contain it. Oligosaccharides can trigger infusion reactions and color changes in soybean lecithin during medical injections; glycoconjugates in the form of glycolipids can also change the physical behavior of lecithin. The molecular components of oligosaccharides and glycoconjugates in soybean lecithin powder were studied in this paper. Three oligosaccharides and 21 glycoconjugates were verified in soybean lecithin powders for the first time. Raffinose, sucrose, and stachyose were detected as the principal components of oligosaccharides by high-performance liquid chromatography (HPLC). Twenty-one glycoconjugates, including four steryl glucosides (SG), 13 acyl steryl glucosides

(ASG), one digalactosyl diacylglycerol (DGDG), one monogalactosyl diacylglyceride (MGDG), one glucocerebroside (Glucer), and one glucose palmitate were analyzed by gas chromatography (GC), gas chromatography–mass spectrometry (GC-MS) and RP-UPLC-Q-TOF-ESI-MS. Glycoconjugates were constructed in soybean lecithin powder after separation by column chromatography, thin-layer chromatography, and color reactions. The determination of molecular species of oligosaccharides and glycoconjugates provided a new direction for the exploration of novel functions and uses of soybean lecithin powder.

Lutein is four times more stable in sunflower oil than olive oil at 40°C

Sattar, Z., *et al.*, *Eur. J. Lipid Sci. Technol.121*: 1800126, 2019, https://doi.org/10.1002/ejlt.201800126.

The thermal degradation of lutein is investigated in refined sunflower and olive oils at a selected temperature (40°C) for 3 months. All experiments are performed with lutein (6 mg ml–1) that is obtained from marigold flowers. Samples of the pigment in oil are incubated at 40°C for up to 3 months and each month, the amount of lutein is monitored by a spectrophotometric method. A kinetic analysis of the data shows that thermal degradation is in accordance with the first-order kinetics. The k values of lutein degradation in sunflower oil and olive oil are estimated to be 44 × 10−4 and 186 × 10−4, respectively. In the presence of vitamin E (15 mg ml–1), the k values are decreased and reach 24 × 10−4 and 72 × 10−4 in sunflower and olive oils, respectively. These results suggest that lutein is approximately four times more stable in sunflower oil than olive oil.

A new statistical approach to describe the quality of extra virgin olive oils using near infrared spectroscopy (NIR) and traditional analytical parameters

Willenberg, I., *et al.*, *Eur. J. Lipid Sci. Technol*. 121: 1800361, 2019, https://doi.org/10.1002/ejlt.201800361.

NIR prediction models are developed for the determination of relevant parameters to evaluate olive oil quality such as acidity (FFA), peroxide value (PV), UV-absorption at 232 and at 268/270 nm, p-anisidine value (AnV), isomeric diacylglycerols (DG), and pyropheophytin A (PPP). In addition, a new NIR method to estimate the age of olive oil is presented. The relevant wavenumbers are given for the calculation of the parameters and the precision data are presented in comparison to the chemical reference methods. The calibration and validation of the methods are executed with independent data sets (test in test instead of cross-validation) to cover the wide range of variability of the analytical parameters including the corresponding accurate analytical results from the reference chemical methods. The correctness and accuracy of the developed NIR methods are verified by analyzing certified materials. Finally, a simple statistical approach has been developed to describe the quality of olive oils using the parameters FFA, PV, K232 and K270, DG and PPP. The probability of presence of a sensory defect (100% ≙ 1; 0% ≙ 0) is calculated using the following equation: Pred (BIN) = 1/(1 + exp(−(−9 + 37 × FFA-0.9 × PV -2.9 × K232 + 14 × K270 + 3.7 × PPP-0.17 × DG))).

Refining process for production of refined palm-pressed fiber oil

Sulihatimarsyila, A.W.N., *et al.*, *Ind. Crop. Prod. 129*: 488–494, 2019, https://doi.org/10.1016/j.indcrop.2018.12.034.

Palm-pressed fiber oil (PPFO) is rich in natural phytonutrients such as carotenes and tocotrienols (vitamin E), which makes it worth further development to enhance its quality. Crude PPFO is currently extracted using solvents without further refining. This study aimed to refine crude PPFO using a combination of processes including degumming, bleaching, and deacidification. Various doses of hot distilled water at 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 v/v% were applied during water degumming to remove soluble and hydratable gummy materials in crude PPFO. Degumming with acids at doses ranging from 0.1 to 1.0 wt% were tested to obtain oil with low phosphorus content. Bleaching earth doses ranging from 0.1 to 1.0 wt% were used to absorb trace metals and other impurities. The bleached PPFO was subjected to deacidification to remove free fatty acid (FFA). The optimum refining conditions were using 5.0 v/v% of hot distilled water at 90 °C for 20 min for water degumming, 1.0 wt% of phosphoric acid at 90 °C for 10 min for acid degumming, 0.1 wt% of natural bleaching earth at 105 °C for 15 min during bleaching, and deacidification at 110 °C at 0.1 mtorr. The refined PPFO (RPPFO) showed a 98% reduction of phosphorus content (from 565 ppm to 13±2 ppm) and FFA removal of 97% (from 5.94% to 0.15%), while deterioration of bleachability index (DOBI) increased by 44% (from 1.99 to 2.87±0.17). In addition, RPPFO was rich in carotenoids (1208±23 ppm) and vitamin E (904±8 ppm) that can be developed into high value products. The RPPFO meets the quality specifications of refined, bleached, and deodorised palm oil (RBDPO) while maintaining the heat-sensitive phytonutrients.

Effects of beta-cyclodextrin on the enzymatic hydrolysis of hemp seed oil by lipase *Candida* sp.99–125

Wang, P., *et al.*, *Ind. Crop. Prod.129*: 688–693, 2019, https://doi.org/10.1016/j.indcrop.2018.11.046.

To enhance the stability of lipases, the additive method is attractive because of its high efficiency and simplicity, of which beta-cyclodextrin (β-CD), as an additive has attracted attention. In the present study, the effects of β-CD on enzymatic hydrolysis of hemp seed oil by lipases were investigated. The stability, spectroscopy, and reusability of Candida sp.99–125 were compared by the addition of β-CD, respectively. The results showed that Candida sp.99–125 could produce the highest yield of α-linolenic acid (ALA, 18.27%, w/w) in the presence of β-CD after 24h, and the thermal stability of lipase was also improved. The UV spectroscopy showed that the absorbance of lipase decreased with increasing concentrations of β-CD and the fluorescence result was similar. Moreover, the reusability of lipase with β-CD was better than free


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lipase. This study revealed that β-CD could increase hydrolysis activity and stability of the lipase, thereby improving the hydrolytic process of hemp seed oil by Candida sp.99–125.

Production of omega-3-rich oils from underutilized chia seeds. Comparison between supercritical fluid and pressurized liquid extraction methods

Villanueva-Bermejo, D., *et al.*, *Food Res. Int. 115*: 400–407, 2019, https://doi.org/10.1016/j.foodres.2018.10.085.

Chia seeds constitute a promising source of alpha-linolenic acid (ALA). An underutilized and cheaper set of chia seeds which were discarded after the harvest according to quality criteria—named in this article as low oil content seeds (LOCS)—were evaluated as a potential source for obtaining PUFA-enriched oils against the commonly studied high-quality chia seeds denoted as high-oil-content seeds (HOCS) in this study. Two efficient and environmental friendly techniques, supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE), were evaluated to optimize the extraction process of chia oil. At 60°C, by using pressurized food-grade ethanol, recoveries close to 100% were achieved from both sets of seeds in a short extraction time (10 min). By using SFE, the greatest oil extraction yield (> 95%) was attained at the highest pressure and temperature conditions (45 MPa and 60°C) after 240 min. At the early stage of SFE extraction, both LOCS and HOCS exhibited a similar kinetic behavior, reaching oil extraction rates of 0.59 g oil/min and 0.64 g oil/min, respectively. No differences were found between the fatty acid profile of the oils extracted from LOCS and HOCS both by PLE and SFE. ALA and linoleic acid (LA) concentrations ranged between 65–68% and 17–23% respectively, and a predominance of high molecular weight triglycerides (≥ CN50), was found in all extracted oils. In conclusion, LOCS might constitute a new suitable raw material for the production of ALA-enriched oils. Concerning the extraction methods assayed, the oil was almost entirely recovered by both PLE and SFE at the used conditions.

Comparative study of different extraction processes for hemp (*Cannabis sativa*) seed oil considering physical, chemical, and industrial-scale economic aspects

Devi, V. and S. Khanam, *J. Cleaner Prod. 207*: 645–657, 2019, https://doi.org/10.1016/j.jclepro.2018.10.036.

Hemp (*Cannabis sativa*) seed oil is a rare source of nourishment for vegetarian diets due to the unique ratio of u-6/u-3 fatty acid as 3:1. It is beneficial for cardiovascular health, skin, hormonal balance, diabetes, and so on. These oil benefits encourage optimization of the quantity and quality of the extraction process. Among the various extraction processes that can be used, such as supercritical fluid extraction, Soxhlet, percolation, ultrasonication, pyrolysis, pretreatment processes etc., none is superior in every respect. The study described in this article compared the industrial-scale economics, extraction yield, oil compositions, and physicochemical properties using different extraction processes. Central composite design was employed to optimize the parameters of supercritical fluid extraction and ultrasonication processes. Quadratic models ($P < 0.05$) for both processes were developed with satisfactory R2 (>0.93). A maximum yield of 37.30% was estimated through an ultrasonication-treated Soxhlet process. Gas chromatography-mass spectrometry demonstrated that Soxhlet offers the optimal u-6/u-3 ratio. Further, gas chromatography-mass spectrometry of hemp bio-oil obtained through pyrolysis identified volatile and flammable materials to assure its suitability as a bio-fuel. Economic analyses for different processes revealed supercritical fluid extraction as the most beneficial followed by Soxhlet, ultrasonication, ultrasonication treated Soxhlet, and Soxhlet treated ultrasonication.

Hemp (*Cannabis sativa L.*) seed oil extraction with pressurized n-propane and supercritical carbon dioxide

Grijó, D.R., *et al.*, *J. Supercrit. Fluid 143*: 268–274, 2019, https://doi.org/10.1016/j.supflu.2018.09.004.

Hemp (*Cannabis sativa L.*) seeds are composed of a high oil content rich in polyunsaturated fatty acids and antioxidants such as tocopherols and carotenes, resulting in an interesting nutritional aspect. Oil from hemp seeds extracted using supercritical carbon dioxide ($scCO_2$) as the solvent preserves the qualities described above. However, the high operating pressures and the low solubility of the oil in $scCO_2$ significantly increase operating costs. Generally, the use of pressurized n-propane as a solvent for extraction of vegetable oils is an alternative to overcome these challenges without changing their nutritional qualities. The main objective of this work was to study the extraction of the oil from dehulled hemp seeds using $scCO_2$, pressurized n-propane and organic solvents at atmospheric conditions, to compare some physicochemical properties of the extracts. The extraction conditions using $scCO_2$ as the solvent were 40 and 60°C, and 30 and 40 MPa. These operating conditions of extraction are similar to those available in the literature. For pressurized n-propane used as a solvent, temperatures of 40, 50 and 60 °C, and pressures of 6, 8 and 10 MPa were used. The values of the extraction pressures with n-propane were defined from the knowledge of the phase behavior measured for the system n-propane/hemp seed oil. The values of the mass percentage yields were similar for both pressurized solvents. However, the solubility of the oil in n-propane was higher than in $scCO_2$. The kinetics of the extractions were satisfactory using Sovová modeling.

Influence of molecular distillation on antioxidant and antimicrobial activities of rose essential oils

Yi, F., *et al.*, *LWT–Food Sci. Technol.102*: 310–316, 2019, https://doi.org/10.1016/j.lwt.2018.12.051.

Chemical compositions and antioxidant and antimicrobial activities of the essential oils (REOs) of roses, including *Rosa damascene* (RD), *Rosa centifolia* (RC), *Rosa pomponia* (RP) and *Rosa chinensis* Jacq "Crimson Glory" H. T. (CG), and their fractions obtained through molecular distillation (MD) were investigated. The major constitutes were: beta-citronellol and nonadecane in RDEO, RCEO, and RPEO; 1-nonadecene and nonadecane in CGEO. After MD, a larger proportion of more volatile compounds existed in the distillates relative to their original oils and residues. The REOs and fractions exhibited not only moderate antioxidant activities in the 1,1-diphenyl-2-picrylhydrazyl (DPPH), 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) and reducing power assays, but also showed obvious broad-spectrum antimicrobial activities towards the seven tested microorganisms. Notably, the higher antioxidant and antimicrobial activities were observed for the distillates of RDEO, RCEO and RPEO. Moreover, the active antioxidant constitutes in the REOs were characterized as eugenol and methyl eugenol, and the potential antimicrobial components were linalool, phenethyl alcohol, beta-citronellol, geraniol, eugenol, and methyl eugenol. Results demonstrated that MD could be used to obtain fractions from REOs with higher antioxidant and antimicrobial activities, and the distillates of RDEO, RCEO, and RPEO have potential to act as novel natural antioxidant and antimicrobial agents.

Effects of tocopherol, rosemary essential oil and *Ferulago angulata* extract on oxidative stability of mayonnaise during its shelf life: a comparative study

Alizadeh, L., *et al.*, *Food Chem. 285*: 46–52, 2019, https://doi.org/10.1016/j.foodchem.2019.01.028.

The purpose of this study was to investigate the effects of tocopherol, rosemary essential oil, and ferulago on the oxidative stability of mayonnaise during storage. Their efficacy was also compared with tertiary butylhydroquinone (TBHQ) and a control group. During the primary oxidation stage, tocopherol was more efficient than TBHQ, while in the secondary oxidation stage it was the same as other antioxidants. At end of storage, samples with added rosemary essential oil and ferulago extract showed peroxide values (2.29 and 2.80 meq O2/kg oil), anisidine values (11.83 and 12.23), and hexanal and heptanal concentrations (510.2, 589.9 and 76.6, 75.2 ng/g), respectively. All values were meaningfully less than those of the control sample (10.44 meq O2/kg, 18.32, 1339.8 ng/g, and 225.5 ng/g, respectively). Based on the overall results, tocopherol and rosemary essential oil can be recommended as replacement for TBHQ. However, further evaluation needs to be performed on the organoleptic properties of Ferulago extract.

Medical/Pharmaceutical Applications

Identification of the first synthetic allosteric modulator of the CB2 receptors and evidence of its efficacy for neuropathic pain relief

Gado, F., *et al.*, *J. Med. Chem. 62*: 276–287, 2019, https://doi.org/10.1021/acs.jmedchem.8b00368.

The development of an allosteric modulator for CB2R may lead to an alternative therapeutic route that modulates pain and other CBR indications. It may also help to ease pressure on using cannabis and cannabis-derived CBR modulators for modulation of pain endpoints.

The direct activation of cannabinoid receptors (CBRs) results in several beneficial effects; therefore several CBRs ligands have been synthesized and tested *in vitro* and *in vivo*. However, none of them reached an advanced phase of clinical development due mainly to side effects on the CNS. Medicinal chemistry approaches are now engaged to develop allosteric modulators that might offer a novel therapeutic approach to achieve potential therapeutic benefits avoiding inherent side effects of orthosteric ligands. Here we identify the first ever synthesized positive allosteric modulator (PAM) that targets CB2Rs. The evidence for this was obtained using [3H]CP55940 and [35S]GTPγS binding assays. This finding will be useful for the characterization of allosteric binding site(s) on CB2Rs which will be essential for the further development of CB2R allosteric modulators. Moreover, the new CB2R PAM displayed antinociceptive activity *in vivo* in an experimental mouse model of neuropathic pain, raising the possibility that it might be a good candidate for clinical development.

Efficient semi-synthesis of natural delta-(R)-tocotrienols from a renewable vegetal source

Ville, A., *et al.*, *J. Nat. Prod. 82*: 51–58, 2019, https://doi.org/10.1021/acs.jnatprod.8b00517.

The importance of using delta tocotrienol in combination with three other naturally occurring isomers is well-documented. Each of these isomers plays an important and discreet role in human physiology. The discovery and synthetic manipulation of these compounds at terminal carbon may lead to a differentiated biological profile which may be completely different from that of parent compounds. One such example has already been observed during the high- throughput screening of naturals (data not reported). Recent studies have highlighted the biological potential of tocotrienols, a vitamin E subfamily. The major natural sources of tocotrienols are complex mixtures requiring particularly challenging purification processes. The present study describes efficient semi-synthetic strategies toward relevant delta-(R)-tocotrienol derivatives, using as a starting material delta-(R)-garcinoic acid,

the major vitamin E derivative isolated from *Garcinia kola* nuts, a renewable vegetal source.

Physicochemical properties and phenolic content of honey from different floral origins and from rural versus urban landscapes

Kavanagh, S., *et al., Food Chem*. 272: 66–75, 2019, https://doi.org/10.1016/j.foodchem.2018.08.035

It is well known that quality, chemical composition, and biological profiles of natural products grown and produced in different environments exhibit differences. The next two abstracts provide data documenting that the quality and biological profile of honey is a function of the source of the natural diversity bees are surrounded with. Hence, traceability of the source and origin of natural products is important in a global supply chain.

The composition of honey influences how beneficial it is to human health. This study evaluated the physiochemical properties and total phenolic content (TPC) of single vs. multi-floral Irish and selected international honeys, and whether properties varied according to hive location. Oilseed rape honey had the lowest TPC of Irish unifloral honeys. Heather honey had the highest TPC, similar to manuka honey (Mean ± SD = 68.16 ± 2.73 and 62.43 ± 10.03 respectively), and the TPC of ivy honey was approximately half that of heather. Urban multi-floral honeys contained higher TPC (28.26 ± 13.63) than rural honeys (20.32 ± 11.54). Physiochemical properties varied according to floral origin, and whether hives were in urban or rural sites. Irish heather honey had similar physiochemical characteristics to manuka honey. This first examination of Irish honey confirms that TPC and physiochemical properties vary with honey type and hive location, and suggests that Irish heather honey should be examined for potential health benefits.

Bioactive components and antioxidant and antibacterial activities of different varieties of honey: a screening prior to clinical application

Combarros-Fuertes, P., *et al., J. Agric. Food Chem*. 67: 688–698, 2019, https://doi.org/10.1021/acs.jafc.8b05436.

This study assessed 16 different honey samples in order to select the best one for therapeutic purposes. First, a study of honey's main bioactive compounds was carried out. Then phenolic profiles were determined and specific compounds quantified using a HPLC system coupled to a mass spectrometer. Then, antioxidant activity, by three *in vitro* methods, and antibacterial activity against reference strains and clinical isolates were evaluated. Great variability among samples was observed regarding ascorbic acid (between 0.34 ± 0.00 and 75.8 ± 0.41 mg/100 g honey; $p < 0.001$), total phenolic compounds (between 23.1 ± 0.83 and 158 ± 5.37 mg/100 g honey; $p < 0.001$), and total flavonoid contents (between 1.65 ± 0.11 and 5.93 ± 0.21 mg/100 g honey; $p < 0.001$). Forty-nine different phenolic compounds were detected, but only 46 of them were quantified by HPLC. The concentration of phenolic compounds and the phenolic profiles varied widely among samples (between 1.06 ± 0.04 and 18.6 ± 0.73 mg/100 g honey; $p < 0.001$). Antioxidant activity also varied significantly among the samples. All honey varieties exhibited antibacterial activity against both reference and clinical strains (effective concentrations ranged between 0.05 and 0.40 g/mL depending on the honey sample and bacteria tested). Overall, samples with better combinations of bioactive properties were avocado and chestnut honeys.

Mannan oligosaccharide protects against the aflatoxin-B1-promoted influenza replication and tissue damages in a toll-like-receptor-4-dependent manner

Sun, Y., et al., *J. Agric. Food Chem*. 67: 735–745, https://doi.org/10.1021/acs.jafc.8b05829.

MOS are naturally expressed mannose polymers secreted by yeast. Availability of the composition and its effects against influenza virus replication is interesting to explore through proper clinical studies. Upon clinical confirmation, the polymeric materials can be incorporated in the food applications for protection against influenza viruses.

Our previous study reported that aflatoxin B1 (AFB1) promoted influenza replication. Mannan oligosaccharide (MOS), derived from the cell walls of yeast, is a potent immunomodulator. Here, we investigated the role of MOS in AFB1-promoted influenza replication and further explored the underlying mechanisms. In vitro and in vivo, the exposure to AFB1 alone resulted in significantly decreased weight gain and increased viral replication as well as lung and spleen damages. Increased influenza replication coupled with increases in toll-like receptor 4 (TLR4), phosphorylated nuclear factor κB, and tumor necrosis factor alpha (TNF-α) levels. However, MOS given in conjunction with exposure to AFB1 significantly reversed these above changes. A further study indicated that MOS activity was abolished by TLR4 knockout or TLR4 overexpression. Surprisingly, TNF-α played no role in the MOS-mediated protective effects. Collectively, our data suggest that MOS alleviates the AFB1-promoted influenza replication, inflammation, and tissue damages in a TLR4-dependent manner.

Dietary fructooligosaccharide and glucomannan alter gut microbiota and improve bone metabolism in senescence-accelerated mouse

Tanabe, K., *et al., J. Agric. Food Chem*. 67: 867–874, 2019, https://doi.org/10.1021/acs.jafc.8b05164.

This study helps explain the traditional use of fiber for gut health and also may provide a firm basis to develop new dietary fibers with higher potency.

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Gut microbiota improved using prebiotics may delay the onset of senescence-related health problems. We hypothesized that prolonged intake of prebiotics delays senile osteoporosis. Forty-five male senescence-accelerated mouse prone 6 (SAMP6) aged four weeks were raised on 5% fructooligosaccharide (FOS), 5% glucomannan (GM), or a control diet for 31 weeks. Gut microbiota were identified using culture-dependent analytical methods. Mineral content in femoral bone was analyzed using atomic absorption spectrophotometry. Bone metabolism and inflammatory markers were measured using enzyme-linked immunosorbent assay. The numbers of *Lactobacillus* and *Bacteroides* in cecal contents were significantly higher in the FOS than in the control group ($p < 0.05$); the number of *Clostridium* was significantly higher in the GM than in the control group ($p < 0.05$). Calcium content was significantly higher in the femoral bones of the FOS group (30.5 ± 0.8 mg) than in the control group (27.5 ± 1.5 mg) ($p < 0.05$). There was no difference between the GM (29.1 ± 2.0 mg) and control groups. During senescence, urinary deoxypyridinoline and serum high-sensitivity C-reactive protein levels significantly decreased in the FOS (1.2 ± 0.2 nmol/3 d and 80 ± 6.1 ng/100 mL) and GM groups (1.2 ± 0.2 nmol/3 d and 80 ± 6.1 ng/100 mL) compared with the control group (1.8 ± 0.5 nmol/3 d and 93 ± 7.4 ng/100 mL) ($p < 0.05$). Thus, dietary FOS and GM modified gut microbiota and reduced bone resorption by reducing systemic inflammation in SAMP6.

Antimicrobial and antioxidant activities of phenolic metabolites from flavonoid-producing yeast: potential as natural food preservatives

Ng, K.R., *et al*., *Food Chem*. *270*: 123–129, 2019, https://doi.org/10.1016/j.foodchem.2018.07.077.

Microbial metabolites may play a larger-than-expected role in the development of a safe, robust, effective, and environmentally friendly natural preservative system.

We analyzed the antimicrobial and antioxidant activities of phenolic metabolites secreted from a naringenin-producing *Saccharomyces cerevisiae* strain (a GRAS organism), against the pure flavonoid naringenin and its prenylated derivatives, to assess their potential as natural food preservatives. Agar disc diffusion assay was used to analyze the antimicrobial activity against *Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 29213, while DMPD chemiluminescence assay was used to analyze antioxidant activity, based on DMPD+-scavenging activity. Our results showed that the engineered yeast metabolites exhibited both strong antimicrobial and DMPD+-scavenging activity, particularly the metabolite phenylacetaldehyde. Pure naringenin had poor antimicrobial and DMPD+-scavenging effects. Prenylated varieties, 6-prenylnaringenin and 8-prenylnaringenin, inhibited only S. aureus, while only 8-prenylnaringenin exhibited moderate DMPD+-scavenging activity. Our results suggested that phenolic metabolites secreted from naringenin-producing yeast would be a sustainable source of natural food preservatives.

An insight into the health benefits of fermented soy products

Jayachandran, M. and B. Xu, *Food Chem*. *271*: 362–371, 2019, https://doi.org/10.1016/j.foodchem.2018.07.158.

The current review was aimed to summarize the nutritional values and various health benefits of fermented soy products. Several previous researches proved that soy products rich in protein can reduce the serum concentrations of total cholesterol, low-density lipoproteins (LDLs), and triglycerides if consumed instead of animal protein. Apart from these lipid-lowering effects, fermented soy products also proved to be effective in attenuating the effects of diabetes mellitus, blood pressure, cardiac disorders and cancer-related issues. The nutritional value of the fermented soy products gains much attention due to its increased levels compared to the non-fermented ones. The origin, compositions, nutritional values of different fermented soy products and health-promoting benefits of fermented soy products were systematically reviewed. Hence the in-depth analysis of the various research findings on fermented soy products, beneficial activities may help the future researchers to derive a conclusion on its beneficial effects on health.

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