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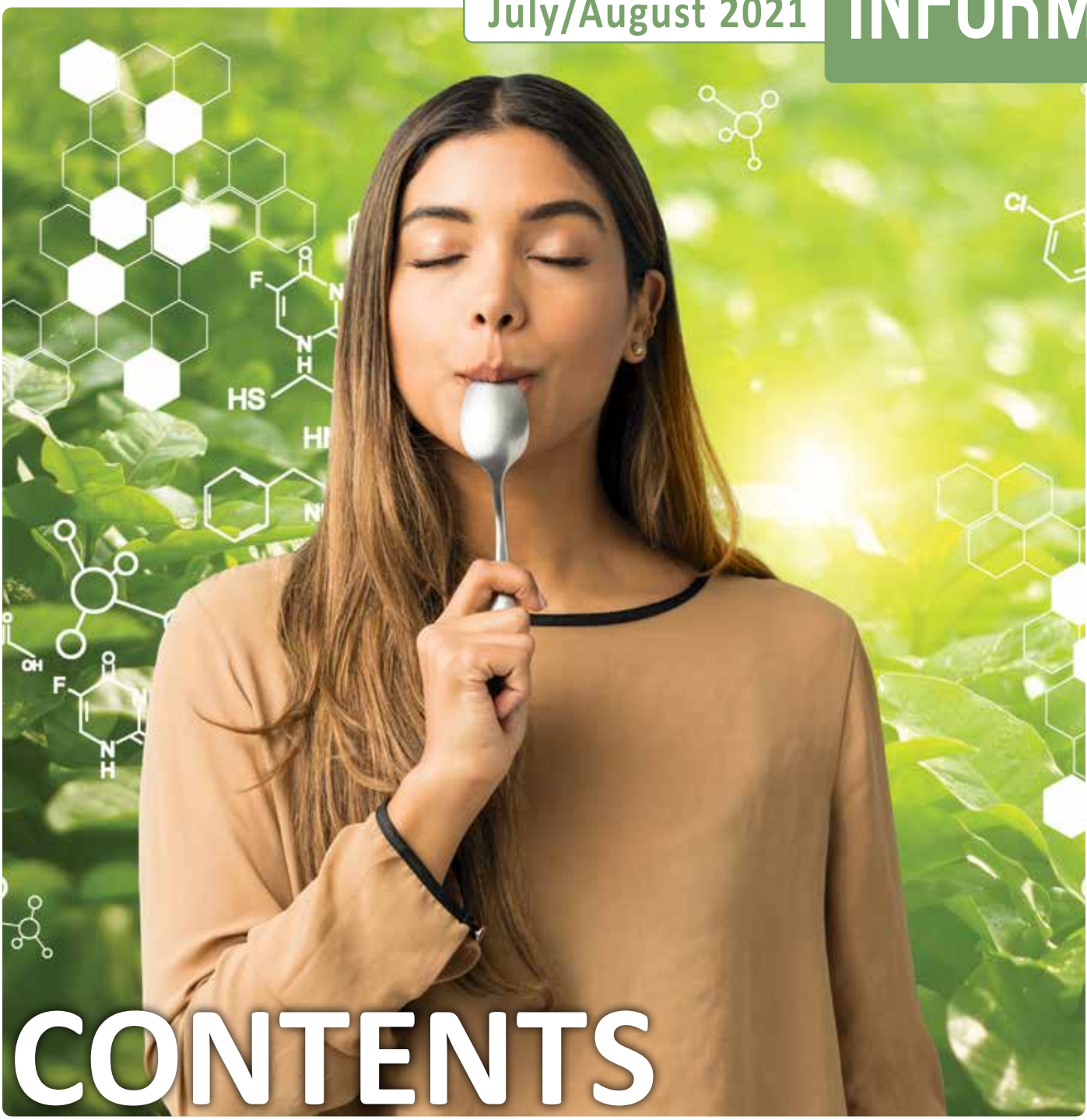

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Can computers make better plant-based foods?

Rebecca Guenard

Until recently, drug development meant addressing the mechanics of a disease. Cancer treatments, for example, were primarily geared toward slowing the rapid division of tumor cells. With the establishment of high-throughput analysis, researchers began approaching drug discovery differently. They turned to producing large volumes of complex and diverse data sets to identify drug targets within individual genes.

- **Instead of replacing the protein source in a formulation and then masking the off-flavors of plant-based ingredients, companies are determining what fundamentally makes a product taste good.**
- **These companies are collecting vast amounts of data on everything from subjective human responses to precise analytical measurements.**
- **They plan to implement statistical modeling and machine learning to determine how to formulate great tasting plant-based foods.**

As they gathered more genetic data, researchers improved statistical models to predict the location of genome mutations and worked out how to synthesize molecular remedies to correct those errors. They wrote algorithms to train computers how to make such predictions faster. Then they gathered more data to fine-tune their algorithms. Data science is now a core discipline in pharmaceutical research, and food companies are beginning to adapt this approach to their industry, particularly in solving the problem of off-flavors in plant-based foods (Fig 1).

"There is a rational development process to determine what works and what does not to get us closer to our goal," says Rick Gerkin, associate professor at the University of Arizona in Tempe. "Our goal is ultimately making something that is appealing to a consumer, is healthy, and is made from plants."

Gerkin collaborates with a Berkeley, California start-up called Climax Foods that is using data science to guide the formulation of plant-based creations for seven of the most popular dairy cheeses. The company is collecting data along every step of their cheese production process and comparing it with the sensory perceptions of tasters who comment on the final product. As their data sets grow, they will use them to build statistical models for the formulation of the ideal plant-based cheese that mimics the taste, texture, and nutrition of a dairy cheese. "There is a list of things that are unavailable to us when making a plant-based, all natural product," says Gerkin. "Under those constraints we have to find new formulations."

FINDING THE RIGHT PROTEIN

Boston-based food ingredient company Motif Foodworks is engaged in a similar pursuit. Dilek Uzunalioglu, Motif's head of product applications, says her company is looking for the fundamental factors that make plant-based foods "cravable". Motif is focused on overcoming the off-flavors

and unpleasant textures consumers commonly describe as part of the plant-based food experience. Uzunalioglu says her company is working on a variety of plant-based applications, such as meat and dairy alternatives, but also new forms of plant-based products.

Through collaborations with different experts, Motif is gaining a better understanding of how to select the optimal protein functionality to contribute to specific properties in a finished product. Motif partners with another Boston company called Ginko Bioworks that retrieves genetic information from an extensive library of sequences and uses that information to design new biological products. After screening over 300 proteins in their database, Ginko designs yeast strains that, through fermentation, can make the proteins Motif identifies as potential product ingredients.

This approach helps them select the plant proteins that are best suited for a specific food application and leapfrogs the myriad physical and chemical modifications needed to make some plant proteins more palatable for food applications. "It is really about gathering the insights and then looking for

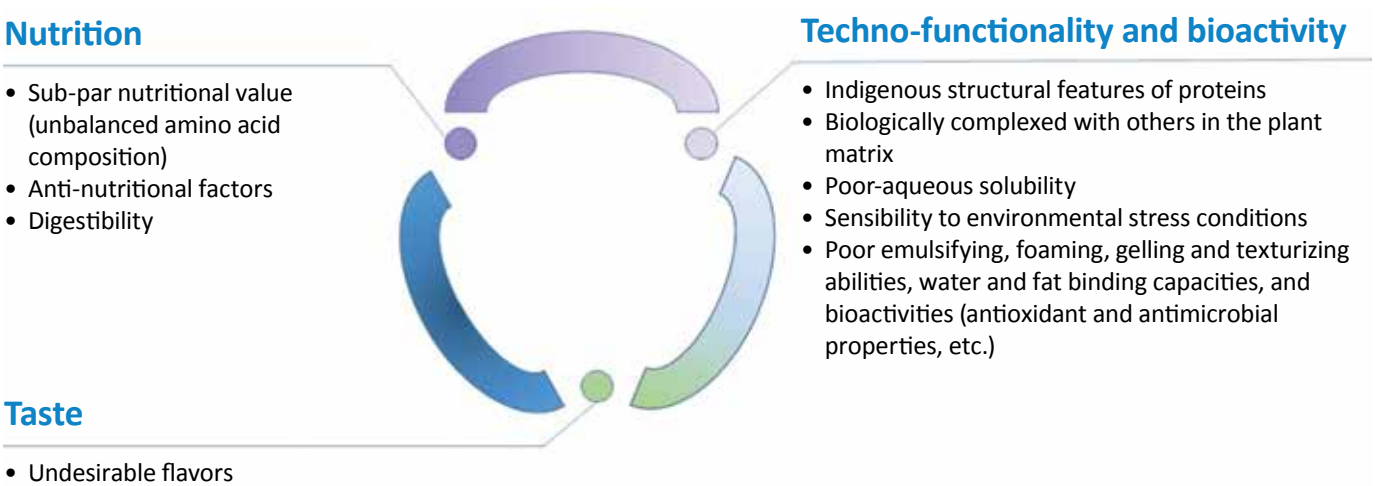

FIG. 1. Challenges facing formulators who use plant-based proteins. Source: Nasradadi, M.N., *et al.*, *Food Hydrocoll.*, *118*, 106789, 2021

gaps where we can design proteins or any other ingredients to remove the gap," says Uzunalioglu. "Scientific biology is one of the tools we use, but it is not the only one." Adding genetic tools to existing analytical techniques, like rheology, helps pinpoint proteins destined to function in food applications while also achieving consumer satisfaction.

Following the drug discovery playbook, Motif is applying high-throughput analysis to characterize a large number of samples at once and screen for the traits that interest them. Automated preparation in multi-well plates followed by simultaneous sample analysis allows pharmaceutical companies to conduct a fast screening of hundreds of potential new product formulations (see *Inform*, March 2020). Drug developers can calculate and optimize experimental conditions, such as buffers, surfactants, sugars, storage temperature, and mechanical stress, much faster using these methods.

Uzunalioglu says, through a collaboration with researchers at the University of Massachusetts, Motif has developed two-gram samples of protein assays for use in high-throughput measurements. The capability allows them to quickly determine the foaming, gelling, and emulsification properties of any protein they produce through fermentation.

The data gathered from these measured properties can then be associated with the traits that consumers describe in a food, such as moistness and chewiness. "For moistness, we measure water holding capacity and oil holding capacity," says Uzunalioglu. "For chewiness, we measure water holding capacity and gelling and foaming, things like that." She says that Motif uses a combination of trained tasters and the general public to gather information on how consumers experience different ingredients.

Motif's strategy of combining their analytical results with consumer satisfaction is indicative of the reality that, ultimately, human perception decides a product's success. Formulators know that fragrances and mouthfeel play a crucial role in perception. Many hope to equate human experience with specific molecules, but measuring perception is complicated.

INTERPRETING SENSORY PERCEPTIONS

Unlike with vision, sound, or touch, which researchers can track from an input to a neurological signal in humans, odor perception is harder to pin down. Instead of proceeding directly to the thalamus like other sensory systems, scent signals first travel to brain regions that process emotions and memory. Smell has a profound impact on how we experience food. For instance, those who lost their sense of smell due to the SARS-CoV-2 virus reported that the taste and texture of food had changed (https://tinyurl.com/3x4p3acj).

One way to improve consumer experience with plant-based foods is to identify the source of unpleasantness and avoid ingredients with a similar molecular structure. But that turns out to be a daunting challenge. Vision operates off of four receptors; scent uses 400. Scientists have not yet deciphered the language our olfactory system uses to decode the estimated trillions of different smells the brain understands. However, they have identified enough correlations between physiochemical features and perception to believe the process is structured and not subjective. Therefore, they continue to search for the fundamental molecular features that combine to create a smell.

Earlier this year, University of California, Riverside researchers were able to increase the number of predictable odorant chemicals perceived by the human olfactory system using computational analysis. Genetics, culture, and lived experience all contribute to a sense of smell, but enough similarities in descriptions of smell for the same chemical exist to imply a common physiochemical basis for their perception among humans. The UC researchers set out to train computers to identify the small group of physiochemical traits that were determined in earlier experiments and, using machine learning, see if the computer could then find other traits.

The team used databases from previous experiments that contained odor character profiles—describing smells such as cooked meat, cooked vegetables, or green vegetables—along with the physiochemical description of the compounds. They wrote algorithms to rank chemical features in terms of their contribution to those descriptors. Then they applied machine-learning models to predict the smell humans were most likely to perceive from specific features.

The group reported that using their statistical models, they were able to extend data from what they referred to as "low-throughput, high-cost human studies" and explore new areas of chemical perception. From a library of 440,000 chemicals, the models were able to predict the descriptions of the

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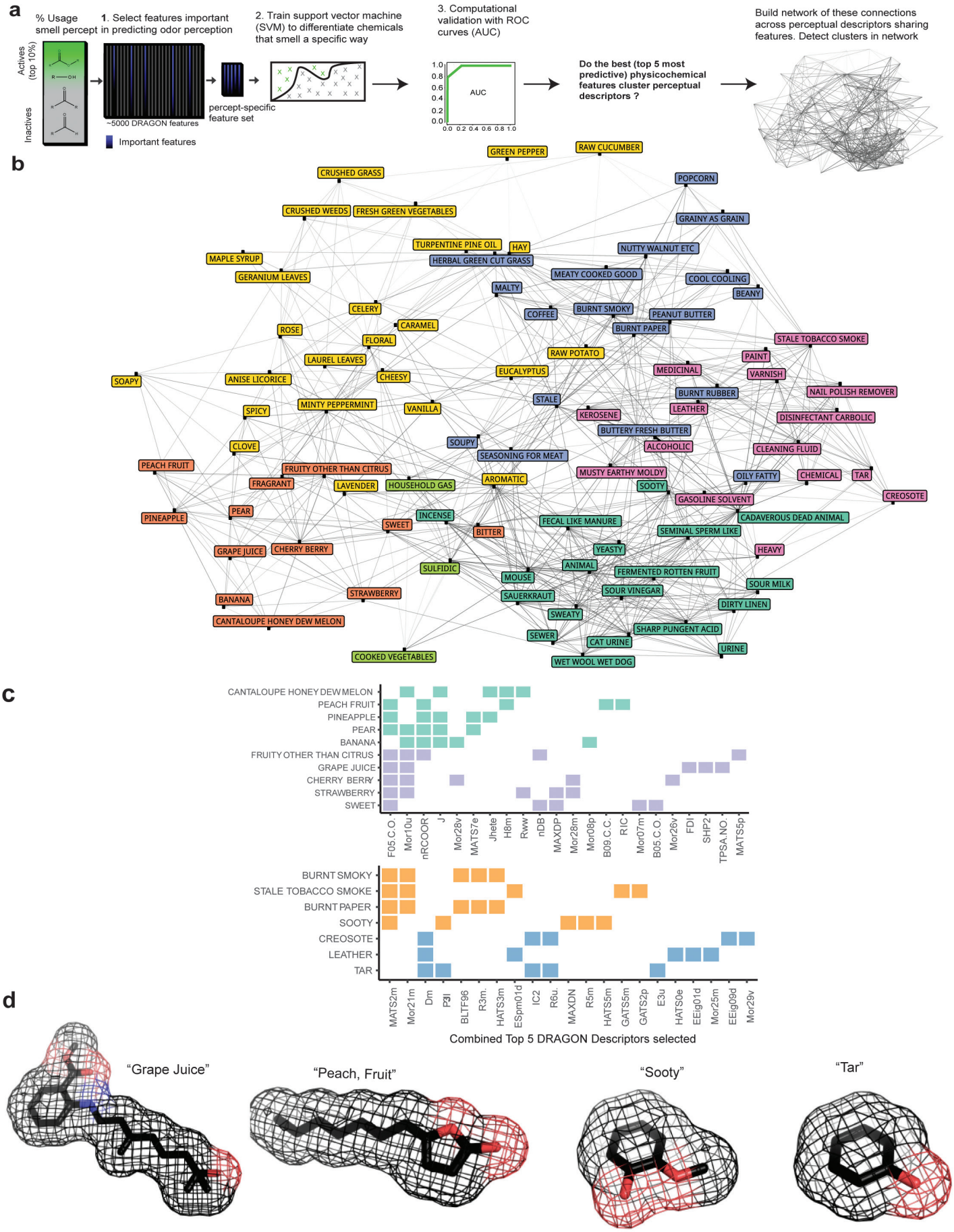

FIG. 2. How to build perceptual descriptor networks for physiochemical features. Source: Kowalewski, J., *et al.*, *Chemical Senses, 46*, 1-13, 2021.

Improving mouthfeel data

Plant-based food manufacturers often want to balance high protein in formulation with low fat and low sugar. Unfortunately, this combination typically leads to a product that consumers describe as chalky or gritty. Over the past decade, researchers have been investigating the components of mouthfeel hoping they might reveal a clue to avoiding unpleasant textures, but a recent review of saliva-protein interaction experiments found more experiments are needed.

The sensory perception and after taste a person experiences when eating is related to saliva's interaction with the food. The bio-lubricant coats mouth surfaces and assists with food processing. Saliva is mostly water, but contains proteins and ionic compounds that influence our perception of texture, especially when interacting with other proteins.

A team of researchers at the University of Leads, Leads, UK, performed what they believe is the first systematic review of protein-saliva studies confirming that these interactions are dominated by electrostatic charges strongly influenced by pH. However, the findings were exclusively for dairy proteins and, according to the researchers, the literature did not yet contain an analysis of plant protein–saliva interaction to predict mouthfeel perception.

Furthermore, the systematic review indicates that the current body of work on protein-saliva interactions is flawed. The review authors suggest that some of the methodology does not reflect a physiologically relevant saliva-to-protein ratio and is, therefore, an inaccurate simulation. In addition, there was a lack of similarity across studies making comparisons difficult. They suggest that in the future, standardization be applied to protein-saliva experiments to improve research quality and enable comparisons.

As data scientists become confident in the application of predictive models, mouthfeel data is likely one of the components they will be interested in incorporating in their statistics. First, they must be certain that data is relevant and reliable.

smells that human participants had given in previous studies. In addition, the researchers introduced 68 million word combinations that describe smells into the model and identified new chemicals that smell like each descriptor (Fig. 2, page 9). This chemical discovery aspect of the research could be lucrative to food and ingredient manufacturers. Machine learning may help unveil previously unknown compounds that remind humans of the smell of freshly cooked meat, for example, even for a meatless product.

MANAGING ALL THE DATA

At the University of Arizona, Gerkin conducts research similar to the work performed by the UC team (though he uses statistical models to interpret neurological activity in response to odor). He has written that the predictive modeling used by the UC team is a valuable way to find new flavor compounds. His collaboration with Climax Foods could signify that the start-up is interested in making such an attempt. However, when asked, Gerkin said, for now the partnership is focused on "trying to figure out what is the very best way to apply the cutting edge of the academic work into industry." That means gathering as much data as possible on the fermentation process of cheese.

"You want to connect the variable that you can control in your process to something you can measure—either by a panel of people evaluating the cheese telling you what they like, or by things you can measure quantitatively," says Gerkin. Like Motif, they are gathering a variety of data from rheology to GCMS and LCMS. He emphasizes the importance of then

knowing what to do with all that data to make it valuable in formulations. Data science is most useful, he says, when you can visualize how all the pieces of information fit together, when you know the uncertainty of all your measurements, and when you can effectively program computers to retrieve valuable predictions from everything you have gathered.

Uzunalioglu says Motif is in the process of data collection that will eventually be used to build predictive algorithms. She confirmed that is the end goal, but for now they are collecting as wide a variety of data as possible. Along with biotechnology and tasting panels, Motif is gathering research on psychology and oral processing (see "Improving mouthfeel data" on adjacent page). Uzunalioglu says, incorporating a breadth of information is part of her company's development philosophy.

During the pandemic, sales of plant-based foods increased due to meat shortages that occurred when outbreaks hit processing plants. Matt Roszell, head of Motif's marketing communications, says that was an opportunity to gain new customers in the plant-based space, but many did not adopt the products permanently because they did not love their experience. "Plant-based foods are never going to be more sustainable or better for people's health if they just do not eat them," he says.

To get to that next level of customer acceptance, food scientists need more options than covering up odd flavors or textures with added sugar and salt to hide the earthiness of plant proteins. And, they want to know if anything other than gums and hydrocolloids can replicate the performance of animal fats.

Uzunalioglu and Roszell say they expect that the arsenal of data and computational power Motif has applied to determining what piques consumers' taste buds will lead to an indistinguishable eating experience between plant-based foods and native meats within one or two years.

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

Information

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Ultrasound-assisted intensified synthesis of designer lipids

Harsh B. Jadhav, Parag R. Gogate, Jyotsna T. Waghmare, and Uday S. Annapure

The modification of natural triglycerides based on various chemical reactions, such as interesterification, alcoholysis, glycerolysis, and acidolysis catalyzed by chemicals or enzymes is an important way to synthesize designer lipids with numerous health benefits [1].

- **Designer lipids are becoming increasingly popular due to their health benefits.**
- **These structured lipids are modified triglycerides that are synthesized by changing the position or composition of fatty acid on the glycerol backbone.**
- **Ultrasound is a promising non-thermal and efficient method for synthesizing designer lipids which intensifies yields, reduces reaction times, and increases operational stability of enzymes, thus making the process more economical for large-scale production.**

The interesterification process involves cleavage of ester bonds to liberate fatty acids. The liberated fatty acids are re-esterified at new positions on the same or another glycerol molecule, thus forming a new triglyceride or a designer lipid.

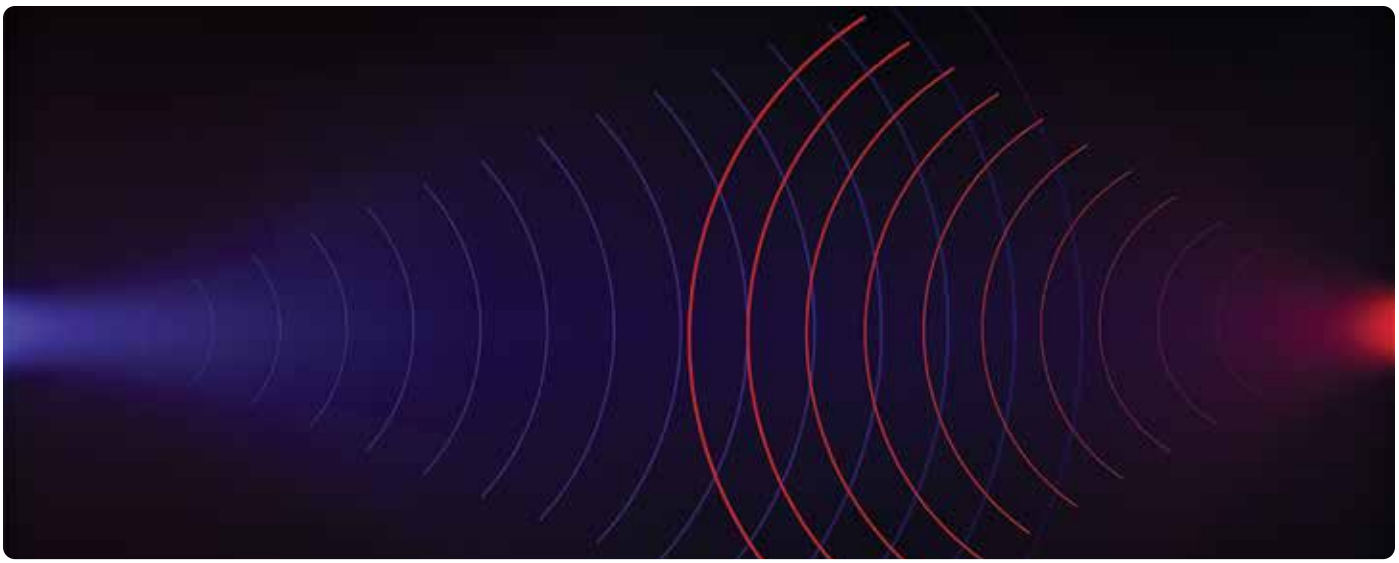
Alcoholysis involves reaction between an alcohol and triglyceride, whereas glycerolysis is based on the reaction of glycerol with triglyceride. Alcoholysis and glycerolysis are not commonly used processes for synthesis of designer lipids since these processes also involve the formation of monoglycerides and diglycerides.

Acidolysis is the most frequently used lipid modification process for the synthesis of designer lipids and involves reaction between triglyceride and fatty acid, which can be selected based on the required characteristics of the final product in the given application. During the reaction, a fatty acid is used as an acyl donor to modify the triglyceride catalyzed most efficiently by location specific enzymes.

ENZYMATIC CATALYSTS

Among the different catalysts used to synthesize designer lipids, enzymes offer many advantages, including good quality products, higher yields, and a green process. Enzymatic synthesis of designer lipids makes use of lipases obtained from a variety of sources, including animal, plant, fungi, bacteria, and yeast. Commercially used lipases are primarily obtained from fungal sources since these tend to be more stable than plant- or animal-based lipases.

Lipases used for enzymatic modification are fatty-acid-specific, stereo-specific, or regiospecific. Fatty-acid-specific lipases have affinity toward specific types or classes of fatty acids irrespective of their position on the glycerol backbone. Stereo-specific lipases hydrolyze ester linkage at the *sn*-1 and *sn*-3 position on the glycerol molecule at different rates, whereas regiospecific lipases are specific to the *sn*-1,3 position on the glycerol molecule, hence these lipases will react only with fatty acids



at the *sn*-1,3 position, while the *sn*-2 position remains unaffected due to steric hindrance.

Enzymatic processes for synthesis of designer lipids are highly recommended since the enzymes are position-specific and yield highly pure products, and because the reaction is carried out under mild reaction conditions so there are fewer chances for undesirable by-products to form.

CHEMICAL CATALYSTS

Chemical synthesis of designer lipids is typically carried out at higher temperatures ranging from 60°C to 150°C, and promoted by a chemical catalyst such as sodium methoxide or sulphuric acid. Since chemical catalysts are not specific to fatty acids or position, the fatty acids will be randomly distributed along the glycerol backbone, forming a mixed designer lipid. Chemical modification involves formation of undesirable by-products, which reduces purity and makes the process less economical since an additional purification process is needed. Additionally, the lipids produced may have limited application due to uneven distribution of fatty acid on the glycerol backbone. The only advantage of a chemical process is that the process is completed in a shorter time. Table 1 provides an at-a-glance comparison of enzymatic and chemical synthesis of designer lipids.

COMPONENT FATTY ACIDS

Different fatty acids are used to synthesize designer lipids, and the component fatty acids and their positions on the glycerol backbone determine the functionality, properties, metabolism, and health benefits of the resulting lipids. Short-chain fatty acids contain two to six carbons and are volatile. These fatty acids are quickly absorbed in the stomach because of their water solubility and shorter carbon chain. Short-chain fatty acids are used to synthesize designer lipids which are usually used as low-calorie fat. The calorific value of short-chain fatty acid is very low (3.5– 7.5 kcal/gm). Salatrim is an example of

TABLE 1. Comparison between enzymatic and chemical synthesis processes for designer lipids

Parameters	Enzymatic process	Chemical process
Types of catalyst	Lipases from different sources	Sodium methoxide, sulphuric acid
Reaction temperature	Lower than 60°C	60°C–150°C
Specificity	Higher specificity	No specificity
By-products	Less or no by-products	Many by-products
Control of reaction	Reaction can be easily controlled by inactivating enzymes.	Reaction is difficult to control.
Product purity	Product is highly pure.	Product quality is low.
Process cost	Cost depends on cost of enzymes; can be lowered by using immobilized enzyme.	Chemical process is economical but requires high temperature.
Environmental concerns	Process is eco-friendly.	Process generates lots of waste and is not eco-friendly.

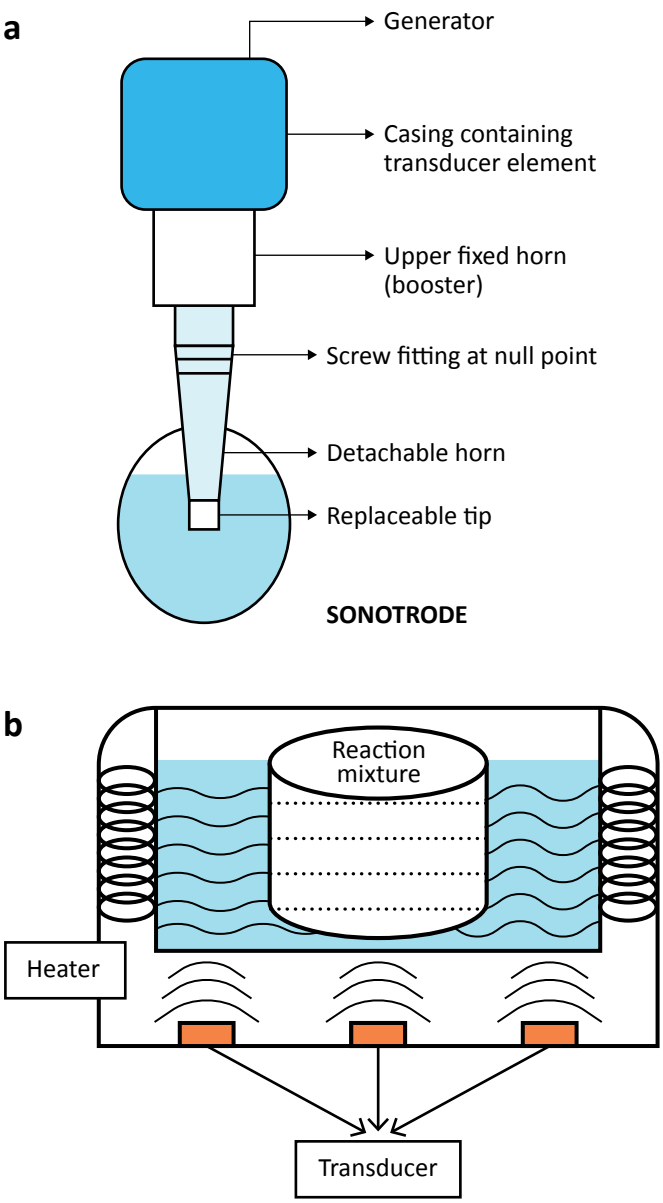


FIG. 1. (a). Ultrasonic horn/sonotrode used in direct methods for synthesis of designer lipids; (b) Ultrasound bath as an indirect method for synthesis of designer lipids

a commercially available low-calorie designer lipid containing short-chain fatty acid.

Medium-chain fatty acids (MCFAs) like caprylic acid (C8), capric acid (C10), and lauric acid (C12) are also used to synthesize designer lipids. MCFAs are metabolized quickly, which provides instantaneous energy, and they are not stored in the body as fat like long-chain fatty acids are. They are used as a supplement in elder nutrition and in the treatment of metabolic syndrome, obesity, diabetes, and other conditions. Medium-chain triglycerides provide 8.3 kcal/gm energy and are used to synthesize low-calorie designer lipids and designer lipids with specific functions. Commercially available designer lipids with MCFAs include Caprenin, Captex, Neobee, and Structolipid.

Essential fatty acids (EFAs) which are not synthesized in human body but are required for normal functioning of the body are also used to synthesize designer lipids. Examples include omega-3 fatty acids, omega-6 fatty acids, and other polyunsaturated fatty acids known to have various health benefits [2].

ULTRASOUND-ASSISTED SYNTHESIS

The disadvantage of conventional enzymatic synthesis is that the process is slow, primarily because of mass-transfer limitations. Usually, a maximum yield of about 80–85% is obtained after 48 hours. To reduce reaction time and to increase yields (%), intensification based on the ultrasound can be applied.

Ultrasound is classified into three categories: power ultrasound with frequencies between 20–100kHz, high-frequency ultrasound with frequencies between 100kHz–1MHz, and diagnostic ultrasound with frequencies from 1MHz–500MHz. In low-frequency ultrasound (20–100kHz), also known as power ultrasound, the physical effects dominate. In contrast, in higher-frequency ultrasound (200–500kHz), chemical effects dominate due to the formation of more active-energetic bubbles. The typical operating intensity of lower-frequency ultrasound is on the order of 10–1000 W/cm^2, but higher-frequency ultrasound has operating intensities lower than 1 W/cm^2.

Higher-intensity ultrasound/power ultrasound is more applicable for intensified synthesis of designer lipids based on the dominant requirement of physical effects for intensification. When the ultrasound passes through the reaction mixture, it generates cavitating conditions leading to high-intensity turbulence, liquid circulation, and acoustic streaming that help in eliminating the mass-transfer resistances. Use of ultrasound also helps to intensify the activity of the enzymes based on the favorable conformational changes. Both these factors lead to higher yields of designer lipids in shorter time periods.

Ultrasound can be applied to a reaction mixture directly by using ultrasonic horn/sonotrode, and indirectly by using ultrasonic bath (Fig. 1). Both these configurations are widely applied when exploring the intensification of different reactions. The scale-up of ultrasonic reactors would be mostly based on use of continuous or recirculation types of reactors using sonotrode or the multiple transducer arrangement with ultrasonic bath as the basis. Flow cells with transducers attached at the wall of the cylindrical or rectangular vessel would also be useful in designing a large-scale operation.

SPECIFIC EXAMPLES OF INTENSIFICATION

There are many studies reported in the literature that highlight the benefits of intensification achieved with use of ultrasound in synthesis of designer lipids using enzyme. One recently published study by Jadhav, *et al.* [3], reported ultrasound-assisted synthesis of palm olein designer lipid using Novozyme 435. The ultrasound-assisted synthesis resulted in a higher yield (%) of 92% in 360 min without affecting the recyclability of the enzyme, whereas conventional synthesis gave only 28% yield in 360 min and took almost 28 h to achieve a 90% yield (Fig. 2).

The recyclability of enzyme is a key parameter in determining the economic and environmental feasibility of large-

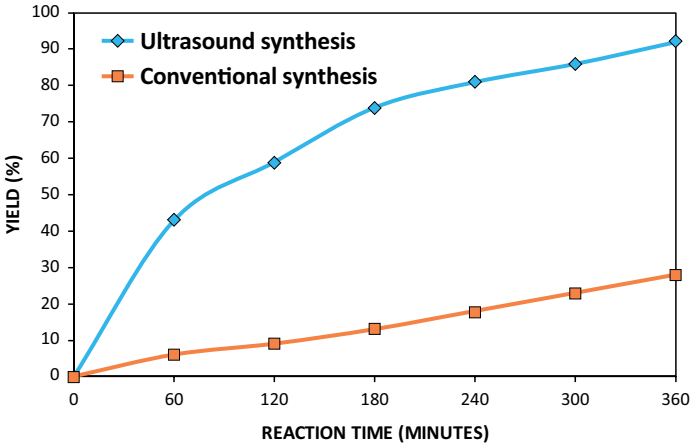


FIG. 2. Comparison between conventional synthesis and ultrasonic-assisted synthesis of palm olein designer lipids [3]

scale industrial production of designer lipids, and recyclability of enzyme is higher in ultrasound-assisted synthesis then in conventional process. Ultrasound additionally improves the operational stability of enzymes. In conventional synthesis, enzymes are exposed to reaction temperatures for more than 48 h, which results in a decrease in enzymatic activity of enzymes and adversely effects recyclability.

More, *et al*. [4], showed that ultrasound-assisted synthesis of designer lipid containing essential fatty acids (EFAs) and medium-chain-fatty acids (MCFAs) using enzyme resulted in an intensified yield (%) of 85% in 9 h, with the conventional process yielding only 77% after 24 h. Yue, *et al*. [5], studied ultrasound pretreatment for synthesis of designer lipid by incorporating caprylic acid in corn oil triglyceride using *sn*-1,3-specific Novozyme 40086 enzyme. Higher incorporation of 45.55% in 6 h of reaction was reported with ultrasound pretreatment using an ultrasonic bath, while conventional synthesis achieved only 32% incorporation of caprylic acid in 10 h. Similarly, Xu, *et al*. [6], studied enzymatic alcoholysis for synthesis of phenolic lipids and reported that ultrasound-assisted enzymatic alcoholysis gave more than 97% conversion (%) at 60°C with 6% Novozyme 435 dosage in 3 h, whereas the conventional process resulted in 63% conversion (%) in 36 h. It was also demonstrated that the conventional process affected the recyclability of novozyme 435 in a negative manner due to prolonged usage in one ~~cy, etc-cle~~ of synthesis.

A novel enzymatic route of MPAs synthesis by the alcoholysis of phenolic acid ethyl esters with glycerol under ultrasound irradiation in solvent free system was developed. Optimization of reaction parameters shows that a high conversion of above 97.4% can be obtained under the following conditions: phenolic acid ethyl esters to glycerol molar ratio of 1:10, with 6% catalyst (Novozym 435, studied enzymatic alcoholysis for synthesis of phenolic lipids and reported that ultrasound-assisted enzymatic alcoholysis gave more than 97% conversion (%) at 60°C with 6% Novozyme 435 dosage in 3 h, whereas the conventional process resulted in 63% conversion (%) in 36 h. It was also demonstrated that the conventional process affected the recyclability of novozyme 435 in a negative manner due to prolonged usage in one cycle of synthesis.

These and other studies reported in the literature clearly show that ultrasound usage is a promising non-thermal and efficient method for synthesizing designer lipids that not only intensifies yields but also reduces reaction times and increases the operational stability of enzymes, thus making the process more economical for large-scale production.

Harsh B. Jadhav and Uday S. Annapure are in the Department of Food Engineering and Technology, Institute of Chemical Technology, Matunga, Mumbai, India. Corresponding author Parag R. Gogate is in the Department of Chemical Engineering, Institute of Chemical Technology, Mumbai, and can be contacted at Tel: 00912233612024, pr.gogate@ictmumbai.edu.in. Jyotsna T. Waghmare is in the Department of Oils, Oleochemicals and Surfactant Technology, Institute of Chemical Technology, Mumbai.

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Microbial biosurfactants in the pharmaceutical industry

Raj Shah, Richard Ashby, Nicholas Douglas, and Nathan Aragon

Surfactants have found many diverse applications because of their emulsification properties, surface and interfacial tension-lowering characteristics, and micellar qualities. Traditionally, surfactants and detergents are produced synthetically from petroleum-based feedstocks. This has resulted in issues associated with their large-scale use, particularly in health and environmental applications. Consequently, there has been much focus recently on the development of microbial biosurfactants. Unlike their petroleum-based analogues, microbial biosurfactants are generally considered to manifest a comparatively low ecotoxicity and to be renewable (thus limiting their carbon footprint) and naturally degradable which alleviates (or at least diminishes) environmental discharge concerns. The pharmaceutical industry has developed several potential applications for microbial biosurfactants, the majority of which are focused on combating infectious organisms and viruses. Promising research has shown a rapid advancement in the utilization of microbial biosurfactants in pharmaceutical-based applications, and because of their valuable properties these biosurfactants stand to benefit millions of people worldwide.

- **As antibiotic resistance becomes more prevalent among potentially pathogenic bacterial strains, new avenues of treatment are continually being sought.**
- **Many microbial biosurfactants have been demonstrated to be effective against specific drug-resistant pathogens and to have potential as immuno-modulating and drug/gene delivery agents.**
- **This article focuses on lipopeptides and glycolipids as they pertain to pharmaceutical applications.**

There are many different classification systems of microbial biosurfactants based on their structural diversity. As such, microbial biosurfactants have been classified based on three distinct criteria. The first is by size. This classification separates microbial biosurfactants into low-molecular-weight biosurfactants (i.e., glycolipids, phospholipids, and lipopeptides) [1] and high- molecular-weight biosurfactants which comprise polymeric and particulate surfactants (i.e., lipopolysaccharides, emulsan). Secondly, low-molecular-weight biosurfactants can be further classified based on their net charge, which allows for differentiation of nonionic, anionic, cationic, and amphoteric biosurfactants. The third classification method is based on absolute structural composition, such as glycolipids, lipopeptides, and proteins. Of these microbial biosurfactants, the most well-known and studied are glycolipids, specifically rhamnolipids (RL) and sophorolip-

ids (SL), and lipopeptides, such as surfactin [1]. In this article, lipopeptides and glycolipids will be discussed as they pertain to pharmaceutical applications.

In the pharmaceutical industry, researchers have found several applications of microbial biosurfactants. These include applications as antimicrobial compounds, immuno-modulating agents, and drug/gene delivery agents [1]. As antibiotic resistance becomes more prevalent among potentially pathogenic bacterial strains, new avenues of treatment are continually being sought to combat the overuse of known antibiotics. Many microbial biosurfactants have been demonstrated to be effective against specific drug-resistant pathogens [1]. Since these pathogens can potentially harm large numbers of individuals if left unchecked, the need for alternative antimicrobial agents, such as microbial biosurfactants, that successfully combat these issues presents a challenge for researchers.

Commonly reported antimicrobial biosurfactant compounds include lipopeptides, which are typically composed of an oligopeptide ring attached to a fatty acid tail. This class of microbial biosurfactants is highly variable structurally and, as such, is composed of many different variants. In fact, lipopeptides belonging to the polymyxin family (A, B, C, D, and E) were some of the first known antimicrobial biosurfactants, with reports of their discovery dating back to 1947 [2]. The two most well-known of the polymyxin lipopeptides are polymyxin B (isolated from the bacterium *Paenibacillus polymyxa*) and polymyxin E (otherwise known as colistin). These two lipopeptides have been classified as antibiotics and have been particularly effective against Gram-negative bacterial infections, but because of their adverse effects on humans, polymyxins are typically only used as drugs of last resort.

In researching their properties, researchers found that the antimicrobial activity of a lipopeptide found in *Streptomyces amritsarensis* sp. Nov showed great promise for the pharmaceutical industry. It showed resilience when exposed to a wide range of bacteria and fungi, and no mutagenic or cytotoxic effects when exposed to Chinese hamster ovary [1]. These properties show promise for lipopeptide biosurfactants to be an effective ingredient in new drugs for the pharmaceutical industry. In addition, researchers also found that the lipopeptide derived from the marine strain *Aneurinibacillus aneurinilyticus* SBP-1 showed promising antimicrobial activity in a low minimal inhibitory concentration (MIC: the measure of the lowest drug concentration that prevents microorganism growth within a confined space [3]) when exposed to different bacteria and fungi, presenting itself as a good candidate in biomedical applications [1].

Due to the growing number of antibiotic-resistant bacteria found in infections, novel lipopeptide-based antimicrobials would be beneficial. Researchers have developed a few theories for lipopeptide-organism interactions. One theory describes the interaction of lipopeptides with bacteria as creating pores through oligomer binding, creating an opening into the cell [4]. Subsequently, transmembrane influxes of sodium

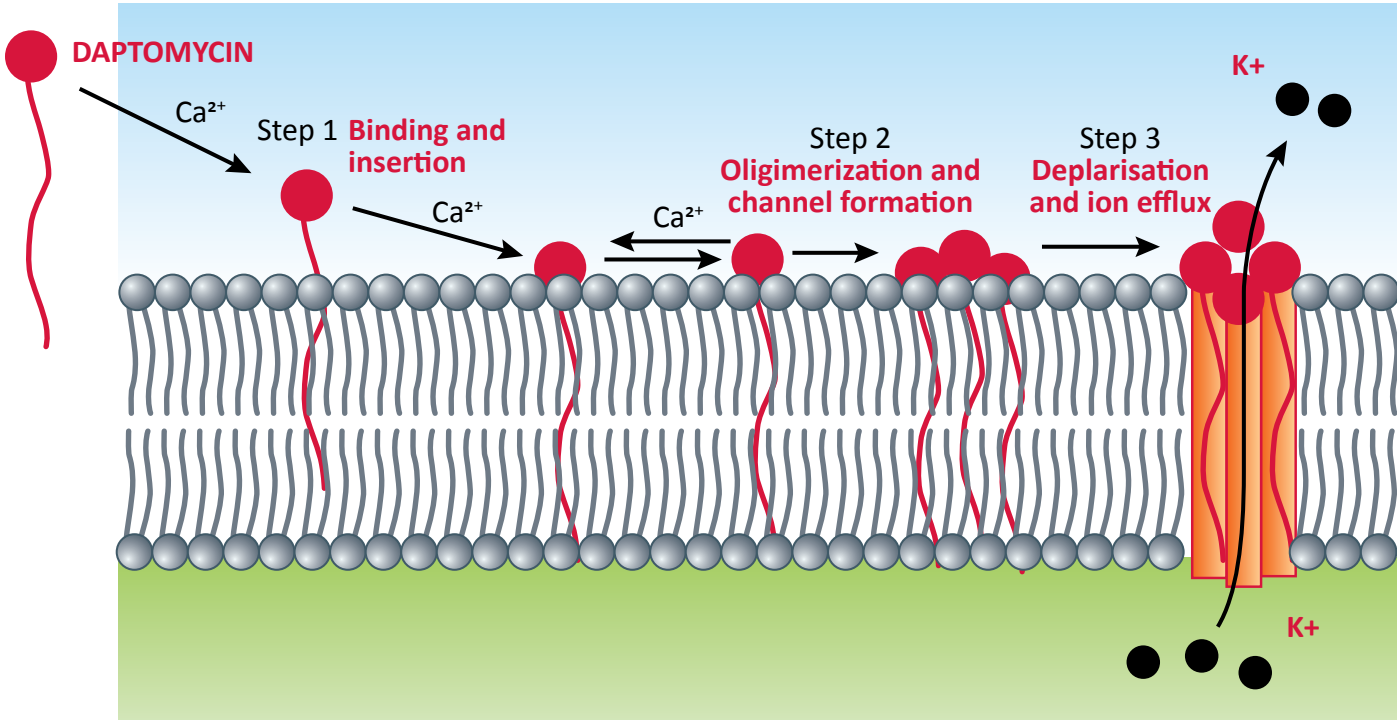

FIG. 1. Mechanism of daptomycin interacting with cell membrane through transmembrane ion influx [5]

and potassium ions may enter the cell, promoting membrane disruption and death [4].

Figure 1 shows daptomycin, a lipopeptide antibiotic primarily effective against infections caused by Gram-positive bacterial strains, interacting with a cell membrane to induce transmembrane ion influx. Membrane penetration causes cell death through interference with cell signaling, prohibiting vital transmissions from being received. As for advantages, lipopeptides have shown potent antibacterial activity, particularly with daptomycin, to drug-resistant bacteria, including penicillin-resistant *Streptococcus pneumoniae* and methicillin-resistant *Staphylococcus aureus* [4]. For researchers, lipopeptides offer a promising solution to a growing problem for many countries, particularly those with high infection rates in Africa and Asia, where approximately 145 million people are infected with drug-resistant bacteria [4]. Research and heavy investment will fuel their application for efficient products.

Surfactin is the most well-known cyclic lipopeptide. It is composed of a seven amino acid ring structure attached to various 3-hydroxy fatty acids, particularly 3-hydroxy-13-methyltetradecanoic acid [6]. It can be efficiently recovered in both batch modes—via acid precipitation due its insolubility at low pH values, and via continuous modes resulting in highly pure molecules [7]. High-purity surfactin can reduce the surface tension of water from 72 to 27.9 mN/m at a concentration of 0.005% [6]. Surface strain is the measure of how much force a material (in this case a microbial biosurfactant) can exert on a cell membrane. By reducing the surface strain, the microbial biosurfactant can interact with a cell and prohibit the transmission of certain proteins and/or DNA through the cell resulting in deleterious responses.

Glycolipids are another common classification of microbial biosurfactants with antimicrobial properties. Composed of a lipid moiety covalently bonded to a carbohydrate head group, glycolipids also contribute to microbial biosurfactant research in the pharmaceutical industry. Glycolipids are classified into several different groups. These include sophorolipids (SL), rhamnolipids (RL), mannosylerythritol lipids (MEL) and trehalose lipids (TL) among others. As with lipopeptides, glycolipid biosurfactants can combat some bacterial and fungal pathogens already resistant to common drugs. A study on a glycolipid from *Staphylococcus saprophyticus* SBPS 15 showed antimicrobial properties when exposed to several bacterial and fungal pathogenic organisms [8]. Low MIC values (from 4-64 microgram/mL) were reported when this glycolipid was tested against *E. coli* (MIC = 12 microgram/mL), *Salmonella typhi* (no value reported), *Vibrio cholerae* (MIC = 64 microgram/mL), and *Aspergillus niger* (MIC = 16 microgram/mL) [8]. By producing such low values, this specific microbial biosurfactant can combat multi-drug resistant bacteria and fungi.

In addition, specific glycolipid biosurfactants have been documented as functional in other pharmaceutical applications. For example, SL, MEL, and RL are also well-known antimicrobial agents particularly effective against Gram-positive bacterial strains. In addition, SL has been shown to exhibit anticancer, anti-inflammatory, antiviral, and spermicidal activity and has been documented to be active in disease treatment, particularly against candidiasis and asthma. In addition to its antimicrobial character, MEL has been demonstrated to promote cell differentiation in the human promyelocytic cell line into granulocytes and has also been demonstrated as a potential therapeutic agent for cancer. RL has been documented to

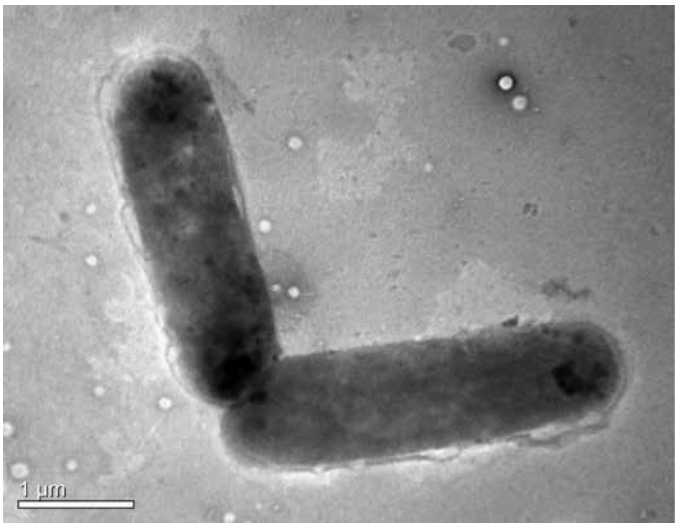

FIG. 2. Electron micrograph of negatively stained cells of mangrove *Bacillus* sp. [10]

possess antimicrobial properties against bacteria, yeasts, fungi, and algae and can cause cell lysis in organisms lacking a protective cell wall.

As immuno-modulating agents, microbial biosurfactants present such properties when dealing with multi-drug resistant bacteria and fungi. Immuno-modulating agents modify an organism's immune response to threats. The immunosuppressive properties of surfactin on macrophages showed great promise for researchers. When bonding to these macrophages, surfactin blocks the NF-κB (the nuclear factor kappa-light-chain enhancer on B cells) and the Akt cell-signaling pathway [1]. The NF-κB protein is vital to macrophage survival due to DNA transcription and cytokine production. Its blockage decreases the macrophage's survivability since no DNA transcription means no information for the macrophage to process. Overall, surfactin's properties in blocking this protein show potential for researchers.

Also, surfactin showed interesting anti-inflammatory properties when interacting with TNF-α and on the overproduction of NO_2 [1]. In this study, researchers found that when analyzing surfactin isomers, they were characterized by their bioactive fraction with *Bacillus* species (sp.) and showed great inhibitory properties on the overproduction of NO_2 and phospholipase A2 [9]. Figure 2 [10] shows *Bacillus* sp. used in this study. Nitric oxide overproduction opens blood vessels throughout many organisms, contributing to an efficient flow and lower blood pressure. In some instances, this overproduction might feed bacteria and promote infection or other disease. This crucial step helps combat overproduction by blocking excessive NO_2, leading to slower spread. As for TNF-α, it is a cytokine that aids in signaling other cells of infection. This leads to necrosis and apoptosis over time. Surfactin alters this by inhibiting this cytokine from altering other cells, which prevents widespread apoptosis [9]. This creates a promising

immuno-modulator by prohibiting TNF-α from alerting other cells of a threat. Cancer and other rampant infections would be suppressed by this action.

Microbial biosurfactants from glycolipids and lipopeptides show great promise for the pharmaceutical industry. To date, the biggest issue is getting to industrial production levels so that millions of people can take advantage of the antimicrobial properties and other characteristics biosurfactants offer as potential treatments. Several advancements have been made, but further research into their production and continuous investment into the industry are needed to develop effective products.

Raj Shah is a director at Koehler Instrument Company in New York, where he has worked for the last 25 years. He is a peer-elected Fellow of IChemE, STLE, AIC, NLGI, INSTMC, CMI, The Energy Institute, and The Royal Society of Chemistry. Shah has a Ph.D in Chemical Engineering from the Pennsylvania State University and is a Fellow from the Chartered Management Institute, London; a Chartered Scientist with the Science Council, UK; a Chartered Petroleum Engineer with the Energy Institute; and a Chartered Engineer with the Engineering council, UK. An ASTM Eagle award recipient, he recently coedited the bestseller, Fuels and Lubricants Handbook*, details of which are available at https://www.astm.org/DIGITAL_LIBRARY/MNL/SOURCE_PAGES/MNL37-2ND_foreword.pdf.*

A 2020 recipient of the illustrious Tau Beta Pi eminent engineer title, Shah is an active volunteer and on advisory board of directors at several US universities. He is a member of the editorial advisory committee for Inform *magazine and has over 300 publications in numerous journals. More information on Raj can be found at https://www.che.psu.edu/news-archive/2018/Alumni-Spotlight-Raj-Shah.aspx. He can be reached at rshah@koehlerinstrument.com.*

Richard Ashby is a senior research scientist in the Sustainable Biofuels and Coproducts Research Unit (SBCP) at the USDA, ARS, Eastern Regional Research Center (ERRC). He has 32 years of research experience in the areas of biopolymer and biosurfactant synthesis and molecular characterization. Ashby currently serves as Senior Associate Editor for the Journal of the American Oil Chemists' Society (JAOCS) *and in an editorial capacity for three additional journals, and recently served as co-editor of the book,* Biobased Surfactants: Synthesis, Properties, and Applications*, 2nd Edition, published by Academic Press and AOCS Press. He is the author or coauthor of 129 publications, 150 presentations, and holder of 7 patents.*

Nicholas Douglas and Nathan Aragon are students in the Department of Material Science and Chemical Engineering at State University of New York (SUNY), Stony Brook, where Shah is an adjunct professor and chair of the External Advisory Board of directors. They are also interns at Koehler Instrument Company.

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Açai oil: physicochemical properties and application potential

Thais Jordânia Silva, Larissa Magalhães Grimaldi, Mayanny Gomes Silva, Fernanda Luisa Lüdtke, Kamila Ramponi Rodrigues de Godoi, Renato Grimaldi, Ana Paula Badan Ribeiro

The açai or açaizeiro (*Euterpe oleracea* Mart.) is a native palm tree of the Brazilian Amazon Rainforest. The fruit of this palm has a dark purple color similar to that of a berry, is grouped in clusters, and measures 1 to 1.4 cm in diameter (Fig. 1). It also has potential health benefits associated with its high antioxidant capacity and phytochemical composition. Açai oil is stored in the mesocarp, in the parenchyma of the lipid reserve. It is extracted by cold pressing from the açai pulp. The oil contained in the açai fruit accounts for ~50% of its total dry matter (Ferreira, Rogez, and Herman, 2018; Pacheco-Palencia *et al.*, 2008a; Schauss, *et al.*, 2006).

- **The Brazilian Amazon is extremely rich and diversified in oil plants.**
- **The unique physicochemical and nutritional properties of these lipid sources demonstrate potential applications in the cosmetic and food industries.**
- **This article looks at the composition, physicochemical properties, and potential applications of açaí oil.**

FIG. 1. Açai fruit (*Euterpe olerace* Mart)

Açai oil has a color between purple and dark green with a high intensity of yellow (28 mg/100g). Upon evaluation, açaí oil had the physical characteristic of a viscous fluid and an aroma characteristic of açaí fruit. It also had approximately 22.91 mg/100g of chlorophylls.

The presence of tocopherol is associated with its excellent antioxidant capacity. The main tocol found in açai oil is alpha-tocopherol (2.38 mg/100g). Polyphenolic compounds and anthocyanins retained in the oil (procyanidin dimers, procyanidin trimers, vanillic acid, and serum acid) also contribute to its significant antioxidant activity. Although the content of carotenoids is low, the oil is less susceptible to oxidation than other unsaturated fatty acids oils due to its high oleic acid content (Bruscatto, *et al*., 2017).

Açai fruit has in its composition proteins, fibers, lipids, vitamins, and minerals. The lipid content of this fruit can reach up to about 41% (Fortuoso, *et al.*, 2020). The predominant fatty acids in açai oil are oleic (omega 9; 55.13%), palmitic (24.44%), and linoleic (11.98%) (Table 1). Palmitic acid is the main saturated fatty acid. Açai oil has a similar composition to olive and avocado oils, with a high content of monounsaturated fatty acids. The content of polyunsaturated fatty acids is less than 12%. This is considered good from the perspective of stability since these fatty acids favor the oxidation lipids (Prisacaru, 2016).

In terms of identity and quality, açai oil has an iodine index of 73.60 gI_2/100g, saponification index of 195.48 mg_{KOH}/g, and acidity of 7.68%. With the increase in the hydrocarbon chain size, a higher saponification index is observed. Other oils from the Brazilian Amazon have a similar saponification index, such as Brazil nuts (187.48 mg_{KOH}/g), pracaxi oil (164.44 mg_{KOH}/g), and pataúa oil (174.85 mg_{KO}H/g) (Pereira, *et al.*, 2019). The acidity index reflects the degree of hydrolytic degradation related to the storage of the fruits and extraction method. This fact can be demonstrated, as an example, when analyzing its classes of glyceride compounds, with 84.55% triacylglycerols, 7.84% diacylglycerols, and 6.66% of monoacylglycerols.

The triacylglycerol composition of açai oil, obtained from its fatty acids composition, is shown in Table 2 (page 24). Açai oil is composed mainly of PSO, POO, POL, and PoOL. Due to the predominance of palmitic (P – C16:0) and oleic (O – C18:1) acids, the main triacylglycerols are composed of these fatty acids. Despite the high content of palmitic, the presence of

TABLE 1. Fatty acid composition of açai oil

Fatty acid (%)	Açai oil
Capric acid (C10:0)	0.03
Lauric acid (C12:0)	0.27
Myristic acid (C14:0)	0.27
Pentadecyl acid (C15:0)	0.03
Palmitic acid (C16:0)	24.44
Palmitoleic acid (C16:1)	3.41
Margaric acid (C17:0)	0.05
Margaric-oleic acid (C17:1)	0.08
Stearic acid (C18:0)	3.01
Oleic acid (C18:1)	55.13
Linoleic acid (C18:2)	11.98
Linolenic acid (C18:3)	0.82
Arachidic acid (C20:0)	0.25
Gadoleic acid (C20:1)	0.07
Behenic acid (C22:0)	0.08
Lignoceric acid (C24:0)	0.08
Saturated fatty acids	28.51
Unsaturated fatty acids	71.49
Saponification index (mg_{KOH}/g)	195.48
Iodine index (gI_2/100g)	73.60

TABLE 2. Triacylglycerol composition of açai oil

Triacylglycerol (%)	Açai oil
PPP/PPPo	0.78
PPS/PPO/PPoO/PPoL	20.28
PSO/POO/POL/PoOL	48.8
SOO/OOO/OOL/OLL	30.13

P: palmitic; Po: palmitoleic; S: stearic; O: oleic, L: linoleic.

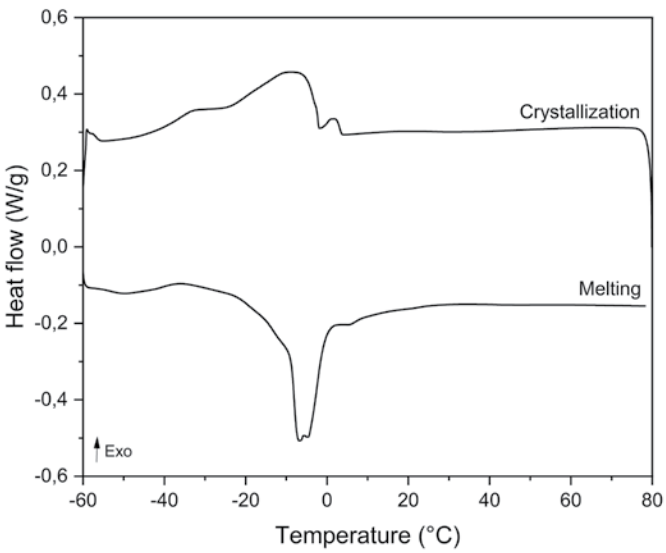

FIG. 2. Crystallization and melting curves obtained by differential scanning calorimeter (DSC) as a function of temperature, for acai oil

tripalmitin was low. It is important to highlight the presence of triacylglycerols containing oleic, stearic, and linoleic acids (SOO, OOO, OOL, and OLL).

Fatty acid and triacylglycerol composition have a direct correlation with the physical properties. Figure 2 shows the crystallization and melting profiles of açai oil. Açai oil has low initial temperatures of crystallization (3.93°C) and melting (-24.62°C) (Table 3), with a single peak of energy release, resulting in its liquid characteristic at room temperature. This feature facilitates its use as a nutraceutical oil, but it hinders its application in food for consumption.

Açaí oil has a high content of unsaturated fatty acids, (71%), which puts this fruit in an attractive condition for the functional food market. Because of its high phenolic content and storage stability, açai oil is a promising new alternative to traditional oils (Pacheco-Palencia, *et al*., 2008b). Açai oil has color and physical characteristics that make its application difficult. Encapsulation using microparticles or nanoparticles could be a solution that would allow this oil to be consumed in everyday products to bring health benefits (Monge-Fuentes, *et al*., 2017).

The authors are with the Laboratory of Oils and Fats, School of Food Engineering, Department of Food Technology, University of Campinas, Campinas, Brazil.

TABLE 3. Thermal behavior parameters of açaí oil

Açaí oil	T_i (°C)	T_p (°C)	ΔH_1 (J/g)	T_f (°C)
Crystallization (peak 1)	3.93	2.12	0.76	-1.62
Crystallization (peak 2)	-2.13	-9.91	23.44	-44.96
Melting	-24.62	-6.75	51.89	12.52

T_i: Initial temperature of crystallization/melting; T_p: Peak temperature of crystallization/melting; T_f: Final temperature of crystallization/melting; ΔH: Enthalpy of peak of crystallization/melting.

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Dry fractionation of cupuassu fat: chemical composition and polymorphic behavior

Virginia Borroni, Roberto Jorge Candal, and Maria Lidia Herrera

- Tropical fats are of great interest for food applications.
- Dry fractionation of cupuassu fat may increase its performance in products.
- S-26 has suitable physical properties for chocolate and a stable β_2-form.

Tropical fats have great potential for many food applications because they originate from plants, are semi-solid at ambient temperature, and contain high percentages of the triacylglycerol (TAG) SOS (S stearic acid and O oleic acid), which is very important in confections and chocolate production (Rodriguez Negrette, *et al.*, 2019).

Cupuassu (*Theobroma grandiflorum*) is a tropical tree of the eastern Amazon region and central South America. It grows in Peru, Bolivia, northern Brazil, and southern Venezuela. Although the cupuassu tree is botanically related to the cacao tree (*Theobroma cacao*), the white aro-

matic fat extracted from its seeds has significant differences in TAG composition compared to the composition of cocoa butter, and these differences give cupuassu fat unique polymorphic and crystallization behaviors.

Despite these differences, cupuassu fat is fully compatible with cocoa butter as shown by nuclear magnetic resonance studies (da Silva, *et al*., 2009), and cupuassu seeds can be processed similarly to cocoa beans to yield a chocolate-like product called "cupulate" (Fernandes Pereira, *et al*., 2017). However, because cupulate has a lower solid fat content (SFC) at ambient temperature and is softer than cocoa butter, its performance for applications may be limited. To increase its potential as a trans-fat alternative and a fat substitute in chocolate production, cupuassu fat may be modified by dry fractionation.

Dry fractionation is a process used to modify the TAG composition of a fat that does not involve a change in the position of the fatty acids on the TAG, as happens with interesterification. In the lab experiments we performed, the original fat was separated into a liquid phase called olein and a solid one called stearin by filtering the crystals under vacuum. Due to differences in TAG composition, these fractions have different physical properties than the original fat. Thus, the original fat melting and polymorphic behaviors may be modified without producing trans-fat.

Dry fractionation is environmentally friendly as it is a thermal process that does not involve solvents. Also, since it is a cheap and simple operation, it should be easy to perform on an industrial scale. Figure 1 is a schematic of a dry fractionation process performed on cupuassu fat. After being melted, cupuassu fat was cooled to 29°C and kept at that temperature for 6 h. Then, a stearin and an olein fraction were separated in a room with temperature control. Subsequently, the olein obtained at 29°C was subjected to a new fractionation step at 26°C to obtain stearin and olein fractions at that crystallization temperature. Finally, the olein obtained at 26°C was further fractionated at 24°C, and two new fractions (a stearin and an olein) were collected at 24°C (Rodriguez Negrette, *et al*., 2020).

The original cupuassu fat used to study the effects of the dry fractionation process had a melting point of 31.6°C ,while stearins crystallized at 24 (S-24), 26 (S-26), and 29 (S-29)°C had melting points of 30.4, 35.0, and 35.2°C, respectively. Dry fractionation raised the melting points of S-26 and S-29 and their solid fat contents (SFC) at temperatures below 30°C, making these fractions more suitable for spreads or confections than the original cupuassu fat. The amount of S-29 obtained after filtering was about 9% in weight of total fat. Olein fraction (O-29) was the main fraction at that temperature. Stearin fractions crystallized at 26 and 24°C represented about 23 and 36% of the initial fat, respectively. S-26 had promising physical properties and was obtained with good yield. A lower percentage of S-29 was obtained, but since it crystallizes faster than cupuassu fat it could be used as a "seed" to accelerate the crystallization process in cupuassu fat (Rodriguez Negrette, *et al*., 2020).

Dry fractionation process allows fractions with TAG compositions different than the original fat to be obtained. In the

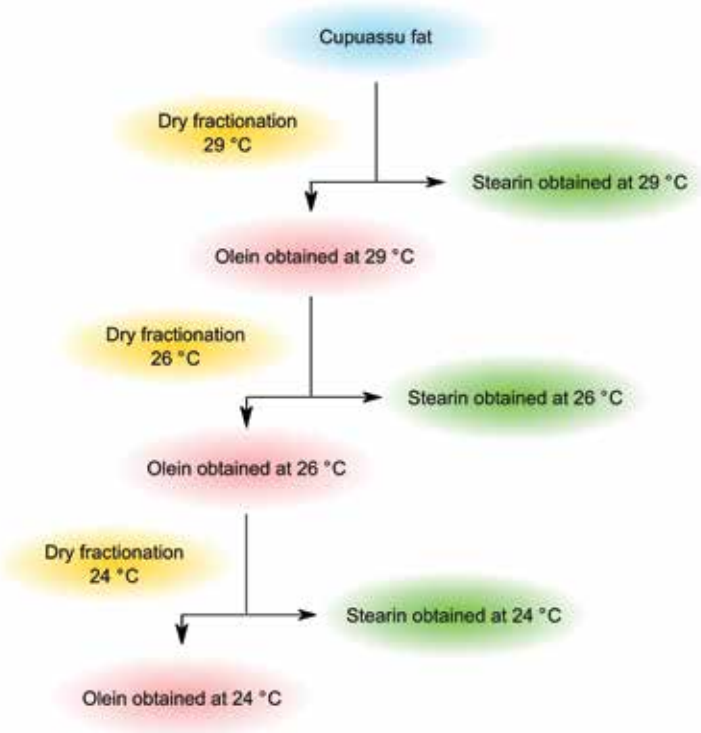

FIG. 1. Schematic of the dry fractionation process

cupuassu fat used in this fractionation study, the TAG that was present at a higher percentage was SOO, with a content of 21.6%, followed by SOS at 18.9%. The TAG SOA (with arachidic acid) was present at 11%, while POP, POS, and SOB (with palmitic acid and behenic acid) were present at 1.4, 9.9, and 1.3%, respectively. The stearin contents of SOS, SOA, and SOB increased as a result of fractionation.

SOA and SOB are solid at ambient temperature, and their percentages in stearin fractions were higher than those reported for the different cocoa butter varieties, where SOA and SOB may be lower than 1%, depending on geographic origin. The main TAGs in cocoa butter—SOS, POP, and POS—have been reported in cocoa butter at percentages varying from 12 to 15, 40 to 47, and 22 to 30%, respectively, with the total fat being 80%.

X-ray scattering analysis performed at small (SAXS) and wide (WAXS) angle is a powerful tool to describe fat polymorphism *in situ* and in real time. This analysis makes it possible to identify polymorphic forms and quantify polymorphic transitions as they occur. Data obtained by this technique allows polymorphic systems to be described in a way that is not possible using conventional techniques, such such as polarized light microscopy (PLM) or differential scanning calorimetry (DSC). Since the physical-chemical properties of fat products are closely related to polymorphism of solid fat, data from synchrotron studies are very important to analyze fat functionality. For example, only form V (β_2) of cocoa butter is used by the confectionery industry as the optimal polymorph in chocolate. Form V provides chocolate products with snap, good demolding properties, good quality in terms of color and gloss, and also resistance to fat bloom. Additionally, only the β'-form is

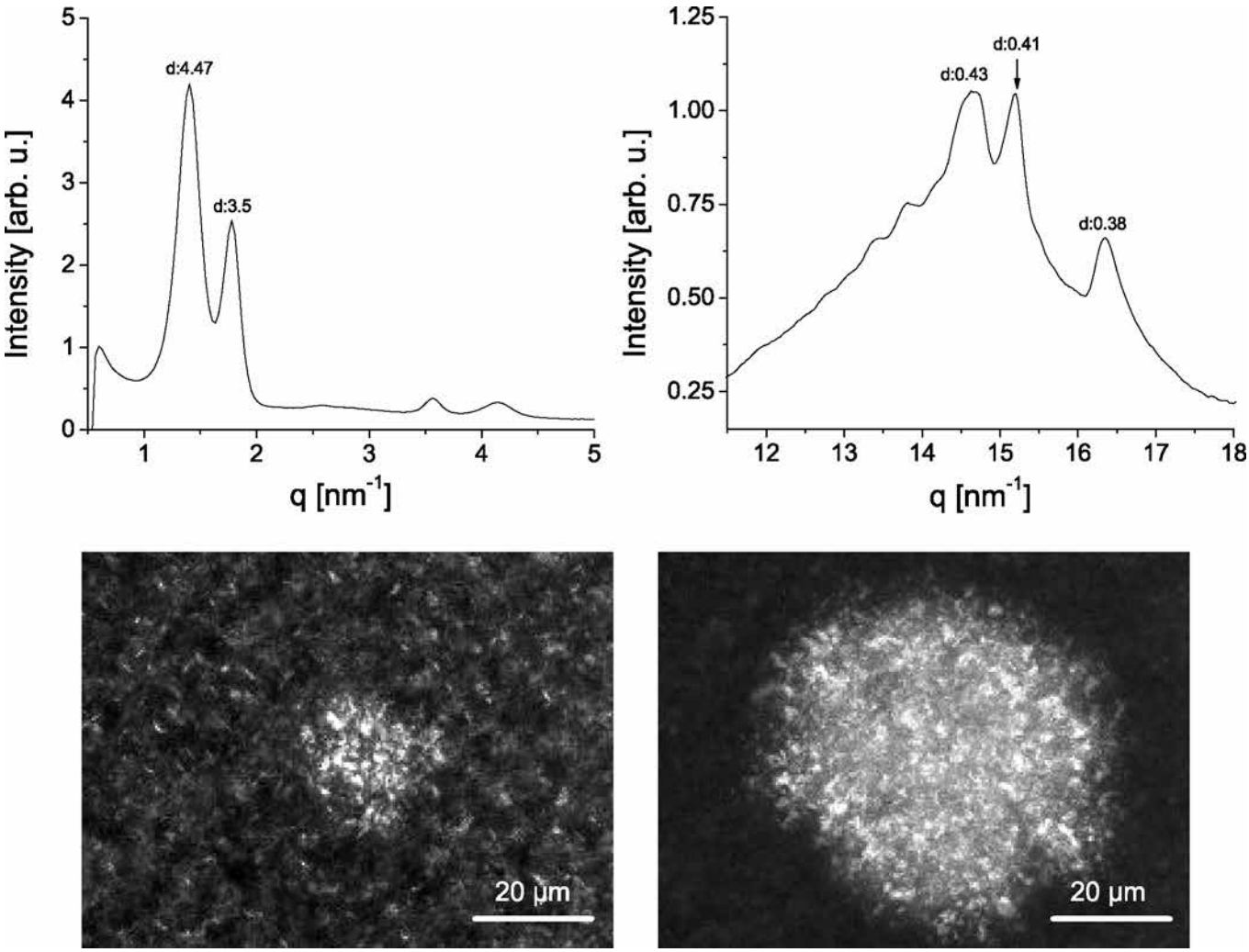

FIG. 2. Stearin fraction obtained at 29°C (S-29) subjected to a thermal cycle. The sample was melted to 60°C and crystallized at 17°C for 90 min. Then, it was heated at 0.5°C min–1 to 23°C, held for 35 min, cooled to 17°C at 0.5°C min–1, and held for 35 min. X-ray studies corresponding to sample crystallized at 17°C for 5 min (final step) appear at the top of the figure. Upper left: SAXS; upper right side: WAXS. Lower left: polarized light microscopy image (PLM)corresponding to the X-ray on the lower left. Lower right: PLM image after 35 min at 17°C (final step).

suitable for margarines and spreads. These crystals form a network that includes small oil droplets that give the product a soft texture.

Silva, *et al.* (2009) provided the first description of polymorphic behavior of cupuassu fat in real time. Depending on processing conditions, they reported four polymorphic forms—γ, α, β′, and β—in increasing order of stability and melting points. Their work described only one β′-form for cupuassu fat that corresponded to the β'_2 polymorph. Although two β-forms were described, the polymorphic transition β_2 àβ_1 was not possible to follow in the isothermal crystallization conditions selected by Silva, *et al.* (2009). Applying a thermal cycle that mimics the chocolate template process, Rodriguez Negrette, *et al.* (2020) reported that the main polymorphic form of cupuassu fat was the β'_2. Even if the β_2-form was the expected one, it did not crystallize. In addition, at the beginning of the cycle, there were trace amounts of the α-form that underwent a polymorphic transformation to β'_1. There were two solid solutions, the main of which crystallized in the β'_2-form. This behavior is different than the one reported for cocoa butter, in which the three main TAGs are compatible in all percentages, even in the β-form, crystallizing in only one solid solution that has a sharp melting peak when analyzing by DSC.

When cupuassu fat was fractionated, S-29 showed a different polymorphic behavior than the original fat. The main polymorphic form that crystallized was the β'_1. Although fractionation changed polymorphic behavior, both the original fat and its fraction crystallized primarily in only one β′-form. Crystallization in one polymorphic form makes these fractions ideal for margarines and spreads since each polymorphic form has a melting point and a microstructure; hence only one crystal morphology would be present at a time, which would likely result in final products with fewer defects.

Figure 2 shows SAXS and WAXS patterns of S-29 crystallized under a thermal cycle. Both β′-forms may be observed in the selected condition. The calculated distances for the β'_2-form were 0.38, 0.43, and 3.5 nm, while those for the β'_1-form were 0.41, 0.44, and 4.47 nm. The corresponding micro-

structure is also shown in Figure 2. The PLM image at the bottom, on the left, corresponds to both β'-forms together, crystallized during the thermal cycle after 5 min at 17°C (final step of cycle). The image on the right was acquired at longer times, after 35 min at 17°C, during the final step of the cycle, revealing a structure with a main crystal morphology. When cupuassu fat was stored at 25°C for 3 months, the β_2-form was the only polymorphic form present. This form was very stable, and no polymorphic transition to the β_1-form was observed. S-29 only crystallized in the β_1-form. In contrast, S-26, which had higher melting point and SFC than cupuassu fat, crystallized in a very stable β_2-form during storage, being more suitable for chocolate manufacture than the original cupuassu fat. Dry fractionation improved S-26 physical chemical properties and its potential for product formulation.

Virginia Borroni and Maria Lidia Herrera are scientists of CONICET at the Institute of Polymer Technology and Nanotechnology, Facultad de Arquitectura Diseño y Urbanismo, University of Buenos Aires-CONICET in Argentina. Herrera can be contacted at Maria mlidiaherrera@gmail.com.

Roberto Jorge Candal is a researcher of CONICET and an Associate Profesor at Instituto de Investigación e Ingeniería Ambiental, Universidad Nacional de San Martín (UNSAM) in Buenos Aires, Argentina.

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The challenge of formulating for skin lipids

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

Rebecca Guenard

After decades of research on the role of lipids in the human body, scientists now appreciate just how critical these compounds are for maintaining human health. Researchers are beginning to understand that lipids fulfill vital duties beyond just membrane composition and energy storage. No place is this more apparent that in the body's largest organ, the skin.

During a talk at the 2021 AOCS Annual Meeting and Expo last May, Apostolos Pappas, currently an adjunct professor at Rutgers University (New Brunswick, New Jersey, USA) who spent many years conducting research for the skincare industry, described the essential function of epidermal surface lipids and explained how interrupting their synthesis leads to abnormalities of the skin and hair. Studies on mice found that when the genes responsible for producing sebaceous lipids were knocked out, the mice did not survive due to an inability to repel water and regulate their body temperature (https://doi.org/10.21748/am21.397).

Luckily, humans will not have to experience such a fate, but animal experiments provide evidence for the important role lipids play in normal skin function. Many questions remain concerning these unique compounds and how cosmetics companies can formulate their products to align with the duties they perform. In particular, with consumers currently focused on sustainability, are there plant-based lipids that match the variety of lipids associated with the skin?

The majority of epidermal surface lipids originate from the sebaceous gland as human sebum, a mixture of triglycerides, wax esters, squalene, and fatty acids with small amounts of cholesterol esters and diglycerides (Fig. 1). However, the outermost, protective layer of the skin itself is composed of equal proportions of free fatty acids, cholesterol, and ceramides produced by keratinocytes close to the skin's surface (https://doi.org10.4161/derm.1.2.7811).

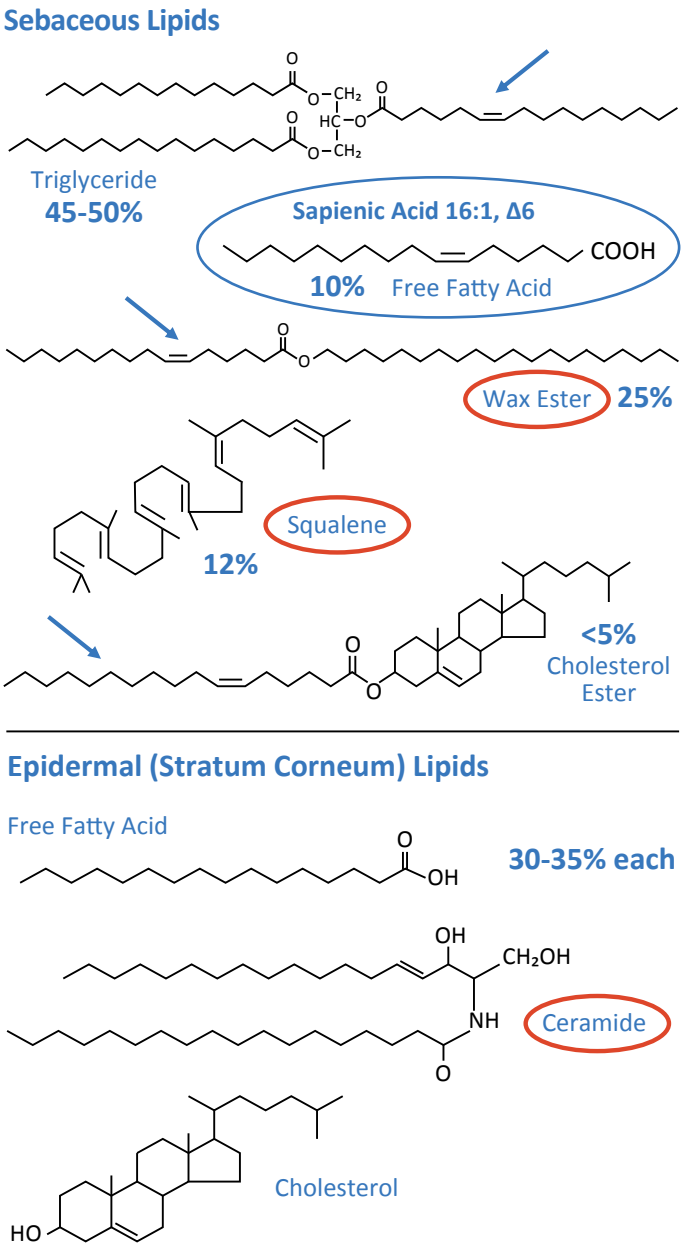

FIG. 1. Chemical structures of the abundant compounds in sebaceous and epidermal lipids. Source: Apostolos Pappas, https://doi.org/10.21748/am21.397.

Benjamin Schwartz is a senior personal care applications specialist at AAK, a fats and oils producer headquartered in Malmö, Sweden. He presented at the technical session following Pappas and described the current state of cosmetic formulations (https://doi.org/10.21748/am21.398).

After water, lipids or lipid derivatives are the primary component of skincare products. However, according to Schwartz, cosmetic chemists are not typically formulating to mimic the multiple lipid classes found natively on the skin's surface. Historically, emollients—ingredients containing fats or oils that soften skin—used in cosmetics were derived from petroleum, because they were inexpensive, easy to obtain, and extremely stable.

Mineral oil is a common ingredient in cosmetics because it can reliably sit on a store shelf for five years without decomposing. Similarly, the industry uses medium-chain triglycerides in formulations because their saturated bonds do not experience oxidation. "That is the incentive to keep using these, not that they are the types of fatty acids you find on the skin's surface," Schwartz said in an interview before his presentation.

Oxidative stability becomes an issue when companies try to reformulate with plant-based ingredients. Companies must weigh the cost/benefit of adding lipids that match the skin's against the complexity of protecting those lipids from oxidation. "You now have a significant challenge built into your formulations that was never something you had to consider before," says Schwartz.

Even if the oxidation issue could be solved, both Schwartz and Pappas indicate that it is only one of many challenges formulators face. When trying to replenish the sebaceous gland lipids with plant-based ones, Schwartz says there is minimal crossover between plant-based triglycerides and the mixture found in human sebum. In terms of plant-based esters, jojoba oil is the only one used in skincare formulations. Therefore, some sort of synthesis would be required to convert the naturally sourced triglycerides and wax esters into a consumer product with a chemical composition which matches that of skin lipids. Phytosterols found in plant oils are structurally and functionally similar to skin lipids, he says, but squalene is too expensive to add to a formulation.

In fact, the more specific to skin chemistry a cosmetic ingredient is, the more a product will cost. "Unless there is some other huge value industry manufacturing these ingredients, it is going to cost quite a bit," Schwartz says. For this reason, the cosmetic industry tries to formulate with ingredients manufactured from edible oils since they are produced on a larger scale.

Again, these are the hurdles for formulating a product to match the lipids on the skin's surface. Addressing the loss of structural lipids that compose the skin barrier is an even bigger challenge. This is an area worth pursuing since these products fall under the lucrative anti-aging category.

The surfactants used in skin cleaners can strip some of the fats from the skin's surface. In addition, the natural production of these fats slows down with age. Consumers are eager for treatments that restore epidermal fats and regenerate a youthful appearance. However, this type of product puts cosmetic companies in a totally different regulatory realm.

Information

Lipid-based formulations in cosmeceuticals and biopharmaceuticals, Ahmad, A., Ahsan, H., *Biomed. Dermatol.* 4, 12, 2020.

New insight into phase behavior and permeability of skin lipid models based on sphingosine and phytosphingosine ceramides, Uche, L.E., *et al.*, *BBA Biomembranes*, 1861, 7, 1317-1328, 2019.

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Epidermal surface lipids, Pappas, A., *Dermatoendocrinol.*, 1(2), 72–76, 2009.

A recent article in *Cosmetics and Toiletries* details how regulations will affect the claims companies can make regarding products designed specifically to interact with the microbiome (https://tinyurl.com/45nnh9s3). A product designed to replace parts of a disintegrating skin barrier would face similar governmental concerns. In general, regulations state that to be considered a cosmetic, a product cannot make any therapeutic claim to modify body functions. There is no international regulatory oversight for cosmetics, and managing the details of the laws in a given country—or a specific state in the United States—adds a layer of complication for manufacturers developing a product whose cosmetics claim could be questioned.

Finally, there is the issue of whether aged skin is structurally viable enough to accept replenishing lipids. The skin loses its fat content as it ages, but it also loses the proteins and polysaccharides that hold those fats in place. More research is needed to determine if the skin can absorb lipids from a topical product and incorporate them into the skin matrix.

Schwartz says the industry has made a lot of progress in the past ten to twenty years in terms of creating functional products with complex formulations. "Just having some of the lipid classes in a finished product is lightyears ahead of when all products were mineral oil with a bee's wax, sodium hydroxide emulsifier as an *in-situ* surfactant," he says.

Maybe ten or twenty years in the future, bioengineering will have the ability to create hyper specific molecules that match the skin. But for now, consumers will have to be satisfied with close enough. "We probably have to accept that what is going to be commercially available will only ever be a decent approximation of what is natively on the skin," says Schwartz.

While we wait for cosmetic products to innovate, Pappas informed his audience that one way skin lipids are replenished is through the fats and oils we eat. Until these lipids come in a jar, the best way to restore them is through our diets.

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

Solvay phases out fluorosurfactant use in the US

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

Leigh Stringer

Belgium-based multinational chemical company Solvay has said it will stop using fluorosurfactants as processing aids in the production of fluoropolymers in the United States by the end of June 2021—a move made possible by new polymerization technology..

Fluorosurfactants—which include perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)—are usually members of the per- and polyfluoroalkyl substance (PFAS) class of chemicals. Fluoropolymers may also be considered PFASs, depending on how the class is defined, but are generally considered to be of lower concern because of their higher molecular weight.

Solvay will use its new process technology to make fluoropolymers for a wide variety of applications, including coatings and sealing adhesives.

The announcement followed initiation in November 2020, of a legal dispute between the company and the New Jersey Department of Environmental Protection (NJDEP) over PFAS emissions from its site in West Deptford.

Fluorosurfactants have long been used as processing aids in emulsion polymerization to make certain types of fluoropolymers.

Some, such as PFOA and PFOS, have been identified as hazardous to the environment and human health. Consequently, certain countries and regions have imposed regulatory measures (the EU, for example, and at the global level under the UN treaty, the Stockholm Convention on Persistent Organic Pollutants).

Furthermore, the entire class of PFASs has come under scrutiny in Europe and the United States, with the former currently considering a restriction for all PFASs, which is expected to enter into force in 2025.

Unregulated fluorosurfactants have largely replaced PFOA and PFOS. However, some of the big fluoropolymer manufacturers have adopted processes that do not require their use.

US-based multinational 3M said it has offered fluoropolymer products that are manufactured without fluorinated surfactant technologies since 1996. However, it continues to use fluorinated surfactants for certain products where manufacturing processes, product performance, or customer needs require their use. In these cases, 3M said it uses "highly efficient capture and recycling technologies in keeping with our commitment to environmental stewardship".

Similarly, US chemicals company, Chemours, said some of its product lines transitioned to non-fluorinated surfactants over a decade ago, but for others used in critical applications that require the highest performance characteristics, such as resistance to corrosive, temperature, and environmental extremes, it is "not aware of any non-fluorinated alternatives that can meet our performance and sustainability requirement". The company said that, despite this, it continues to invest in research projects to "explore options".

Stockholm University professor, Ian Cousins, who is also the lead for the Global PFAS Science Panel, told *Chemical Watch* that—based on the information in Solvay's press release— it looks as if the company has "made a step in the right direction."

The release of fluorosurfactants during manufacture of fluoropolymers was one the biggest environmental concerns of fluoropolymers during their lifecycle, he said.

However, fluoropolymers themselves are still PFASs and are highly persistent, added Professor Cousins. "There will therefore be end of life issues with regard to waste management."

Solvay confirmed to *Chemical Watch* that it used process aids containing PFOA at the West Deptford site until 2003—and used PFNA until 2010—but after this it continued to use alternative PFASs.

According to the complaint filed by the NJDEP, the company has blocked attempts to make public the specific identities of those substances, claiming such information is confidential and proprietary.

Leigh Stringer is global business editor for Chemical Watch.

2022 AOCS Awards Call for

Get ready – award nominations open July 1, 2021!

Society Awards

NOMINATION DEADLINE ▶ AUGUST 15, 2021

A.R. Baldwin Distinguished Service

Recognizes long-term, distinguished service to AOCS in positions of significant responsibility. The Society's highest service award. Sponsored by Cargill.

$2,000 honorarium, $1,500 travel allowance and a plaque

AOCS Award of Merit

Recognizes an AOCS Member who has displayed leadership in administrative activities, meritorious service on AOCS committees or performed an outstanding activity or service.

Plaque and recognition during the AOCS Annual Meeting

AOCS Fellow

Recognizes achievements in science or extraordinary service to the Society.

Fellow membership status, a plaque and custom medal

Scientific Awards

NOMINATION DEADLINE ▶ AUGUST 15, 2021

Alton E. Bailey

Recognizes outstanding research and/or exceptional service in the field of lipids and associated products.

$750 honorarium and a plaque

AOCS Young Scientist Research

Recognizes a young scientist who has made a significant and substantial research contribution in one of the areas represented by the Divisions of AOCS. Sponsored by the International Food Science Centre A/S.

$1,000 honorarium, $1,500 travel allowance and a plaque

Stephen S. Chang

Recognizes a scientist, technologist or engineer who has made decisive accomplishments in research for the improvement or development of products related to lipids. Provided by the Stephen and Lucy Chang endowed fund.

$1,500 honorarium and a jade horse

Supelco AOCS Research

Recognizes outstanding original research in fats, oils, lipid chemistry or biochemistry. Sponsored by MilliporeSigma, a subsidary of Sigma-Aldrich Corp.

$10,000 honorarium, $1,500 travel allowance and a plaque

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Division Awards

NOMINATION DEADLINE ▶ AUGUST 15, 2021

ANA Division Herbert J. Dutton

Recognizes an individual who has made significant contributions to the analysis of fats, oils and related products.

$1,000 honorarium, $1,000 travel allowance and a plaque

BIO Division Ching Hou Biotechnology

Recognizes a scientist, technologist or leader who has made contributions to the advancement of the Biotechnology Division's area of interest.

$1,000 honorarium and a plaque

EAT Division Timothy L. Mounts

Recognizes research related to the science and technology of edible oils or derivatives in food products, which may be basic or applied in nature.

$750 honorarium and a plaque

EAT Division Outstanding Achievement

Recognizes a scientist, technologist or leader who has made significant contributions to the Division's area of interest or to the advancement of edible oils.

$500 honorarium and a plaque

H&N Division Ralph Holman Lifetime Achievement

Recognizes an individual who has made significant contributions to the Division's area of interest, or whose work has resulted in major advances in health and nutrition.

$500 honorarium, $1,000 travel allowance, a signed orchid print and a plaque

H&N Division New Investigator Research

Recognizes a young scientist who is making significant and substantial research contributions in one of the areas represented by the Health and Nutrition Division of AOCS.

$1,000 honorarium and a plaque

IOP Division ACI/NBB Glycerine Innovation

Recognizes outstanding achievement for research in new applications for glycerine with emphasis on commercial viability. Sponsored by the American Cleaning Institute (ACI) and the National Biodiesel Board (NBB).

$5,000 honorarium and a plaque

PCP Division Lifetime Achievement Award

Recognizes significant contributions to the advancement of protein and co-products through research and applications.

$1,500 travel allowance and a plaque

Nominations

PRO Division Distinguished Service
Recognizes and honors outstanding and meritorious service to the oilseed processing industry.
$1,000 travel allowance and a certificate

S&D Division Samuel Rosen Memorial
Recognizes a surfactant chemist for significant advancement or application of surfactant chemistry principles. Initiated by Milton Rosen and this Division.
Plaque

S&D Division Distinguished Service
Recognizes outstanding and commendable service to the surfactants, detergents and soaps industry.
Plaque

Student Awards
NOMINATION DEADLINE ▶ OCTOBER 1, 2021

Honored Student
Recognizes graduate students in any area of fats and lipids. To receive the award, a candidate must remain a registered graduate student and must not have received a graduate degree or have begun career employment before the Society's Annual Meeting.
$500 travel allowance for U.S. and Canada residents [$1,000 travel allowance for recipients residing outside of those countries], complimentary AOCS Annual Meeting registration and lodging, and a certificate

Hans Kaunitz
Recognizes a student conducting research related to fats, oils and detergent technology.
$1,000 honorarium, $500 travel allowance and a certificate

Lipid Chemistry and Nutrition
Recognizes outstanding performance and achievement of a graduate student conducting research in lipid chemistry and nutrition. Sponsored by Seawit Co., Inc.
$1,000 honorarium, $550 travel allowance and a plaque

Lipid Processing and Biotechnology
Recognizes outstanding performance and achievement of a graduate student conducting research in lipid processing and biotechnology. Sponsored by Myande Group Co., Inc.
$1,000 honorarium, $550 travel allowance and a plaque

Ralph H. Potts Memorial Fellowship
Recognizes a graduate student conducting research related to fatty acids and their derivatives, such as long-chain alcohols, amines and other nitrogen compounds. Sponsored by Nouryon.
$2,000 honorarium, $500 travel allowance and a plaque

AOCS Division Student Awards
Recognizes over 20 students from any institution of higher learning, who are studying and doing research towards an advanced degree in fats, oils and related materials.
Awards range from $50 to $1,000 and a certificate

Each award has its own specific and unique nomination requirements. Please refer to the website for full details.

The award recipient must agree to attend the AOCS Annual Meeting & Expo and present an award lecture. The 2022 AOCS Annual Meeting will be held in Atlanta, Georgia, USA, from May 1–4, 2022.

Meet Fred Holzhauer

Member Spotlight is a slice of life that helps AOCS members get to know each other on a more personal level.

Fred Holzhaur at Sonoma Plaza in 2017, just prior to going on stage at the weekly Valley of the Moon Certified Farmers' Market, for an audience of around 2,000 persons.

Fast facts

Name	Fred Holzhauer
Joined AOCS	1991
Education	B.Sc. in metallurgical engineering from the Colorado School of Mines (Golden, Colorado, USA)
Job title	Technical Marketing Manager
Employer	Brenntag Group (Santa Fe Springs, California, USA)
Current AOCS involvement	Presenter, 2018 AOCS Annual Meeting

PROFESSIONAL

What's a typical day like for you?
My days vary a lot. In general, as a professional product developer, being a tech rep at a chemical distributor is like playing in the biggest sandbox with the most toys: You are expected to show the younger kids which tools work best for the kind of castle they are building. You get to design your own castles and work on them with your friends. And adults honor your needs; they listen when you ask for other toys for the next castle.

My favorite part of my job is…
Imparting the craft to eager folk and taking care of the planet while I do it. (They don't teach what we do in school.)

Flash back to when you were 10 years old. What did you want to be when you grew up?
I wanted to build rockets and went crazy with model rockets for years.

Why did you decide to do the work you are doing now?
Because I get to help people grow and I get to do meaningful work for the planet. Further, I get to fix or build things and I have fun doing all of it.

Is there an achievement or contribution you are most proud of? Why?
I was pretty much the poster child for Attention Deficit Hyperactivity Disorder (yah, it's real). Surviving a disciplined engineering school like the Colorado School of Mines was a stratospheric reach for me. I'm glad for the great education there, as well as the senses of growth, realization, and relief that came with the accomplishment.

What event, person, or life experience has had the most influence on the direction of your life?
Hands down, that goes to my Dad. He was an engineer and machinist; he taught me how to fix almost anything. And fishing…

PERSONAL

How do you relax after a hard day of work?
I read something every day and get outdoors for something. I also like to cook. Plus, I'll do a couple Sudoku puzzles before I retire.

What is the most impressive thing you know how to do?
I'm a fairly skilled guitarist, still appearing in regional bands.

What skill would you like to master?
So many to choose from… I'd like to pick up a language by immersing for a while in another country.

What are some small things that make your day better?
Speaking with an industry friend on the phone brightens my day. An uninterrupted block of time makes for a hugely good lab day.

What are you looking forward to in the coming months?
Vaccination.

PATENTS

Use of a mixture of a complex ester with a monocarboxylic acid to reduce friction

Zorn; M., BASF SE, US10927319, February 23, 2021

The present invention relates to the use of a mixture comprising (I) at least one complex ester obtainable by an esterification reaction between (A) at least one aliphatic linear or branched C.sub.2-to C.sub.12-dicarboxylic acid, (B) at least one aliphatic linear or branched polyhydroxy alcohol with 3 to 6 hydroxyl groups, and (C) as a chain stopping agent (C1) at least one aliphatic linear or branched C.sub.1-to C.sub.30-monocarboxylic acid in case of an excess of component (B), or (C2) at least one aliphatic linear or branched monobasic C.sub.1-to C.sub.30-alcohol in case of an excess of component (A), and (II) at least one aliphatic monocarboxylic acid having from 12 to 30 carbon atoms in a weight ratio of (I):(II) of from 20 to 80:80 to 20 as an additive in a fuel for different purposes.

Lipid-based ophthalmic emulsion

Ketelson, H.A., *et al.*, Alcon Inc., US10925892, February 23, 2021

The present invention is directed to a lipid-based ophthalmic emulsion. The emulsion has an increased amount of a mucoadhesive galactomannan polymer that promotes a long-lasting protection against desiccation and moisture retention.

PVC plasticizers and methods for making thereof

Wei, X., *et al.*, Kraton Polymers U.S. LLC, US10927234, February 23, 2021

A plasticized PVC composition free of phthalate is disclosed. The composition comprises a tertiary diamide plasticizer prepared from biorenewable feedstock such as fatty acid selected from tall oil fatty acids, tall oil fatty acid monomers, fatty acids derived from tall oil fatty acid, and mixtures thereof. The tertiary diamide plasticizer is a reaction product of a reactant mixture comprising the fatty acid and one or more monocyclic diamines.

Composition for transdermal delivery, comprising nanoemulsion and modified layered double hydroxide

Lee, J.H., *et al.*, H&A Pharmachem Co., Ltd., US10925816, February 23, 2021

The present invention relates to: a composition for transdermal delivery, comprising 1) a nanoemulsion comprising an active ingredient, saturated lecithin, phytosteryl/behenyl/octyldodecyl lauroyl glutamate, a polyol, and water, and 2) a modified layered double hydroxide; and a preparation method therefor.

Toothpaste composition and method of making same

Price, G., *et al.*, EWC & Associates, LLC, US10925828, February 23, 2021

A toothpaste composition having a plant oil constituent together with white or a close shade of white coconut shell activated charcoal constituent is disclosed herein.

Soy protein and carbohydrate containing binder compositions

Lester; U., *et al.*, Johns Manville, US10934646, March 2, 2021

Soy protein and carbohydrate containing binder compositions are described. The binder compositions may include a carbohydrate, a nitrogen-containing compound, and a soy protein. The binder compositions may also optionally include thickening agents such as modified celluloses and polysaccharides.

Surfactant-free water-free foamable compositions, breakable foams and gels and their uses

Tamarkin; D., *et al.*, Vyne Pharmaceuticals Ltd., US10946101, March 16, 2021

A substantially surface-active agent free composition which includes a hydrophobic solvent, and/or a petrolatum, a paraffin wax and/or a fatty alcohol, a fatty acid and/or a wax and/or shea butter, with and without a propellant. A substantially surface-active agent free composition, further comprising, a tetracycline antibiotic, or a vitamin D derivative, or one or more other active agents. A method of treatment using a substantially surface-active agent free composition.

Stabilization of cosmetic compositions comprising fish oils and hydroxylated fatty acid and/or its derivatives

Tomashevskaia; M., *et al.*, Conopco, Inc., US10945945, March 16, 2021

Stabilized skin care compositions are described. The compositions comprise a fish oil component that yields a product of oxidation and the component is stabilized with a radical scavenger, a peroxide decomposer and hydroxylated fatty acid and/or a derivative thereof.

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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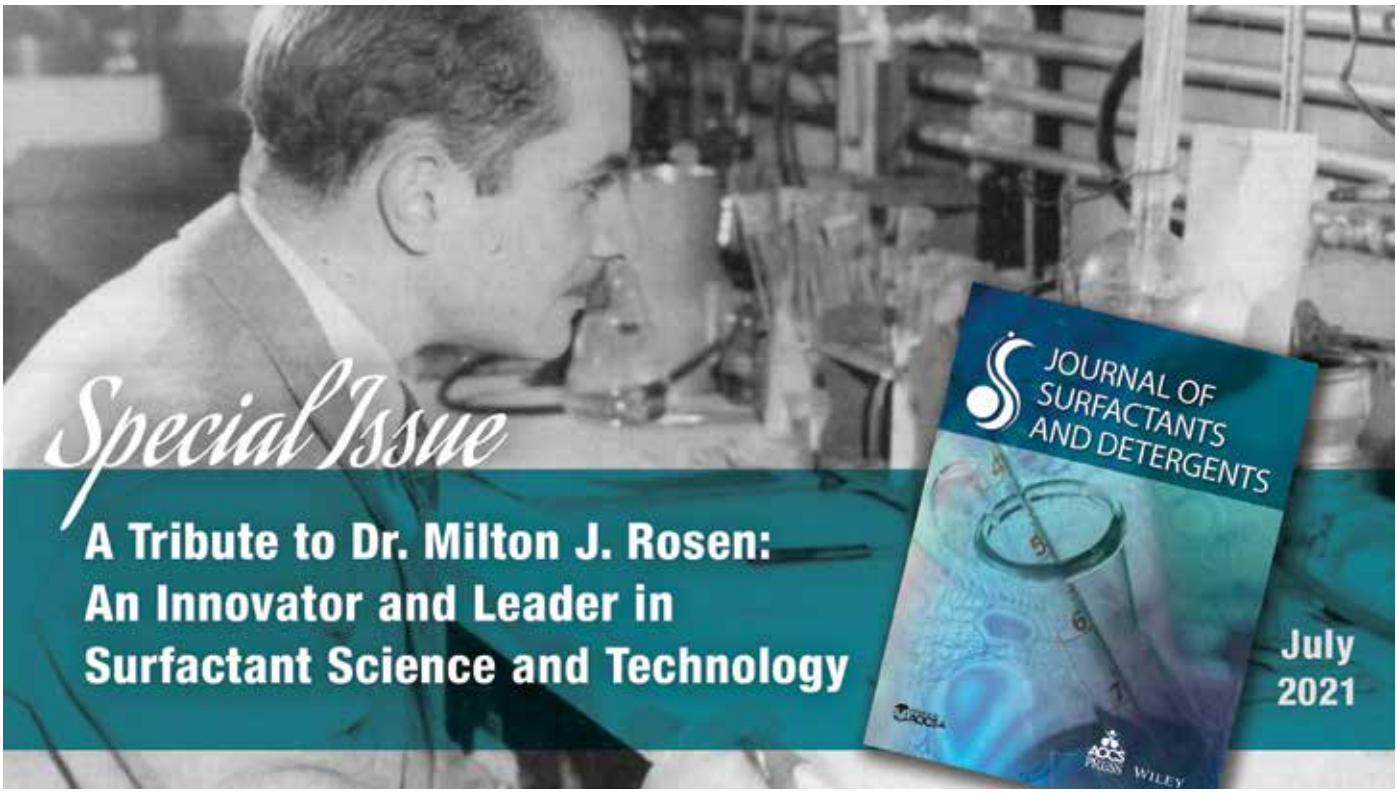

JSD special issue honors Milton J. Rosen

In July of 2021, the *Journal of Surfactants and Detergents (JSD)* will commemorate Professor Milton J. Rosen's contributions to surfactant science and industrial application of surfactants with a special collection of papers. The collection includes a biography of Dr. Rosen's life and accomplishments, including a list of publications, patents, and some unpublished photographs taken over his career (Zhu, Vinson, Smith and Hayes, 2021).

For those who work in the field of surfactant science, Professor Rosen is a legendary figure whose memorable contributions include structure-property relationships of surfactants, surfactant synergy and the infamous beta parameter, and his work on Gemini surfactants.

"What happens when we vary the size and shape of the hydrophobic and hydrophilic groups is still the main concern in surfactant science, and Dr. Rosen's work has formed the basis of our modern thinking and approaches," says *JSD* Editor-in-Chief Douglas Hayes.

Dr. Rosen was also deeply concerned about the impact of surfactants on humans and the environment, and once said: "Surfactants should be based on renewable resources like fats and proteins, not petroleum or other things like that. They must have practically no significant impact on the environment and must be mild or have no effect on skin surfaces."

During his over 65 year career, Dr. Rosen published more than 100 journal articles and nine books. *Surfactants and Interfacial Phenomena*, which many refer to as the "Bible of Surfactants," is a handy reference found on almost every surfactant scientist's desk. Now in its fourth edition, the book explains in simple, straightforward terms how surfactants behave in interfacial processes such as foaming, wetting, emulsification and dispersion, solubilization, and detergency. The book is usually the first place to look when encountering some unexpected result in the laboratory, and people new to the field use it to become familiar with the use of surfactants in virtually every application area of modern life.

A QUICK PREVIEW

Review articles

- Naskar, *et al*. (JSDE12503, https://doi.org/10.1002/jsde.12503), present an unambiguous method for determining critical micelle concentration (CMC) using derivative plots and use the values obtained to calculate surfactant synergy using the Rubingh and Rosen approach. Interaction parameters are discussed in relation to detergency, foaming, solubilization, and cloud point.
- Synergy of anionic and cationic surfactant mixtures is reviewed by Sabatini, *et al*. (JSDE12512, https://doi.org/10.1002/jsde.12512), in relation to minimizing surfactant precipitation, microemulsion formation, and enhanced solubilization.
- A study on synergistic effects between anionic and sulfobetaine surfactants for stabilization of foams tolerant to crude oil in foam flooding was presented by Cui, *et al*. (JSDE12501, https://doi.org/10.1002/jsde.12501). The study illustrates that the foam stability in the presence of oil can be greatly improved by use of a mixture of anionic surfactants such as SDS and AES with sulfobetaines, with a long alkyl chain performing better. The improved foam stability is attributed to the synergistic interaction of the anionic surfactants and sulfobetaines in view of the negative β values. Furthermore, the improved foam stability in the presence of oil is discussed by use of the factors of Entering coefficient (E), Spreading coefficient (S), and Bridging coefficiency (B).

Gemini surfactants

- The equilibrium and dynamic surface properties of Gemini salts of linear alkyl benzene sulfonate were determined by surface tension, conductivity, pendant drop and spinning drop methods by Smith, *et al*. (JSDE12496, https://doi.org/10.1002/jsde.12496). Performance in foaming, hard surface cleaning, and laundry detergency are discussed in relation to the surface properties.
- The surface, micellar, and aggregation behavior of non-cytotoxic imidazolium Gemini surfactants were determined by Shaheen, *et al*. (JSDE12472, https://doi.org/10.1002/jsde.12472), using a variety of different experimental techniques. The superior aggregation properties and non-cytotoxic nature of the imidazolium Gemini surfactants has application in biomedical and pharmaceutical sciences.
- Synthesis and characterization of zwitterionic Gemini surfactants is presented by Mansha *et al*. (JSDE12474, https://doi.org/10.1002/jsde.12474). These new Gemini surfactants have potential in oilfield applications due to their ability to build viscosity.

Three-phase micellar systems at optimal salinity

- Effect of ethylene oxide group in the anionic–nonionic mixed surfactant system on microemulsion phase behavior is discussed by Kittithammavong, *et al*. (JSDE12475, https://doi.org/10.1002/jsde.12475). The findings from this work provide an understanding of how to formulate mixed anionic–nonionic microemulsion systems using the hydrophilic-lipophilic difference (HLD) model for oils that possess a wide range of equivalent alkyl chain lengths (EACN).
- Phase behavior of nonionic surfactant mixtures with medium chain triglyceride in water is discussed by Wettig, *et al*. (JSDE12510, https://doi.org/10.1002/jsde.12510). Surfactant interaction parameters were determined for surfactant mixtures and related to Winsor microemulsion formation for drug delivery applications.
- The role of micelle solubilization on enhanced oil recovery was examined by Feng, *et al*. (JSDE12488, https://doi.org/10.1002/jsde.12488), using naphthalenic arylsulfonates (NAS). The solubilization capacity of NAS micelles increases with increasing concentration to almost 40% indicating that micelle solubilization can increase oil recovery efficiency even without ultralow IFT.
- Incorporation of membrane proteins (MP) into bicontinuous microemulsions (BμEs) at optimum salinity was discussed by Hayes, *et al*. (JSDE12500, https://doi.org/10.1002/jsde.12500). The study suggests that successful MP encapsulation in BμEs is highly dependent on the level of synergy between MP and the particular microemulsion system being employed. These results are intriguing and additional research is warranted to better identify approaches for MP encapsulation for use in biochemical reactions.
- The interfacial rheology of SOW systems at optimum formulation were determined by a modified spinning drop tensiometer. In this work, Marquez and Salager, *et al*. (JSDE12502, https://doi.org/10.1002/jsde.12502), used model oils and high asphaltene crude oil solubilized by salinity scans and by varying the ratio of nonionic surfactant mixtures. The findings confirm that at optimum formulation the interfacial tension, and interfacial elastic moduli show a deep minimum consistent with the observed decrease in emulsion stability at optimum formulation.
- A novel approach to studying surfactant solubilization was discussed by Kocherginsky and Sharma (in press during time of production). Biomimetic membranes were constructed by impregnating nitrocellulose filters with fatty acid esters and triglycerides. When used as a membrane separating pure water from surfactants solution, a transmembrane electric potential is observed which is proportional to the log of the surfactant concentration. At surfactant concentrations near the CMC, spontaneous oscillations in transmembrane potential are observed. At concentrations above the CMC, the potential disappears which is explained by washing out of the fatty acids from the pores of the membrane.

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Keshun Liu, U.S. Department of Agriculture, Agricultural Research Service, USA

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IOP Industrial Oil Products
PRO Processing
PCP Protein and Co-Products
S&D Surfactants and Detergents

Review Articles

PRO EAT IOP Improving sustainability of palm oil production by increasing oil extraction rate: a review

Chew, C.L., *et al.*, *Food Bioprocess Technol. 14*: 573–586, 2021, https://doi.org/10.1016/j.foodres.2021.110312.

Tremendous efforts have been devoted to improving the sustainability of palm oil production. One strategy is to improve the oil extraction rate (OER) during the milling process. The average OER in Malaysia has remained stagnant between 19 and 21% for the past 40 years. Based on the world production of palm oil in 2018, approximately 3 million metric tons of additional palm oil can be produced globally with a 1% increase in OER. This article presents the current status of the palm oil milling process and the factors affecting the OER. Subsequently, methods to improve the OER are reviewed.

H&N IOP A comprehensive review on different classes of polyphenolic compounds present in edible oils

Zeb, A., *Food Res. Int.143*: 1103312, May 2021, https://doi.org/10.1016/j.foodres.2021.110312.

Edible oils are used as a frying medium and in food preparation. Triacylglycerols are their major components, while other compounds are classified as minor constituents, including polyphenols. This class of compounds plays an important role in the thermal stability and quality attributes of finished industrial food products. In addition to antioxidants, the desired thermal stability of edible oil is achieved by fortifying or mixing edible oils. This comprehensive review was therefore aimed to review the different classes of polyphenolic compounds present in commonly consumed edible oil. The edible oils reviewed include soybean, olive, rapeseed, canola, sunflower, flaxseed, sesame, cottonseed, palm, almond, peanut, chestnut, coconut, and hazelnut. The identified classes of polyphenolic compounds, such as simple phenols, hydroxybenzoic acids, phenylethanoids, hydroxycinnamic acid, esters of hydroxycinnamic acids, coumarins and chromans, stilbenes, flavonoids, anthocyanins, and lignans are discussed. It was observed that a single edible oil from different origins showed the varied composition of the different classes of phenolic compounds. Among the oils, soybean, sunflower, olive, and brassica, received higher attention in terms of polyphenol composition. Among the different classes of phenolics, hydroxybenzoic acids, hydroxycinnamic acid, and flavonoids were the most widely present compounds. Phenolic compounds in edible oils possess antioxidant, antibacterial, anti-viral, anti-inflammatory, anti-tumor, cardioprotective, neuroprotective, anti-diabetic, and anti-obesity properties.

Original Articles

BIO IOP PCP Depolymerization and conversion of lignin to value-added bioproducts by microbial and enzymatic catalysis

Weng, C., *et al.*, *Biotechnol. Biofuel.*, *84*, open access, 2021, https://doi.org/10.1186/s13068-021-01934-w.

Lignin, the most abundant renewable aromatic compound in nature, is an excellent feedstock for value-added bioproducts manufacturing, but intrinsic heterogeneity and recalcitrance has hindered efficient lignin biorefinery and utilization. Compared with chemical processing, bioprocessing with microbial and enzymatic catalysis is a clean and efficient method for lignin depolymerization and conversion. Generally, lignin bioprocessing involves lignin decomposition to lignin-based aromatics via extracellular microbial enzymes and further converted to value-added bioproducts through microbial metabolism. This review discusses the most recent advances in degradation and conversion of lignin to value-added bioproducts catalyzed by microbes and enzymes and includes a comparative analysis of the lignin-degrading microorganisms of white-rot fungi, brown-rot fungi, soft-rot fungi, and bacteria under aerobic and anaerobic conditions. The paper discusses the catalytic metabolism of the microbial lignin-degrading enzymes of laccase, lignin peroxidase, manganese peroxidase, biphenyl bond cleavage enzyme, versatile peroxidase, and beta-etherize, and reviews the microbial metabolic process of H-lignin, G-lignin, S-lignin based derivatives, protocatechuic acid, and catechol. Lignin was depolymerized to lignin-derived aromatic compounds by the secreted enzymes of fungi and bacteria, and the aromatics were converted to value-added compounds through microbial catalysis and metabolic engineering. The authors propose new insights for future work to overcome the recalcitrance of lignin and convert it to value-added bioproducts by microbial and enzymatic catalysis.

BIO IOP PCP Role of copper in the enhancement of astaxanthin and lipid coaccumulation in *Haematococcus pluvialis* exposed to abiotic stress conditions

Guo, H., *et al.*, *Bioresour. Technol.* 335: 125265, 2021, https://doi.org/10.1016/j.biortech.2021.125265.

This study investigated the effects of copper (Cu) on astaxanthin and lipid biological synthesis in unicellular alga *Haematococcus pluvialis* under high-light (HL) and nitrogen-deficient (ND) conditions. During a 15-day cultivation period, the astaxanthin and lipid contents reached peak values (3.32% and 47.72%) under 6 micromolar Cu treatment, respective increases of 66.87% and 34.99% compared to the nontreated group. The application of Cu also increased the transcriptional expression of biosynthesis genes and antioxidant enzyme-related genes, increased the intracellular calcium (Ca^{2+}) level, but led to a decrease in reactive oxygen species (ROS) levels. Additionally, Cu treatment induced the activation of calcium-dependent protein kinases (CDPKs) and mitogen-activated protein kinases (MAPKs). This approach simultaneously facilitated astaxanthin and lipid production, and the role of Cu were elucidated on the regulation of signal transduction (e.g., Ca^{2+}, CDPK, MAPK and ROS) in the carotenogenesis and lipogenesis in *H. pluvialis*.

BIO PCP Creating biotransformation of volatile fatty acids and octanoate as co-substrate to high-yield medium-chain length polyhydroxyalkanoate

Li, D., *et al.*, *Bioresour. Technol.* 331: 125031, 2021, https://doi.org/10.1016/j.biortech.2021.125031.

Using mixed microbial consortium (MMC) to accumulate polyhydroxyalkanoate (PHA) is an effective strategy to reduce high production cost and excess sludge. In this study, a process for the production of short-chain-length and medium-chain-length PHA using volatile fatty acids (VFAs) from pretreated wood hydrolysate synergistic with octanoate as co-substrate was proposed. The effects of co-substrate ratios on PHA accumulation ability and physical properties were investigated. The incorporation of co-substrate accelerated the time of PHA and 3-hydroxyoctanoate, reaching maximum production (1834 and 280 mg COD/L). The highest PHA content was 53.0% (w/w), which was equivalent to that reported previously. The biopolymer films possessed high tensile strength, Young's modulus, and could be used in the field of water vapor barrier requirements. The accumulation strategy applied for

converting fermentation products VFAs and octanoate co-substrate into high value and yield PHA could potentially demonstrate the valuable for low-cost large-scale production.

EAT PRO The encapsulation of hydroxytyrosol-rich olive oil in Eudraguard® protect via supercritical fluid extraction of emulsions

Tirado, D.F., *et al.*, *J. Food Eng. 290*: 110215, 2021, https://doi.org/10.1016/j.jfoodeng.2020.110215.

The SFEE technology was used to micronize the food-approved-biopolymer Eudraguard® protect. After setting the ratio of emulsion phases to 20:80 ethyl acetate:water, higher surfactant (0.1–10.0%) and lower polymer (1–10%) concentrations reduced the size of the particles. By halving the stirring speed to 1250 rpm during the homogenization of the emulsion, larger particles were formed. All these manipulations allowed the creation of particles ranging from 10 nm to 200 nm. A higher viscosity of the organic phase, achieved with 2% vitamin E, increased the particle size to 300 nm. Afterwards, SFEE was used to encapsulate hydroxytyrosol-rich olive oil (HT-oil), obtained from alperujo, in Eudraguard® protect for its preservation. Spherical non-aggregate particles were formed with an average of 230 nm. High degrees of encapsulation were possible (up to 99%) resulting in loadings of HT-oil in the obtained particles of 39% with 0.7 mg HT per g of particle.

EAT LOQ Recovery of ascorbic acid, phenolic compounds, and carotenoids from acerola by-products: an opportunity for their valorization

Poletto, P., *et al.*, *LWT 146*, 111654, 2021, https://doi.org/10.1016/j.lwt.2021.111654.

Ascorbic acid, phenolic compounds, and carotenoids were extracted from acerola (*Malpighia emarginata* DC.) by-products using gas-expanded liquids (GXLs) based on carbon dioxide expanded ethanol at 40°C and 7 MPa. The by-products generated in the processing of acerola: bagasse (seed and peel) and non-pomace (from the juice clarification step), were studied separately. The overall extraction yields obtained were 3.8 and 12.9 g/100 g for bagasse and non-pomace, respectively. Ascorbic acid was not detected in the bagasse extract, while 158.2 mg/g extract was found in non-pomace extract, and 193.7 mg/g was found in the acerola juice powder. The higher the concentration of ascorbic acid, the higher the antioxidant activity of the extracts. The phytochemical profile obtained by LC-Q-TOF-MS/MS showed a higher number of phenolic compounds (hydroxycinnamic acids and flavonoids) in the bagasse and non-pomace extracts when compared to acerola juice. In addition, GXL promoted the extraction of a pool of carotenoids (lutein and beta-carotene), pheophytin, and chlorophyll derivatives detected by LC-APCI-MS/MS. The obtained extracts, rich in bioactive compounds, open an opportunity for the valorization of acerola by-products, meeting the current demand for natural nutraceuticals rich in vitamin C and polyphenols.

EAT PRO Minimizing hazardous impact of food waste in a circular economy—advances in resource recovery through green strategies

Usmani, Z., *et al.*, *J. Hazard. Mater 126154*, online May 19, 2021, https://doi.org/10.1016/j.jhazmat.2021.126154.

This review brings together some of the recent progress made in the green strategies toward food waste valorization. Under circular economy principles food waste can be used as a sustainable supply of high-value energy, fuel, and nutrients through green techniques such as anaerobic digestion, co-digestion, composting, enzymatic treatment, ultrasonic, hydrothermal carbonization. Recent advances made in anaerobic co-digestion are helping in tackling dual or even multiple waste streams at once with better product yields. Integrated approaches that employ pre-processing the food waste to remove obstacles, such as volatile fractions, oils, and other inhibitory components from the feedstock to enhance their bioconversion to reduce sugars. Research efforts are also progressing in optimizing operational parameters, such as temperature, pressure, pH and residence time, to enhance further the output of products such as methane, hydrogen, and other platform chemicals, such as lactic acid, succinic acid, and formic acid.

EAT LOQ Antimicrobial, antioxidant, and physical properties of chitosan film containing *Akebia trifoliata* (Thunb.) Koidz. peel extract/montmorillonite and its application

Jiang, Y., *et al.*, *Food Chem. 130111*, online May 15, 2021, https://doi.org/10.1016/j.foodchem.2021.130111.

A novel active packaging film was prepared in this study that incorporated *Akebia trifoliata* (Thunb.) Koidz. peel extracts (APE) and montmorillonite (MMT) into chitosan (CH) films. Compared with the pure CH film, the CH/APE film showed significantly higher tensile strength, elongation at break, UV light resistance, and antibacterial activity; the CH/MMT film displayed significant increases in contact angle, antioxidant activity, oxygen permeability, and thermal stability. SEM and AFM analyses showed that the additions were well-distributed into the CH matrix, but MMT induced a more compact and rougher structure. The CH-based film formula was optimized using the single-factor test and Box-Behnken design and was 0.15 % MMT, 0.15 % APE, and 1.50 % CH. Besides, the optimized coating was applied in the postharvest preservation of A. trifoliata fruits, which yielded a significant effect on the delaying crack and mature of the fruits during 35 days of storage at 5°C.

LOQ H&N Enrichment of mayonnaise with a high-fat fish oil-in-water emulsion stabilized with modified DATEM C14 enhances oxidative stability

Yesiltas, B., *et al.*, *Food Chem 341*: 128141, 2021, https://doi.org/10.1016/j.foodchem.2020.128141.

Enrichment of mayonnaise using delivery emulsions (DEs) containing 70% fish oil versus neat fish oil was investigated. DEs were produced with combined use of sodium caseinate, diacetyl tartaric acid esters of monoand diglycerides (DATEM), and/or modified DATEMs with different length (C12 or C14) and covalently attached caffeic acid. Physical and oxidative stability of the mayonnaises were analyzed based on parameters including droplet size, viscosity, peroxide value, volatile compounds, and sensory properties. DEs addition to mayonnaise resulted in larger droplets and lower viscosity compared to neat fish oil. However, zeta potential was higher in mayonnaises with DEs containing DATEMs. Mayonnaise containing DATEM C14 had higher protein surface load leading to a thicker interfacial layer, lower formation of hexanal, (E)-2-hexenal, and (E)-2-heptenal as well as lower rancid odor intensity compared to mayonnaise containing DATEM and free caffeic acid, and thus benefitted from the location of the antioxidant at the interface.

PCP Green bioprocessing of protein from *Chlorella vulgaris* microalgae towards circular bioeconomy

Azim bin Azmi, A., *et al.*, *Bioresour. Technol. 333*: 125197, 2021, https://doi.org/10.1016/j.biortech.2021.125197.

This study studied the potential of producing a system with high microalgal protein recovery and separation using a one-step or integrated downstream process, which could, in turn, enable green biorefinery of protein and contribute to a circular bioeconomy while reducing energy, labor, and cost. By using electric three phase partitioning flotation system, high protein recovery yield, R of 99.42 ± 0.52%, and high separation efficiency, E of 52.72 ± 0.40% system was developed. Scaling up also showed high protein recovery yield with R value of 89.13 ± 1.56%. Total processing duration (extraction, separation, and purification) was also significantly reduced to 10 min. This system showed remarkable potential in reducing processing time, alternatively cost of production, benefiting microalgal downstream processing. Concisely, through this system, microalgal bioprocessing will no longer be complex allowing a wide array of potentials for further studies in this field.

PRO IOP One-pot fungal biomass-to-biodiesel process: influence of the molar ratio and the concentration of acid heterogenous catalyst on reaction yield and costs

Bento, H.B.S., *et al.*, *Fuel*, *300*, September 15, 2021, https://doi.org/10.1016/j.fuel.2021.120968.

This work evaluates a microbial-based biodiesel production process through simultaneous esterification and transesterification of the lipid-rich fungal biomass using ethanol as both extractor and acyl acceptor. Two of the most influential parameters were evaluated, the molar ratio of ethanol to the oil, and the concentration of a heterogeneous acid catalyst (H_3PMo/Al_2O_3), with responses in terms of conversion to ethyl esters and an estimated cost of the process variables. Fungal biomass of *Mucor circinelloides* was cultivated in sugarcane molasses media, and the obtained oleaginous cells were used as the source of acylglycerols and free fatty acids for the trans/esterification reactions in a pressurized stainless-steel reactor at 200°C for 6 h. Our results demonstrate that the effects of the two factors analyzed were significant, with an indication that increases in the molar ratio and catalyst favor the reaction yield. In the reaction system, a molar ratio of 120:1 (ethanol: oil) and 15 wt% of catalyst yielded 96.6% of ester content, which meets the minimum limit established by the international standards. Production costs were estimated in function of ethanol and catalyst price and indicated the selected parameters reflected the adequate configuration to reach the stablished minimum ester content.

PRO IOP Biocrude upgrading in different solvents after microalgae hydrothermal liquefaction

Xu, D., *et al.*, *Ind. Eng. Chem. Res., May 8, 2021,* https://doi.org/10.1021/acs.iecr.1c00145.

Hydrothermal liquefaction of the third-generation biomass represented by microalgae can produce biocrude. However, the directly obtained biocrude has a high heteroatom content and a low higher heating value (HHV), which cannot meet the standards of biofuel. In this work, water-insoluble biocrude which was directly gained from microalgae hydrothermal liquefaction (HTL) was upgraded under four kinds of solvents (i.e., methanol, ethanol, acetone, and H_2O) and one type of catalyst (H_2O + Ru/C) at 240–400 C for 1 h. The results show that the HHV and C and H contents of upgraded bio-oil increased and the O/C ratio decreased significantly after solvent upgrading. The highest upgraded bio-oil yield appeared in the case of ethanol upgrading and reached the maximum value of 82.8 wt % at 360°C. The upgraded bio-oil yield of acetone upgrading increased from 45.8 to 68.2 wt % as the temperature increased within 240–400°C. Also, esterification reactions between alcohol and acid in the supercritical system remarkably reduced the content of carboxyl-containing organic matter.

PRO EAT IOP BIO Deacidification of microalgal oil with alkaline microcrystalline cellulose

Li, Q., *et al.*, *Appl. Biochem Biotechnol. 193*: 952–964, 2021, https://doi.org/10.1007/s12010-020-03457-w.

Microalgal oil is considered a promising candidate for edible oils. However, investigation of the refining processes for microalgal oil has been limited, especially deacidification. In this work, microcrystalline cellulose (MCC) was pretreated using different methods and utilized for the first time in the deacidification of microalgal oil. Detection results from FTIR and XRD indicated alkali pretreatment had a significant effect on the structure of MCC. Some inter- and intramolecular hydrogen bonds in AMCC (alkali pretreated MCC) were destroyed, and crystallinity index of cellulose decreased, which increased its adsorption capacity and the reaction of OH groups with free fatty acids. Some NaOH was adsorbed into AMCC through cellulose swelling, which also contributed to de acidification. The interaction with oil was also improved with many cracks and voids on the surface of AMCC. AMCC could reduce the acid value to about 2 mg KOH/g. Comparatively, original MCC and MCC pretreated with microwave or ultrasound did not exhibit the ability to deacidify. Furthermore, the conditions of alkali treatment were optimized. Treatment with 20% NaOH for 20 min was optimal. Compared with other adsorbents, such as sodium silicate and chitosan treated with alkali and resin, only AMCC could effectively reduce acid value while maintaining high lipid recovery. Therefore, AMCC was considered a better adsorbent for the deacidification of microalgal oil.

PRO IOP A new process for biodiesel production from tall oil via catalytic distillation

Albuquerque, A.A., *et al.*, *Chem. Eng. Res. Design 170*: 314–328, June 2021, https://doi.org/10.1016/j.cherd.2021.04.014.

In this work, the techno-economic feasibility of a new process for biodiesel production from crude tall oil (CTO) was investigated. A solid acid-catalyzed (SAC) route based on esterification of free fatty acids (FFA) using a catalytic distillation column (CDC) with Relite CFS as the catalyst was employed. CTO purification was needed to achieve biodiesel standard specifications. A base case and an alternative process for CTO purification from four and three distillation columns were designed, optimized and techno-economically assessed. The alternative process was technically feasible for biodiesel production and also more economical and eco-friendly. Therefore, this process was investigated for biodiesel production by the SAC process using a CDC and a catalytic divided-wall column (CDWC). The CDWC process was not technically feasible, so that the CDC process was globally optimized based on six inputs. Finally, the effect of CTO composition was also investigated, so that a final design was obtained for biodiesel production using CTO coming from the United States of America, Canada, and Scandinavia.

PRO EAT Influence of protein and solid fat content on mechanical properties and comminution behavior of structured plant-based lipids

Dreher, J., *et al.*, *Food Res. Int. 145*: 110416, 2021, https://doi.org/10.1016/j.foodres.2021.110416.

An approach has been developed to structure plant-based lipids to mimic animal fat tissue in processed meat products or analogues. This study investigated the comminution behavior in a bowl chopper of such structured lipids with varying mechanical properties. For products like salami-type sausages, these systems need to withstand comminution to yield particles for inclusion in product matrices. Therefore, samples were prepared from protein suspensions with 6%, 8%, 10%, and 12% soy protein isolate (SPI) and 70% (w/w) total fat with varying solid fat contents (0-30%, w/w). The hardness of samples prepared with 6% and 8% SPI varied between 4.5 and 35.9 N. When comminuted in a bowl chopper, these structures had insufficient mechanical strengths to facilitate the formation of small particles and yielded a coarse paste. Higher concentrations of protein increased hardness (15.9-76.2 N and 15.6-96.1 N, for 10% and 12% SPI, respectively). These samples retained their structural integrity upon comminution yielding individual intact particles. The size of these particles increased with sample firmness, i.e., with increasing amount of protein. The shape of the particles was more elongated the higher the solid fat content as indicated by a higher aspect ratio. Taken together, results show that structural characteristics of the gelled emulsions can be tuned to yield desired fat particles after comminution.

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