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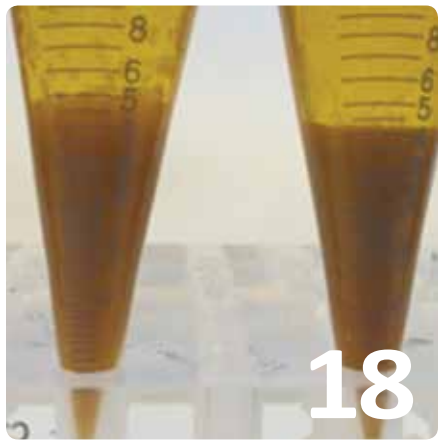

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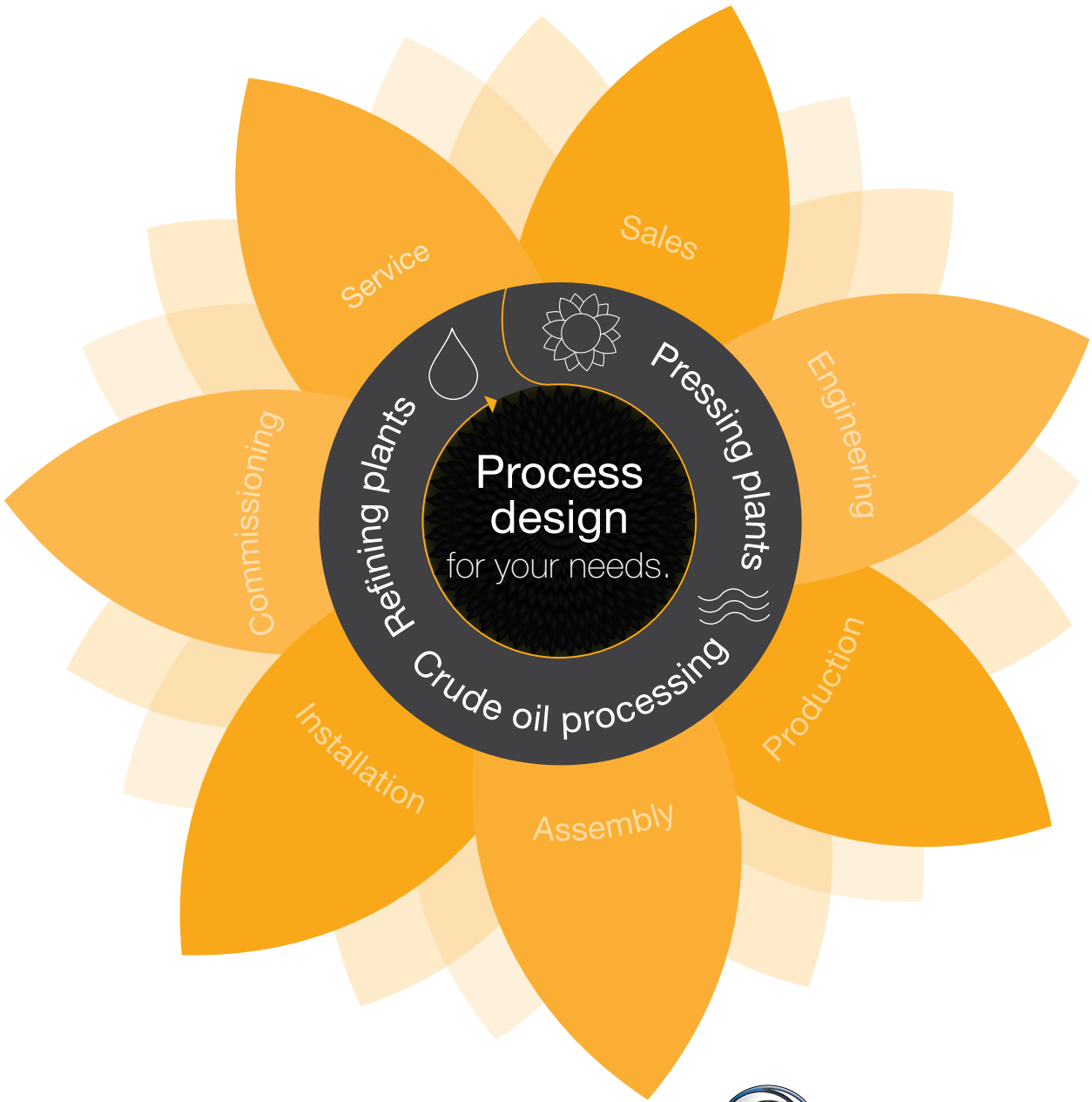

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What makes your shortening suitable for fancy croissants, puff and Danish pastry?

Braulio A. Macias-Rodriguez and Alejandro G. Marangoni

Shortenings are fats used for many applications, including cakes, icings, and laminated doughs, among others. As indicated by their name, their main role is to "shorten" baked products by preventing interaction of gluten and starch particles. Other important functions include structuring, lubricating, foaming, emulsifying, and so on. According to the functional requirements, shortenings fall into various categories including those intended for roll-in applications.

- **Roll-in shortenings are firm yet malleable specialty fats used in the manufacture of laminated doughs.**
- **Their functionality or mechanical performance is largely determined by their bulk rheological properties at large deformations.**
- **Large oscillatory shear tests reveal that roll-in shortenings are more effective at dissipating energy than other bakery fats, a property that explains their ability to bear stresses during lamination.**

A roll-in shortening, used in laminated doughs, serves as barrier by forming continuous thin fat films that prevent fusion of dough layers. To do so, this roll-in material must "survive" deformations imparted during co-extrusion, sheeting, and folding of dough. If the shortening is too soft, it will be absorbed into the dough or squeezed out; if it is too firm and brittle, it will rupture the dough. Either case yields the same disastrous result: small pastries with poor crumb structure, low lift and volume.

To achieve good roll-in functionality, formulation and crystallization conditions are adequately customized to meet a set of physical criteria. Roll-in shortenings are formulated with higher contents of tri-saturated, and tri-unsaturated triacylglycerols (TAGs) consisting of trans fatty acids in some cases. This represents a major shortcoming as the industry aims to rid fat products of industrial trans fats to comply with the current regulatory framework.

Roll-in shortenings are crystallized under substantial cooling and shear conditions using a scraped-surface heat exchanger, worker units, and extrusion passages, which contribute to breakage of crystal aggregates, and their orientation into layer-like microstructures. Some of the physical parameters that are believed to describe roll-in functionality include higher solid fat content and melting points, β′ polymorphism, and high yield values. Nevertheless, it was recently found that bakery shortenings may share similar physical properties. For example, an icing shortening may share a similar melting point, solid fat content (though wider melting ranges), and polymorphic behavior with a roll-in shortening. Likewise, viscoelastic attributes, such as yield values, could not be cor-

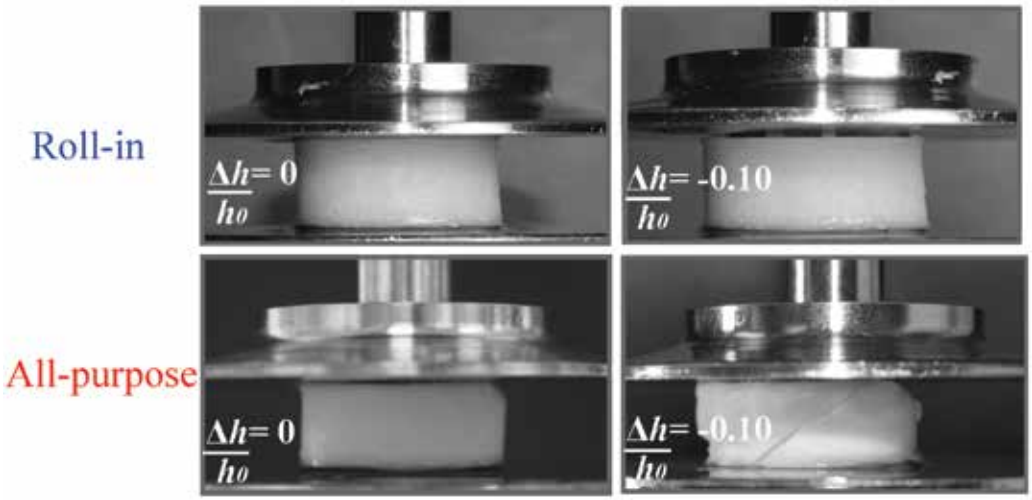

FIG. 1. Side views of shortenings during compression. A roll-in shortening deforms plastically without forming cracks, whereas an all-purpose shortening displays macroscopic cleavage fracture.

related with the usability of shortenings. These findings were particularly important (yet puzzling) since these properties had been long used to design for baking functionality.

Rheologically speaking, a glimpse into the differences among shortenings may be gained partly by tactile perception (using the so-called "thumb or finger" test) and partly by visual observation during deformation—still common industry practices. A roll-in shortening may be perceived as firm yet malleable ("shape" retaining) during handling in contrast to an all-purpose shortening that would be perceived as a firm yet brittle material. Indeed, during compression a roll-in shortening does not seem to develop visible cracks, whereas an all-purpose shortening does (Fig. 1). These characteristics are important factors in determining the quality of lamination, and whether the dough bakes into a puff and flaky pastry.

So far, a direct measure of these properties has been impossible, partly because of continued reliance on subjective or empirical tests established over half a century ago [1]. These tests have been used to determine "hardness," "spreadability," the "consistency" index, and similar attributes typically found in the industry lexicon. The challenge in using such tests lies not so much in their ill-defined physical properties, as in the degree to which such properties can be said to exist at all. This motivated the search for alternative tests or physical measures of roll-in functionality.

Considering that roll-in shortenings (and fats in general) experience substantial deformations during use, it seemed relevant to investigate their nonlinear rheological behavior. For this purpose, large amplitude oscillatory shear (LAOS) tests were conducted and applied to understand yielding dynamics of a wide range of soft matter and complex fluids. Unlike more traditional large deformation tests (cone penetrometry or compression), LAOS oscillations provide controlled yielding, allow the decomposition of elastic and viscous moduli, and better resemble the flow experienced in use as they probed strains and frequencies relevant to lamination. For example, under small amplitude oscillatory shear (SAOS), bakery shortenings behave in a similar fashion; i.e., both fats act as soft viscoelastic solids ($G' > G''$) with similar viscoelastic moduli, critical strains, and stresses uncorrelated to solid fat content. Rohm and Weidinger [2] reached similar conclusions in commercial butters. Nevertheless, visualization of the same data in strain *versus* stress curves makes it possible to realize rheological differences between samples.

Beyond $\gamma_{critical} \approx 0.05\%$, both shortenings reached yield stresses (taken as stress maximums) of $\tau_1 \approx 4000$Pa (roll-in) and $\tau_1 \approx 4900$ (all-purpose), respectively. Above the yield stress (failure point), the stress in roll-in exhibits a plateau compared to an all-purpose shortening in which the stress undergoes abrupt decrease and quick stress relaxation. Strong stress

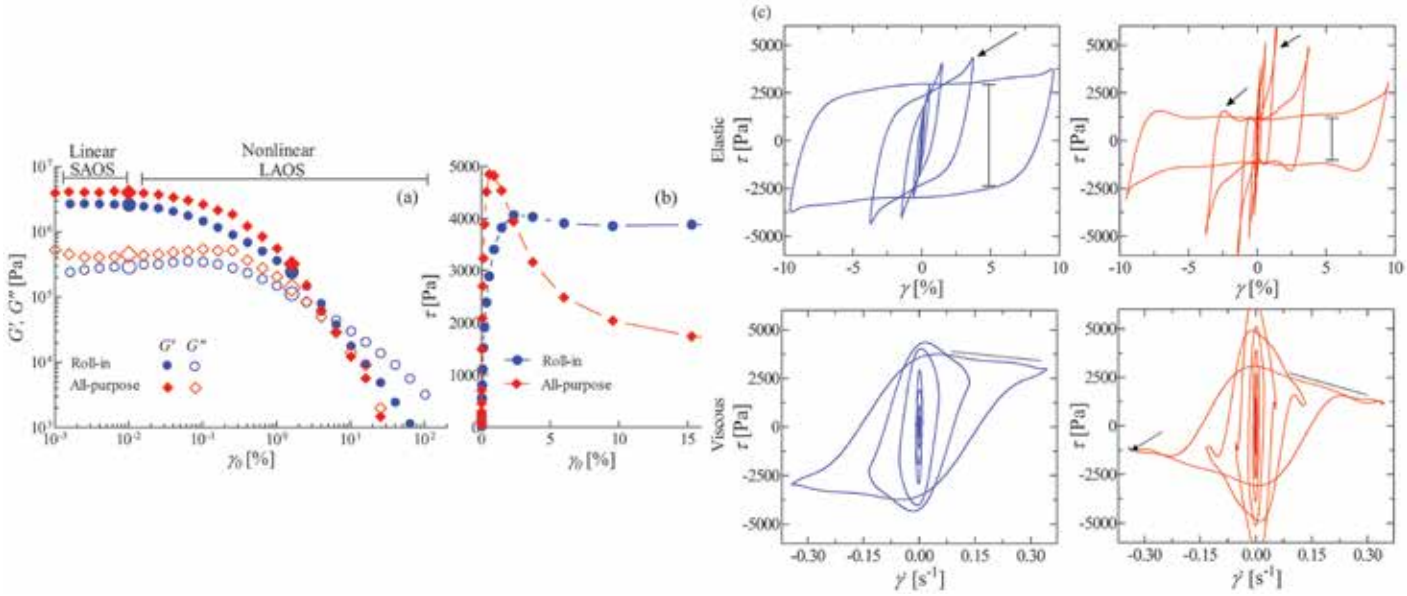

FIG 2. (a) Viscoelastic moduli G′ and G″ as a function of strain input γ_0. Enlarged data points reflect average responses (G′, G″) calculated from the raw waveforms. (b) Stress versus strain as obtained from (a) for strain deformations $\gamma_0 \leq 15\%$. (c) Curves of stress versus strain–elastic projection, and shear rate–viscous projection recorded at $\omega = 3.6$ rads^{-1} and $\gamma_0 = 0.01$-10 % for laminating and all-purpose shortenings. Arrows highlight the observed qualitative differences. Adapted from [5].

overshoots result from the growth of macroscopic fractures in the nonlinear regime, as shown in Fig 1.

To capture the observed behavior, several methods have been proposed to analyze the nonlinear LAOS response. These include Lissajous-Bowditch (L-B) curves and Fourier-transform (FT) rheology, and stress-decomposition via FT-Chebyshev polynomials, among others. For a comprehensive review on the fundamentals, analysis, and applications of the technique, readers can consult the work of Hyun, *et. al.* [3], while readers wanting to know more about use of the technique in lipid materials may refer to Macias-Rodriguez and Marangoni [4].

L-B are parametric plots of strain *versus* stress (elastic perspective) or strain-rate *versus* stress (viscous perspective) that appear as ellipsoidal shapes in the linear regime, but progressively distort in the nonlinear regime (Fig. 2). In the nonlinear regime, both shortenings display similar features; i.e., stress "upturns" and stress "bends" within an oscillatory cycle, specially at maximum strains or shear rates (local measures). However, it seems that a roll-in shortening experiences less local strain stiffening; i.e., milder stress upturn, and less shear-thinning, higher viscosity as seen by larger area enclosed by the elastic L-B figures, and weaker stress bending shown in the viscous L-B figures.

Quantification of these responses can be done via a Fourier transform (FT) analysis to reconstruct the LAOS waveforms. In the linear regime, Fourier series show the presence of one or "fundamental" harmonic (n=1), whereas in the nonlinear regime, higher-order odd harmonics (n=1, 3, 5…) grow unboundly in the nonlinear regime. Fig 2 shows the intensity of the leading-order harmonic (n=3) as a function of strain. Compared to an all-purpose shortening, roll-in shortenings

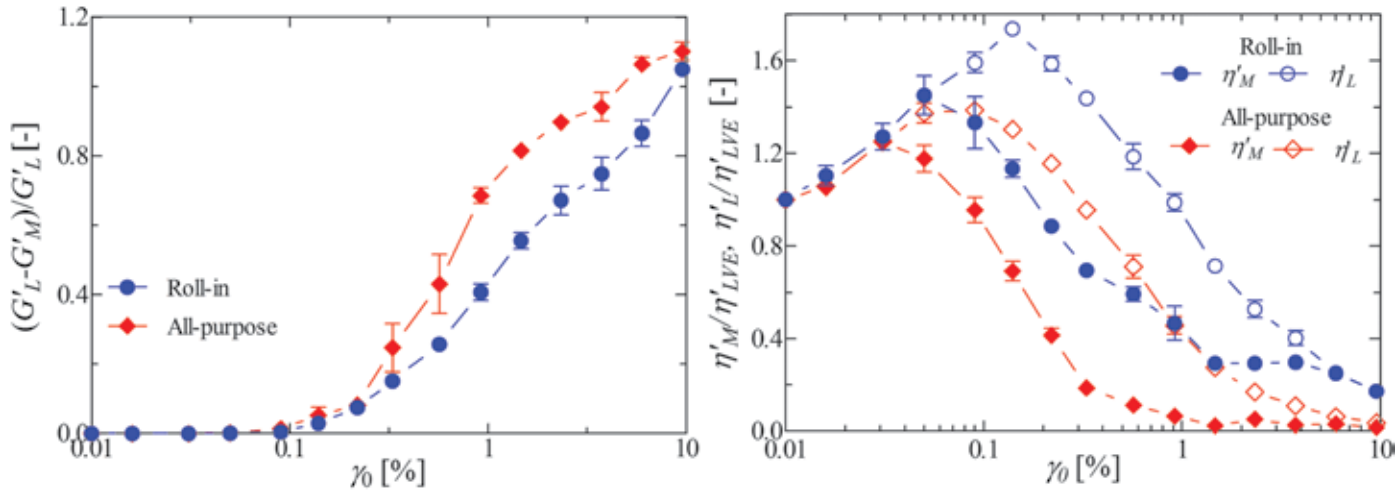

FIG. 3. Nonlinear elastic and viscous local measures at $\omega = 3.6$ rads^{-1} and $\gamma_0 = 0.01$-10 % for roll-in and all-purpose shortenings. Viscous measures are parametrized by the linear dynamic viscosity η_{LVE}' at $\gamma_0 = 0.01\%$. Inset shows absolute values of dynamic viscosities. Adapted from [5].

gradually transition into the nonlinear regime, suggesting superior ability to bear stresses for the primer.

To gain physical insight into the nonlinear regime, we use the FT-Chebyshev framework to isolate storage- and loss-energy mechanisms in the stress response (Fig. 3). While minor differences appear in the local elastic response (G_L'-G_M')/ G_L', substantial variations, such as dynamic viscosities at minimum- (η_M') and maximum- (η_L') shear rates, show in the viscous response (viscosities are related to plastic flow). To illustrate, a roll-in shortening exhibits at least twice the relative dynamic viscosities than an all-purpose shortening does. Increased viscosities mean that a roll-in shortening dissipates energy more effectively during deformation than an all-purpose shortening does, and thus the primer withstands higher stresses than is the case when using all-purpose shortening. Remarkably, it has been found that multiple formulations (e.g., palm-oil based, soybean-oil based, trans-containing, trans-free) meet the same rheological criteria. This suggests that novel and functional roll-in shortenings may be designed as long as the rheological properties are adequately matched.

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Unraveling the fusty/musty off-flavor in native cold-pressed rapeseed oil by application of the molecular sensory science concept

Katrin Matheis and Michael Granvogl

- Sensomics combines sensory and instrumental analytical techniques to analyze odorants.
- The molecular sensory science concept uses the sensomics approach to identify, quantify, and simulate the characteristic aromas of specific foods.
- In this article, 2017 AOCS Analytical Division Student Award winner Katrin Matheis and her Ph.D. supervisor Michael Granvogl describe how they used this concept to identify marker compounds that can be used to develop a quick method for determining the quality of native cold-pressed rapeseed oil.

The molecular sensory science concept is aimed at identifying, quantifying, characterizing, and, finally, simulating the characteristic aromas of specific foods. This state-of-the-art sensomics approach for the analysis of key odorants combines sensory and instrumental-analytical techniques. The first step is a gentle isolation of the volatiles using high-vacuum distillation at temperatures of 35°C to prevent artifact formation either caused by degradation of present aroma-active compounds or by formation of odorants from other present compounds, such as thermolabile precursors.

Next, aroma extract dilution analysis (AEDA) as a screening method via gas chromatography-olfactometry (GC-O) is applied to reduce the large number of volatiles to a smaller set of characteristic aroma-active compounds. This is followed by identification experiments based on comparison of retention indices on two GC columns with different polarities, odor quality and intensity, and mass spectra in electron ionization (EI) and chemical ionization (CI) mode obtained for the analytes and their respective reference compounds. A precise quantitation using stable isotope dilution analysis (SIDA) in combination with the calculation of so-called odor activity values (OAVs; ratio of concentration to the respective odor threshold) and, finally, simulation of the aroma in a respective food matrix finalize the concept.

In the first part of the study, this approach was applied to native cold-pressed rapeseed oil (NPC, native positive control). The volatiles

were isolated by a two-step high-vacuum distillation consisting of thin-film distillation, followed by the so-called solvent-assisted flavor evaporation (SAFE) technique [1] to remove remaining oil droplets. After gently concentrating the obtained distillate using a Vigreux column, the concentrate (~ 100 µL) was stepwise diluted 1+1 (v+v) with solvent and AEDA was applied, which yielded so-called flavor dilution (FD) factors. The FD factor correlates with the dilution step and represents the highest/last dilution, in which the respective odorant was perceivable at the sniffing port during GC-O for the last time.

In NPC, 52 aroma-active compounds with FD factors between 8 and 2048 were detected and identified by their aroma qualities and intensities, retention indices on two GC columns of different polarities, and mass spectra (EI and CI mode) using data of reference compounds available in an in-house database containing more than 1,000 aroma-active volatiles. Thirty-one odorants with an FD factor ≥ 64 were quantitated by stable isotope dilution analysis (SIDA), the most accurate methodology, especially for volatile and/or reactive compounds. In addition, odor thresholds in oil were determined and used to calculate the corresponding OAVs.

Only 11 compounds showed concentrations above their respective odor thresholds and, thus, contributed to the overall aroma of NPC. High OAVs were obtained for 2-isopropyl-3-methoxypyrazine (330) and dimethyl trisulfide (37), followed by butanoic acid, dimethyl sulfide (both 7), 2-isobutyl-3-methoxypyrazine (5), 2-*sec*-butyl-3-methoxypyrazine, octanal (both 3), hexanal, 3-hydroxy-4,5-dimethylfuran-2(5*H*)-one (sotolon), and 3-methylbutanal (all 2).

For aroma reconstitution, all odorants showing OAVs ≥ 1 were added in their naturally occurring concentrations to an odorless oily matrix (refined rapeseed oil). The comparison of this reconstitution model with the original oil using the odor descriptors cabbage-like, nutty/fatty, earthy/pea-like, malty, sweaty, and seasoning-like matched very well [2].

The characterization of the key odorants in native cold-pressed rapeseed oil with desired sensory attributes was the basis for unraveling the odorants responsible for the fusty/musty off-flavor in a native cold-pressed rapeseed oil (NOF, native off-flavor oil). In the next step, the key odorants evoking the fusty/musty off-flavor in NOF were characterized by application of the molecular sensory science concept. Eighteen aroma-active compounds with OAVs ≥ 1 were found and, again, the reconstitution model was in perfect accordance with the original oil. Thereby, 12 compounds were increased at least by a factor of five compared to NPC and showed OAVs ≥ 1 including 2-*sec*-butyl-3-methoxypyrazine (earthy, pea-like), dimethyl trisulfide (cabbage-like), ethyl 2-methylbutanoate (fruity), 2-isobutyl-3-methoxypyrazine (bell pepper-like), 2- and 3-methylbutanal (both malty), 2- and 3-methylbutanoic acid (both sweaty), 2-methoxyphenol (gammon-like, smoky), and 4-methylphenol (fecal).

In addition to the reconstitution model, a spiking experiment was performed to further validate that the odorants responsible for the musty/musty off-flavor had been characterized correctly. Therefore, the 12 compounds clearly increased in NOF were added in the respective amounts to NPC. In parallel, butanoic acid, (*E*,*E*)-2,4-decadienal, dimethyl sulfide, 2-isopropyl-3-methoxypyrazine, and octanal were added to NOF to compensate for slightly higher concentrations in NPC. Finally, the sensory panel was not able to distinguish both model solutions (A: NPC + 12 compounds present at higher concentrations in NOF; B: NOF + 5 compounds present at higher concentrations in NPC) using the six odor attributes mentioned above for evaluation.

Next, omission experiments were performed to verify if all 18 odorants with OAVs ≥ 1 are necessary to evoke the characteristic fusty/musty off-flavor. Therefore, single as well as groups of odorants were systematically left out in the model solution. In a triangle test, this “omission sample” was compared to the full recombinate using the forced-choice prin-

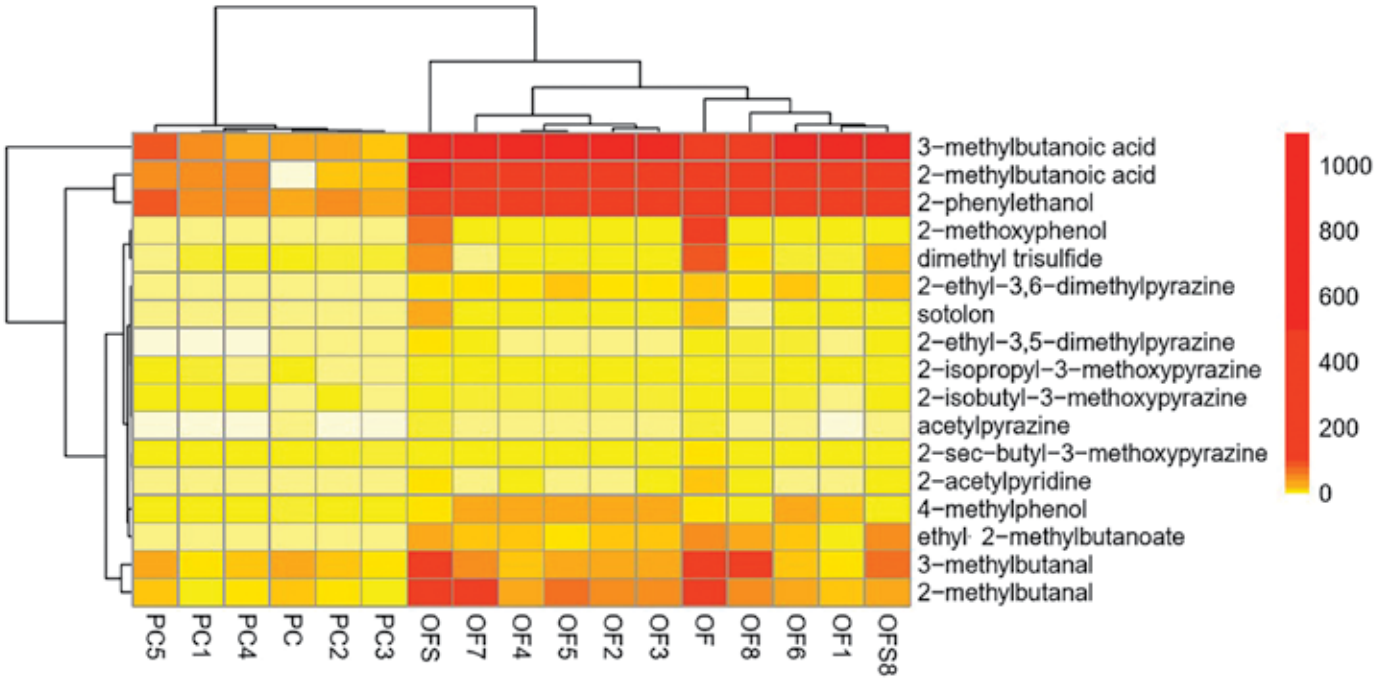

FIG. 1. Heat map illustrating the clustering of oil samples with desired sensory attributes (PC, PC1-PC5) or a fusty/musty "off-flavor" (OF, OF1-OF8), as well as the two corresponding seeds (OFS and OFS8), from which OF and OF8 were pressed. Concentrations (µg/kg) are displayed in colors with the highest in red and the lowest in white.

ciple. In summary, the sensory experiments revealed that a mixture of the six odorants dimethyl trisulfide, 2-methoxyphenol, 4-methylphenol, 2- and 3-methylbutanoic acid, and sotolon in their naturally occurring concentrations was not distinguishable (at a significance level of $\alpha = 0.05$) from the full recombinate containing all 18 odorants. Thus, these six odorants are responsible for the formation of the fusty/musty off-flavor in cold-pressed rapeseed oils [3].

To find marker compounds for oils eliciting the fusty/musty sensory defect, all compounds, which showed a clearly increased concentration in NOF, were quantitated in another eight rapeseed oils eliciting the off-flavor and in five oils with the desired sensory attributes. These data, clustered pairwise in a heat map, showed that all of the off-flavor oils showed a very similar pattern—as was also the case with the good rapeseed oil samples. Additionally, the above-mentioned increase of selected odorants in the off-flavor oils was clearly visible. Interestingly, the pattern of the seeds (OFS and OFS8), from which the off-flavor oils (OF and OF8) were pressed, and the pattern of the oils OF

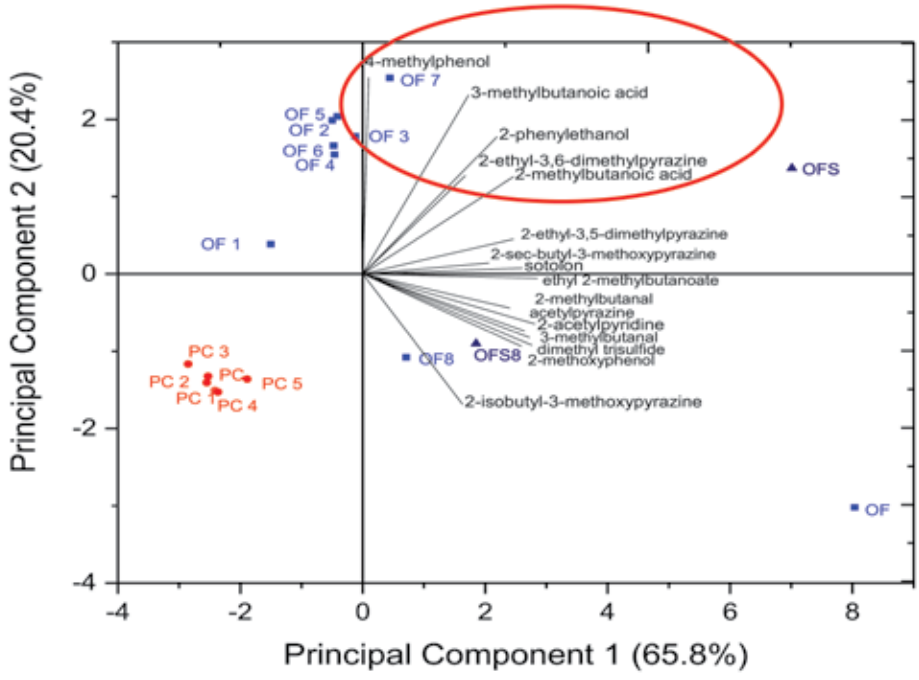

FIG. 2. Biplot of the PCA showing a clear separation of oil samples with desired sensory attributes (PC, PC1-PC5) and with a fusty/musty "off-flavor" (OF, OF1-OF8), as well as of the two corresponding seeds (OFS and OFS8), from which OF and OF8 were pressed.

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3. Matheis, K. and M. Granvogl, Characterization of key odorants causing a fusty/musty off-flavor in native cold-pressed rapeseed oil by means of the sensomics approach, *J. Agric. Food Chem*. *64*: 8168–8178, 2016.

and OF8 themselves were very similar (Fig. 1). Due to the fact that exactly the same key odorants were characterized in the seeds, an influence of the pressing process on the oil quality could be excluded.

It was noticeable that all compounds that increased in the oils eliciting the sensory defect can be formed from respective precursors, such as amino acids or phenolic acids, via degradation pathways caused by microorganisms, yeasts, or fungi. Consequently, the storing temperature and the residual moisture in the seeds play a crucial role in the off-flavor formation [3].

Additionally, data obtained for the off-flavor oils were statistically evaluated using principal component analysis (PCA). The right top quarter in the biplot shows the compounds, which revealed the highest increase in the off-flavor samples; therefore, 2- and 3-methylbutanoic acid, 4-methylphenol, and 2-phenylethanol were proven to have a high influence on the separation of the group containing the off-flavor oils and the group containing the oils eliciting good sensory attributes. Again, the seeds and the corresponding oils were likewise coordinated representing their similarity (Fig. 2).

In a final step, the above-mentioned marker compounds were used for the development of a quick method based on headspace-solid phase microextraction-high resolution gas chromatography-mass spectrometry (HS-SPME-HRGC-MS) to determine the quality of rapeseed, which can be used as a prediction tool for the quality of the corresponding native cold-pressed rapeseed oil.

Katrin Matheis, a graduate student in the Department of Chemistry at the Technical University of Munich, received the 2017 AOCS Analytical Division Student Award. She can be contacted at katrin.matheis@tum.de. Her Ph.D. supervisor is Michael Granvogl, Chair for Food Chemistry in the Department of Chemistry at the Technical University of Munich. He can be contacted at michael.granvogl@ch.tum.de.

Production of food-grade canola proteins by membrane-based process

Bih-King Chen and Levente L. Diosady

- A patented process developed by our research group was used to isolate protein from defatted canola meal. The process involves a series of well-designed unit operations. In the bench-top experiments, all of these individual steps were optimized to ensure the quality and yield of the final products.
- The process yields three products: a precipitated protein isolate with 83% protein, a soluble protein isolate with 91% protein (both are on dry basis, N×6.25), and a meal residue with 26% protein suitable for animal feed. The isolates are light in color and bland in taste. They are essentially free of glucosinolates, and have very low phenolics content.
- The process was readily scaled up, resulting in a precipitated protein isolate and a soluble protein isolate with qualities similar to the lab products.

Canola with very low erucic acid (0.01% in oil) and glucosinolate (10 µmole/g seed) levels is now grown in Canada. With its high oil content (45%), low concentration of saturated fats (7%), and balanced amino acid profile, it is Canada's most valuable oilseed crop. So far the most valuable part of canola is its oil, which is considered to be one of the healthiest edible vegetable oils. At present, canola oil is produced by prepress solvent extraction [1]. In this process, the seed is cleaned, preconditioned, and flaked; then its oil is removed by mechanical pressing followed by solvent extraction. After the hexane is recovered from the miscella, the crude oil is degummed and then refined to produce edible oil. The meal is desolventized, then toasted to remove any residual solvent. Due to its poor taste, unattractive dark color, and antinutrients, the defatted meal produced is used only as animal feed despite its high nutritional value.

The high protein content (35–40%) in canola meal, along with its balanced amino acid profile, makes it attractive for food applications. In this article we describe, though not at length, our investigation into converting canola meal to food-grade protein products. One of the major interests of our research group is developing processes to isolate proteins from *Brassica* oilseeds. Patents [2, 3] have been granted after years

of research optimizing the process, which yields two main products: a soluble protein isolate (SPI) and a precipitated protein isolate (PPI). It also yields a third product, meal residue (MR), which can be used as a food ingredient if made from mustard meal, and as animal feed from canola meal.

The process involves a series of unit operations: protein dissolution, chemical treatment, centrifugation, membrane operations of ultrafiltration and diafiltration, isoelectric precipitation, and drying. While each step plays its role in the production, the operations indispensable for the high quality of the final products are centrifugation and membrane operations. Effective centrifugation eliminates fine suspended particles, resulting in a clear protein extract. This is doubly important, as a clear solution with no fine solid particles makes membrane filtration much less prone to clogging, and the protein isolates have a higher quality since they contain no undissolved meal residue. Membrane filtration is a powerful tool used to separate micro-molecules from macro-molecules in a true solution, diverting them into two separate streams. Once the membrane with correct pore size is selected, and the process liquid is appropriately pre-treated, the dual operation of ultrafiltration and diafiltration will remove essentially all small, low-molecular-weight antinutritional components, and thus purify the protein solution.

Defatted meals were acquired from different suppliers: (1) two commercial meals from two different suppliers (pressed, hexane-extracted, desolventized, and toasted during manufacturing), (2) non-toasted meal (pressed, hexane-extracted, desolventized, but not toasted), and (3) expeller-pressed meal (pressed twice, without solvent extraction). Aside from these materials, a meal was also prepared in our lab by defatting the ground seeds with hexane, followed by air-drying. Table 1 presents the protein extractability at pH 11.5 and room temperature (21–25°C).

Compared to the non-toasted meal or the lab-prepared meal, the commercial meal and the expeller-pressed meals had significantly decreased extractability. Obviously, this was due to the thermal damage to the meal caused by toasting or extensive mechanical pressing. Given that the expeller-pressed meal had very low protein extractability, it was not processed further.

In a typical bench-scale experiment, 80g of defatted meal was used for protein isolation. The processing started with aqueous alkaline extraction at pH 11, which was maintained by 25% or 50% NaOH solution. The extraction of non-toasted meal or lab-prepared meal was carried out at room temperature (21°C). However, the commercial meal was extracted at 50°C to achieve higher protein solubility and higher product yield. (At 50°C and pH 11 its protein extractability was 65.0%.)

The addition of ascorbic acid reduced oxidization during the extraction stage. After completing an extraction that lasted for 45 min, centrifugation separated the alkaline extract solution from the wet solids, which were immediately washed twice with water. The extract solution and the two wash solutions were combined. The wet solids were freeze-dried to produce the meal residue. NaCl was added into the alkaline extract solution, and heated at 50–55°C for 30 min. Then the solution was cooled to 45°C, without exceeding the maximum operating temperature of our ultrafiltration membrane.

The membrane was made of polyethersulphone, with a molecular weight cut-off of 5,000 Daltons. The extract solution was split into two streams by ultrafiltration: The retentate containing largely concentrated protein and some micro-mo-

TABLE 1. Protein extractability from various canola meals at pH 11.5

Meal	Commercial meal	Non-toasted meal	Expeller-pressed meal	Lab-prepared meal
Extractability	45.5%	68.2%	28.5%	64.0% (at pH 11)

TABLE 2. Protein content in the starting meals and their final products

	Commercial meal*	Non-toasted meal#	Lab-prepared meal#
Starting meal	35.3%	37.8%	37.0%
Products:			
Meal residue (MR)	24.9%	23.0%	25.4% (25.9% dry basis)
Precipitated protein (PPI)	76.5%	90.7%	79.3% (83.0% dry basis)
Soluble protein (SPI)	81.6%	89.4%	86.1% (90.6% dry basis)

* Meal was extracted at 50°C
\# Meal was extracted at room temperature (21°C)

lecular impurities, and the permeate containing undesirable low molecular weight impurities. The protein in the retentate was further purified by subsequent diafiltration, in which fresh 0.05M NaCl solution (adjusted to pH 11) was continuously added into the retentate while the permeate was removed.

The pH of the diafiltration retentate was lowered to 4 by the addition of 6M H_3PO_4. This precipitated the proteins. The solid slurries collected after the centrifugation were washed with water, centrifuged, and then freeze-dried to produce the precipitated protein isolate. The clear liquid, which contained the acid-soluble proteins, was ultrafiltered to reduce its volume, and then diafiltered with fresh water. The retentate was freeze-dried to produce the soluble protein isolate.

Table 2 shows the crude protein content (N×6.25, as is) of the starting meals and the products made from them.

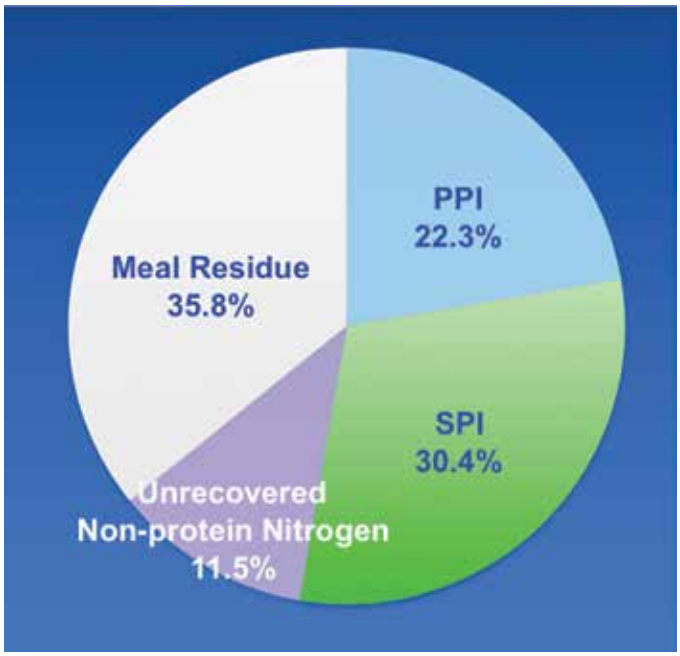

FIG. 1. Protein distribution among products from lab-prepared defatted canola

The two major final products from the commercial meal were noticeably lower in protein content; they were also darker in color, and moderately harsh in taste. The protein isolates from the non-toasted or the lab-prepared meal were beige in color and bland in taste. They were essentially free of glucosinolates and had a very low phenolics content (~0.15%). The process recovered 88.5% of the protein present in the lab-prepared meal; more than 50% was distributed in two isolates, and 35% in the meal residue. The protein distribution among the three products from this meal is shown in Figure 1.

A semi-pilot scale experiment of protein isolation was conducted with defatted Estonian rapeseed, resulting in two major final products, PPI and SPI, with 84% and 91% protein, respectively. Very similar to canola, the seed also contains low concentrations of erucic acid and glucosinolates. The meal used for this scale-up test was prepared by defatting the ground seeds with hexane, followed by air-drying. It was not heated during desolventization.

Higher protein extractability and better final protein products are attainable if the starting meal is:

- low in oil content;
- low in residual solvent;
- free of contaminants, such as other seeds, weeds, leaves, stems, soil, or sand;

References

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[2] Diosady, L.L., L. Xu, and B-K. Chen, Production of high-quality protein isolates from defatted meals of *Brassica* Seeds, US Patent 6,905,713 (2005).

[3] Diosady, L.L., L. Xu, and B-K. Chen, Production of high-quality protein isolated from oil seeds, US Patent 8,048,463 (2011).

- finely ground;
- dehulled; and
- not thermally damaged.

This work clearly points out that currently available commercial canola meal or expeller-pressed meal is not a suitable starting material for the process of protein isolation. However, we have clearly demonstrated that, when our scaleable process is used, high-quality food-grade protein isolates can be made from canola seed that has been gently defatted and desolventized.

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AOCS MEETING WATCH

May 6–9, 2018. AOCS Annual Meeting & Expo, Minneapolis Convention Center, Minneapolis, Minnesota, USA.

September 6, 2018. JOCS AOCS Joint Symposium, Kobe Gakuin University, Arise Campus, Kobe, Japan.

October 28–31, 2018. Fabric and Home Care World Conference, Boca Raton Resort & Club, Boca Raton, Florida, USA.

May 5–8, 2019. AOCS Annual Meeting & Expo, Cervantes Convention Center at America's Center, St. Louis, Missouri, USA.

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

From laboratory to full-scale degumming: a new efficient phospholipase A

P.M. Nielsen

Enzymatic degumming is a robust process that consistently ensures a low level of phosphorous (P) in degummed oil while achieving a higher yield than other physical refining processes. The yield increase is a result of releasing fatty acids from the phospholipids and reduced binding of neutral oil in the gum phase.

- **Enzymatic degumming is a highly effective technology to remove phosphorous from oil with limited yield loss.**
- **Phospholipase A Lecitase® Ultra has been widely used since 2003. In 2016, a new thermostable and acid-stable enzyme called Quara® LowP was introduced.**
- **This article describes the development of Quara® LowP, including the properties and benefits that have been documented in Novozymes laboratories and full-scale trials.**

The enzymatic degumming process was first introduced using the expensive porcine pancreatic phospholipase in 2000 [1, 2]. A few years later, a microbial phospholipase A1 (PLA1), Lecitase Ultra, was introduced to refineries globally (Fig. 1), and 5–6 years ago Verenium introduced a phospholipase C (PLC) for the water degumming application. In water degumming, the PLC cleaves off a diglyceride (DG) and significantly increases the yield. However, the PLCs available today do not react with all phospholipids.This has led refineries to use a PLC/PLA combination enzyme product to achieve the highest possible yield and DG—within acceptable enzyme costs.

A new PLA for full degumming has been in development for some time and was launched as Novozymes Quara LowP in November 2016. Since June 2016, full-scale testing has been running successfully at our partner plant in the United States.

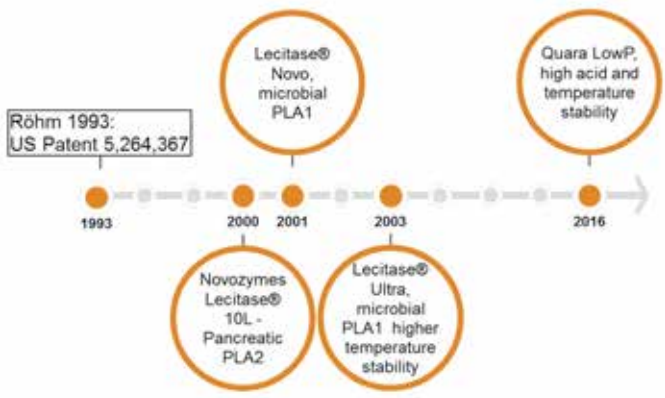

FIG. 1. The historical development of phospholipase A in refining

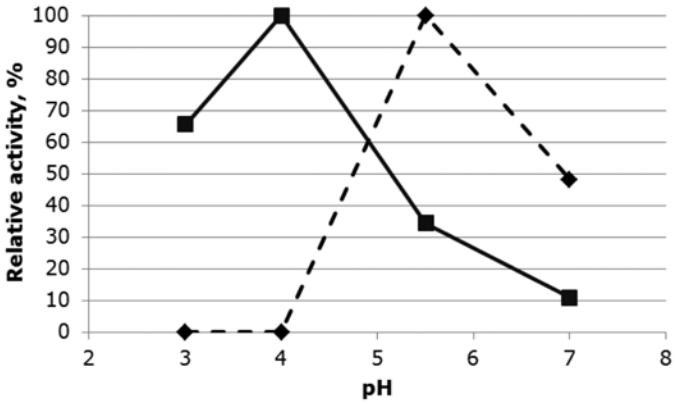

FIG. 2. Relative activity of Lecitase Ultra (dotted line) and Quara LowP (solid line)

BACKGROUND ON DEGUMMING

There are many different technologies available for physical refining of vegetable oils. The oil yield increase is what makes enzymatic degumming attractive. The enzyme's hydrolysis of phospholipids changes the properties of these molecules dramatically, making it possible to wash out the gums without losing much oil. So the higher the phospholipid content in the crude oil, the larger the savings will be.

Today there are several suppliers of enzymes for degumming. The enzymes differ with respect to specificity and optimum operational conditions. PLA releases free fatty acids (FFA) together with additional neutral oil yield, while PLC produces DG. The most important parameters for a successful enzyme reaction are temperature and pH in the water phase.

The reaction temperature for enzymatic degumming has historically been 50–55°C, which corresponds with the enzyme's thermostability. It has therefore been necessary to cool and heat the oil during the process to get the temperature right for the acid chelating step, the enzyme reaction, and the separation. The pH in the water phase is also dictated by the optimum conditions for the enzyme, and normally caustic must be added to adjust the pH. When adding caustic, a small amount of soap formation, which can impact the centrifugation efficiency, is unavoidable.

Recent R&D work addresses some of the challenges of using enzymes for degumming. This has resulted in development of a new phospholipase—Quara LowP—which originates from the thermophilic microbe *Talaromyces leycettanus.* This PLA's heat-denaturation temperature is 17°C higher than Lecitase Ultra, making it fully active at 70°C and both active and stable at low pH. The activity at pH 3–7 compared with Lecitase Ultra is illustrated in Figure 2.

With the increased heat stability and the activity at low pH, the process becomes simpler and easier to control. This is evident from the typical process layout for enzymatic degumming (with Quara LowP); see Figure 3.

Quara LowP simplifies the process by eliminating the temperature-controlling steps after acid treatment, although the temperature still needs to be increased to 85°C during centrif-

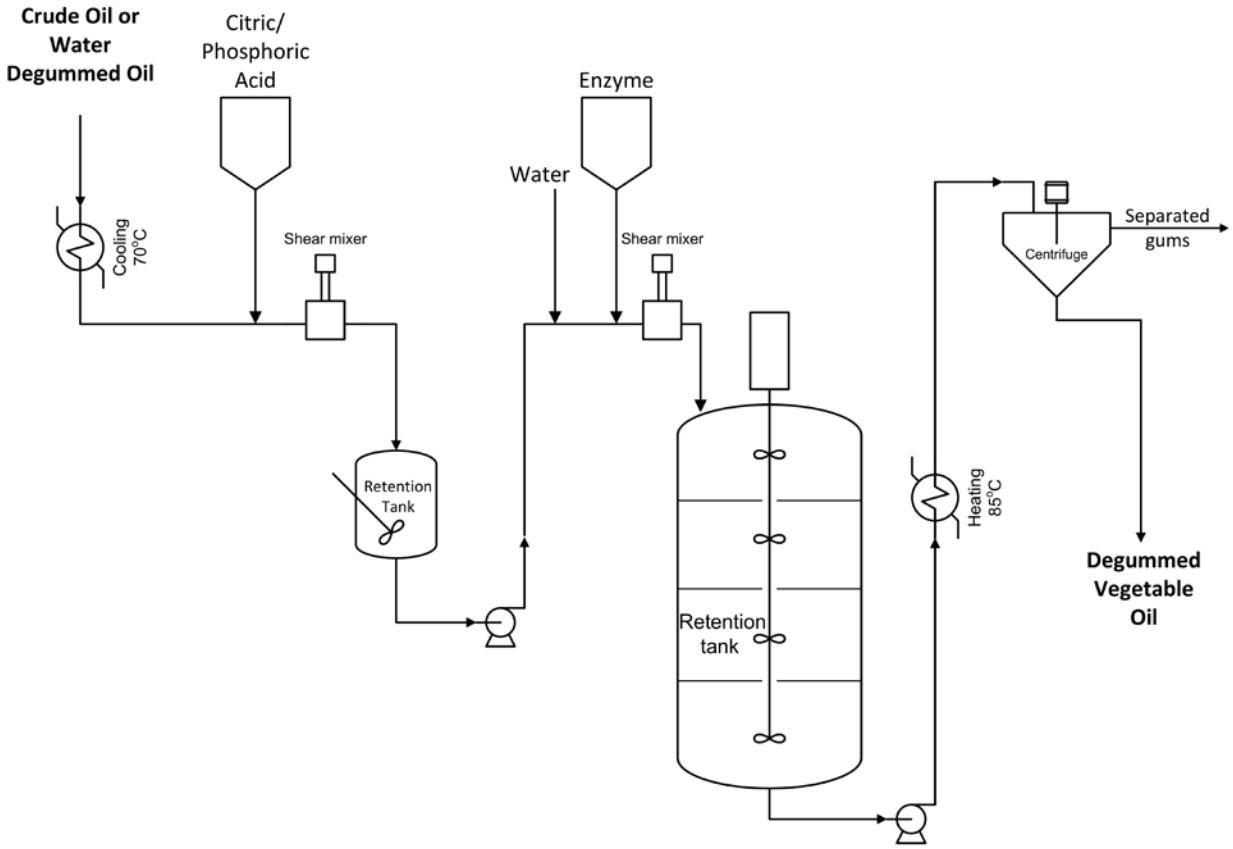

FIG. 3. Process layout for enzymatic degumming using Quara LowP

ugation for optimum separation and to deactivate the enzyme. Furthermore, there is no need to add caustic to control the pH. The low pH coming out of the reaction is expected to reduce fouling of downstream equipment such as heat exchangers and centrifuges. In cases when enzymatic degumming is performed at higher pHs, fouling can be prevented by adding acid after degumming [3].

Quara LowP for full enzymatic degumming has also demonstrated a significant oil yield increase in laboratory testing (Fig. 4). The figure shows the gum phase in the centrifugation tube after degumming using Lecitase Ultra (55°C) and Quara LowP (70°C), respectively. The difference in oil yield is 0.8%. Why is that?

First, there is a clear difference in FFA-release during the reaction. The FFA content in oil is typically 0.3% higher with Quara LowP. This is because of more efficient hydrolysis of the phospholipids. Table 1 illustrates how the reaction rate of each type of phospholipid differs for the two enzymes. This data was collected from a reaction test at 40°C, and we expect a significant increase in the reaction rate for both enzymes when they are used at their respective recommended temperatures of 55°C (Lecitase Ultra) and 70°C (Quara LowP). In addition, the new enzyme is hydrolyzing off fatty acids from the lyso-phopsholipids.

FULL-SCALE TESTING

The US-based soybean plant, which has been using Lecitase Ultra for three years, has experienced a simple and robust process with enzymatic degumming that consistently delivers less than 20 ppm phosphorous after one-step centrifugation. The degumming section consists of three reactors with four compartments each. These make up the efficient continuously-stirred tank system with a total of 5 hours retention time.

In the trial, different dosages of Quara LowP were tested to identify the minimum dosage needed to achieve the same performance as the plant could achieve with the Lecitase Ultra standard dose of 30 ppm. The process conditions were changed to meet the temperature and pH optimum of the new PLA (70°C and pH of 4 in the water phase). The parameters measured were:

- FFA
- P-content by ICP
- Centrifuge test
- Yield by flowmeter

Samples were collected on a daily basis, and the conversion of the phospholipids was confirmed by NMR analysis.

The Quara LowP test formulation was used at different dosages ranging from 40 to 10 ppm.To be able to deliver a low flow rate, the low dosage at 10 ppm required changes in the dosage pump This confirmed that the enzyme should be formulated in accordance with the dosage of 30 ppm that fit the dosage pumps in the plants.

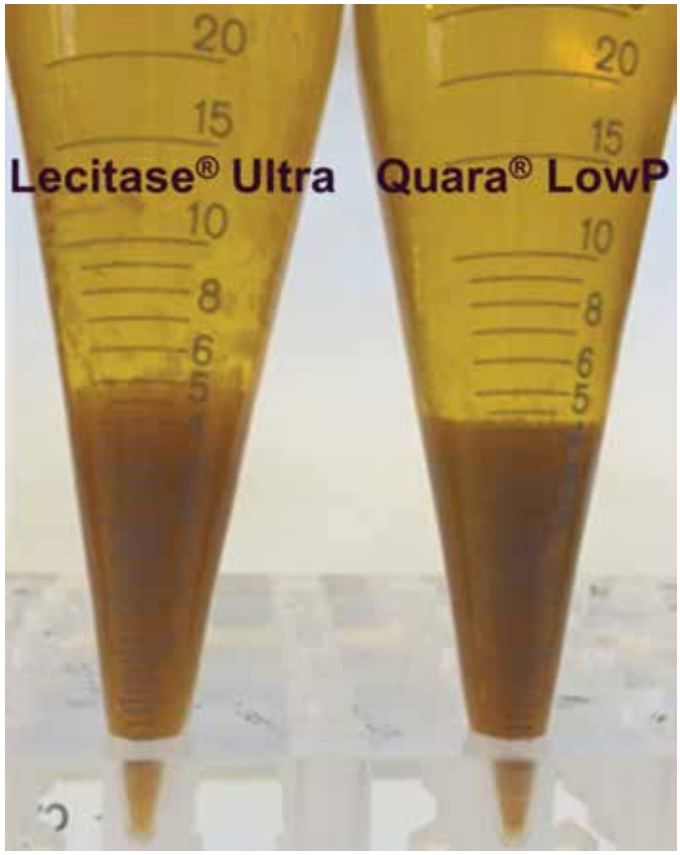

FIG. 4. Degumming of crude soybean oil using Lecitase Ultra and Quara LowP

It was immediately evident that Quara LowP produced higher FFA than Lecitase Ultra. Further, the new enzyme changed the gum properties so that viscosity was lower, which impacted the centrifuge. It was then necessary to lower the water content in the gums for better operation of the centrifuge. This turned out to be a benefit, because water usage was reduced from 2.5% to 2.2%. During the first two months of trials with the new enzyme, the plant sent samples to the Novozymes laboratory for analysis. The data analysis combined with plant data documented an FFA increase of 0.3%, and a yield increase of 0.4%, which meant that the yield increase was partly FFA (75%) and partly neutral oil (25%). The additional FFA produced by Quara LowP came from the reaction with lyso-phospholipids (Fig. 5). The first part of the reac-

TABLE 1. Initial reaction rate for degumming crude soybean oil with Lecitase Ultra and Quara LowP at 40°C measured as ppmP/(Minutes*ppm enzyme protein). Analyzed by ^{31}P-NMR.

	PC	PE	PI	PA
Lecitase Ultra	3.25±0.02	3.50±0.12	0.06±0.03	2.50±0.14
Quara LowP	12.30±0.02	9.85±0.17	1.04±0.10	2.04±0.08

Laboratory tests confirmed that Quara LowP is more efficient than Lecitase Ultra. The next step was full-scale testing at a soybean oil plant located in the United States.

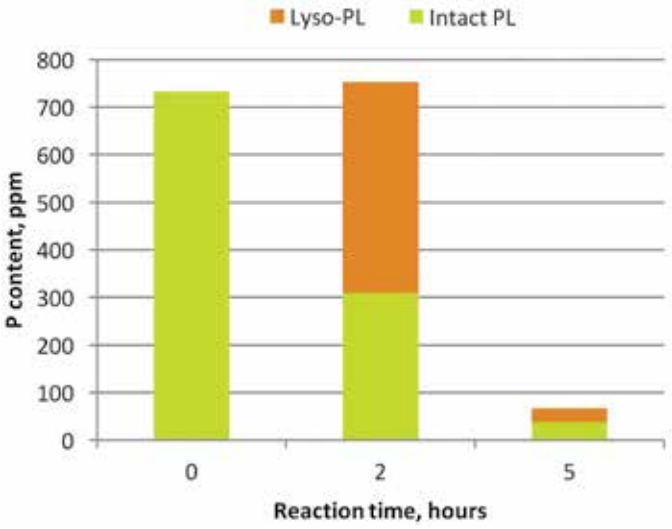

FIG. 5. Reaction data from converting phospholipids in crude soybean oil 20 ppm dosage of Quara LowP. Analyzed by P-NMR.

tion produces lyso-phospholipids, which are hydrolyzed during the last part of the reaction.

Because Quara LowP operates at a lower pH, it is expected to lead to several benefits in addition to yield gain. First, NaOH dosing becomes redundant, which means that plants can eliminate soap formation and save pumps and piping. Second, the low pH can reduce deposits in centrifuge and heat exchangers [2]. These benefits will take more time to prove, but during the test period there were no signs of fouling of equipment, and 2.5 months of operation without a need to clean the centrifuge indicates a significant reduction in deposits.

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2. Galhardo, F. and Dayton, C. Enzymatic degumming. AOCS web August 2016: http://lipidlibrary.aocs.org/content.cfm?ItemNumber=40324.

3. Dayton, C.L.G., Staller, K. and Berkshire, T.L. Process for improving enzymatic degumming of vegetable oils and reducing fouling of downstream process equipment, US Patent 7,713,727 (2010).

The simplest analytical tools are required: FFA-analysis to control the reaction of the enzyme, centrifuge test to check centrifuge performance, and the ICP for P-content analysis.

Thanks to the trials in the laboratory and at full scale, Quara LowP was formulated to be used at the standard dosage of 30 ppm enzyme/ton of oil.

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Extraction of proteins and active substances from microalgae

Halime Idakiev and Steffi Baecker

- Today, microalgae are mainly used to produce high-priced products, such as dyes, antioxidants, and unsaturated fatty acids. They are also sold in dried form as a food supplement.
- Although proteins are a major constituent of microalgae biomass, they are currently not viewed as a quality product—even though many are enzymes with diverse functional characteristics. Better use of the proteins in microalgae (between 30 and 60% [w/w]), could make microalgae processing more profitable, and is an important step in realizing the concept of a microalgae biorefinery.
- The study described in this article focuses on recovering proteins in microalgae alongside the recovery of existing high-price products.
- Optimal conditions for the production of protein and biopigment (phycocyanin, phycoerythrin) from *Arthrospira platensis* and *Porphyridium purpureum* were determined during laboratory tests. A process flow chart is presented, and possible applications are discussed.

Microalgae offer incredible potential as renewable raw material due to their ability to synthesize numerous valuable ingredients through photosynthesis-based growth, and to bind massive amounts of CO_2. Their ability to reproduce quickly allows them to realize yields far superior to those of classical land plants. Consequently, algae biotechnology is developing into a major global industry.

To date, 40,000 species of microalgae have been discovered. Of these, only a few hundred species are characterized biochemically, and only 15 strains are used industrially. Therefore, while the use of microalgae offers enormous potential, current use of this renewable raw material remains far behind what is possible.

Most of the products obtained from microalgae are high-value products, such as cosmetic ingredients, dyes and other fine chemicals, antioxidants, and unsaturated fatty acids. Intact algae are also marketed in dried, pressed form, or as food supplements.

More recent developments aim at mass markets such as the fuel market. Research projects in this area tend to focus on optimizing the use of individual key components. Meanwhile, other components that are present in microalgae in relatively high concentrations, such as proteins (Fig. 1), are generally disposed of, released for anaerobic digestion in biogas plants, or used to fuel the combustion process.

This is unfortunate, as many microalgae proteins have a high-quality amino acid spectrum that would be of interest to manufacturers of human nutrition, animal feed, cosmetics, and other products. For this reason, Pilot Pflanzenöltechnologie Magdeburg e.V. (PPM), Magdeburg, Germany, initiated a project to develop biorefining technologies for isolating proteins

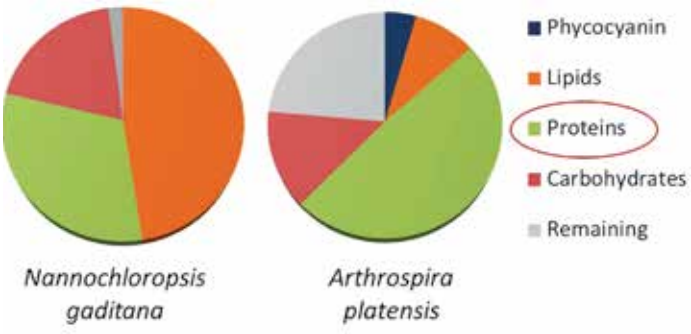

FIG. 1. Approximate composition of microalgae *Arthrospira platensis* and *Nannochloropsis gaditana* (Miyamoto, 1997; Radakovits, *et al.*, 2012, original data)

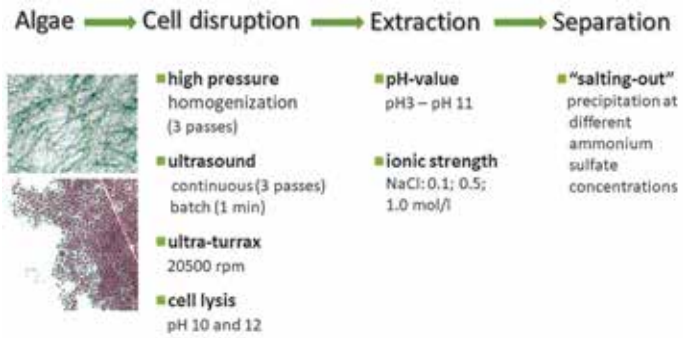

FIG. 2. Trial design for determining the optimal conditions for the production of pigments and proteins from *Arthrospira platensis* and *Porphyridium purpureum*

and other potentially valuable co-products in tandem with the production of lipids or other active substances. The premise was that a more holistic use of microalgae could improve the viability of microalgae cultivation.

MICROALGAE SELECTION CRITERIA

The intent of the project was to investigate five microalgae species with different structural compositions and valuable products, to see how the isolation procedures would differ. The algae were selected based on their:

- high content of valuable ingredients (a prerequisite for commercial production);
- ability to be produced on a technical scale; and
- different cell wall structures and compositions, which would result in the application of different extraction methods.

The microalgae species selected are illustrated in Table 1. All are commercially available and have a high application potential. The first two microalgae species are currently being evaluated, as the project is still ongoing.

ARTHROSPIRA PLATENSIS AND *PORPHYRIDIUM PURPUREUM*

The most important active substances in the microalgae *Arthrospira platensis* and *Porphyridium purpureum* are phycocyanin and phycoerythrin, respectively. These are accessory pigments in photosynthesis and belong to the phycobili-

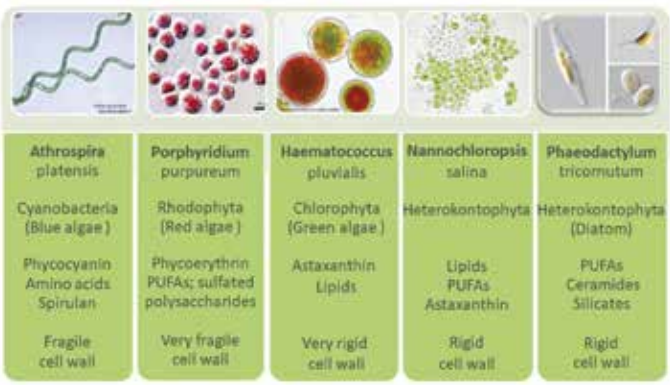

TABLE 1. Tested microalgae (free-access photos assembled from Culture Collection of Algae (SAG) at Goettingen University)

proteins (pigment-protein complexes). Both pigments are therefore water soluble, which we considered to be an important factor in selecting an appropriate extraction process. Phycocyanin (blue pigment) and phycoerythrin (red pigment) have fluorescent and antioxidant properties. Thus, *A. platensis* and *P. purpureum* are cultivated for the production of these pigments, which are marketed as high-priced fluorescent dyes in biological and biomedical research, and as food supplements and natural dyes in the food and cosmetics sectors.

The process for extracting functional proteins in conjunction with phycocyanin and phycoerythrin extraction from *Arthrospira platensis* and *Porphyridium purpureum* was investigated in laboratory tests, in which various methods of cell disruption, such as high-pressure homogenization, ultrasound treatment, ultra-turrax homogenization,and cell lysis were applied. The solubility behavior of proteins and pigments at various pH values and ionic strengths was determined, and the extracted proteins and pigments were also separated by precipitation at different ammonium sulfate concentrations using a salting-out method. Figure 2 provides an overview of the methods and testing parameters that were used.

The optimal cell disruption method for *A. platensis* turned out to be high-pressure homogenization. Phycocyanin has maximum solubility at pH 6, and is unstable within the alkaline pH range, where the majority of other proteins are most soluble. The proteins of *A. platensis* are also highly soluble at pH 6 and maximally soluble at pH 10. Therefore, the optimum pH for extracting both substrates together is 6. Ion concentration does not increase phycocyanin and protein solubility. Therefore, to solubilize them more selectively, cell disruption can be conducted at pH 6 without adding salts. The phycocyanin and proteins in the obtained extract can then be separated from each other—for example, by precipitation at different ammonium sulfate concentrations. The salting-out process for microalga *A. platensis* is presented visually in Figure 3 (page 28). Phycocyanin can be separated from proteins at higher ammonium sulfate concentrations (25% and 35%), as the phycocyanin fractions are distinguished by their typical blue color. However, the addition of ammonium sulfate introduces obstacles (eg., the high cost of adding and recovering ammonium sulfate, possible impairment of solubility in water) which could be avoided with another separation method. Another possibility would be to use ultrafiltration. In

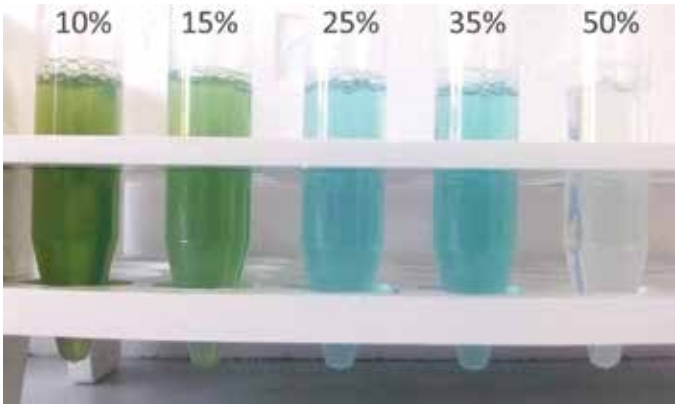

FIG. 3. Phycocyanin and protein separation by precipitation at different ammonium sulfate concentrations

this case, using membranes with different molecular weight cut-offs could achieve effective separation, as the pigment and protein have different molecular weights.

The residue from cell disruption still contains a large portion of the proteins, which can be subsequently extracted under basic conditions. The protein solution recovered by centrifugation can also be purified by precipitation at the isoelectric point (pH 4) or, alternatively, by ultrafiltration. The process diagram for extraction of proteins and phycocyanin from *A. platensis* is shown in Figure 4.

In the case of *P. purpureum* microalga, most of the cells can be disrupted using ultrasound. Phycoerythrin is maximally soluble at pH 7, unstable at the alkaline pH range, and less soluble in saline solution. In contrast, *P. purpureum* proteins are poorly soluble at a neutral pH range. They are most soluble at pH 11 and less soluble in saline solution. Therefore, these two products cannot be extracted simultaneously. By applying successive extraction, both products can be obtained with high yields and quality. In this case the *P. purpureum* cells should be disrupted first at pH 7 to solubilize phycoerythrin more selectively. Since just small fraction of *P. purpureum* proteins will be recovered, separation can be omitted if high purity is not desired. The extract obtained by centrifugation can be marketed as a phycoerythrin-rich product.

The residue can be subsequently extracted under basic conditions to obtain the proteins. The protein solution recovered by centrifugation can be further purified by precipitation at the isoelectric point (pH 3) or by ultrafiltration. The process scheme for extracting proteins and phycoerythrin from *P. purpureum* is presented in Figure 5.

Using the processes shown in Figures 4 and 5, proteins were obtained as co-products of phycocyanin and phycoerythrin extraction. Moreover, the techno-functional properties of the proteins obtained can be studied, and their application possibilities determined based on their functionality. The extraction of other valuable compounds such as sulfated polysaccharides, PUFAs remaining in the residue should also be considered. These steps are necessary to use the full potential of the microalgae *Arthrospira platensis* and *Porphyridium purpureum*.

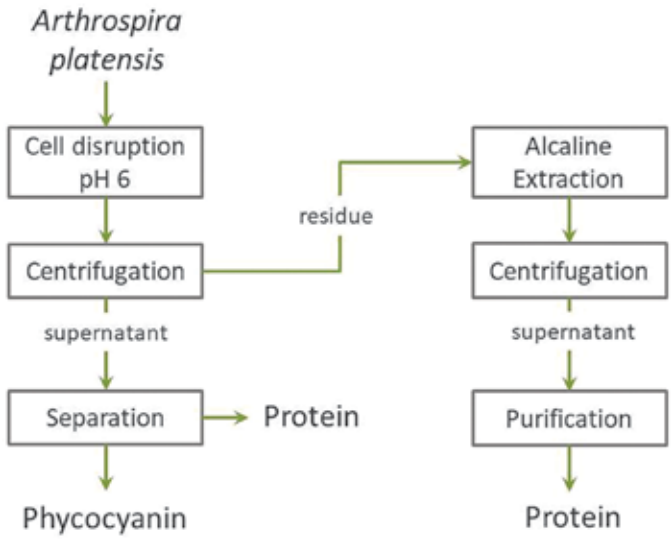

FIG. 4. Process design for obtaining the phycocyanin and proteins from *Arthrospira platensis*

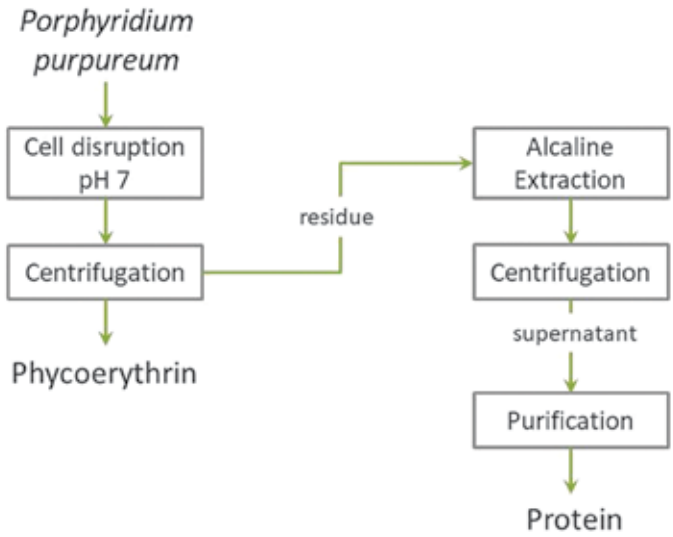

FIG. 5. Process design for obtaining the phycoerythrin and proteins from *Porphyridium purpureum*

MICROALGAE PROTEINS AND THEIR POSSIBLE APPLICATIONS

Today, the techno-functionality of proteins of only a few microalgae species (*Tetraselmis* sp., *Chlorella vulgaris*, and *Arthrospira platensis*) is known.

Protein extracted from the microalga *Tetraselmis sp.* are completely soluble at pH values of 5.5 and higher, independent of ionic strength. Such Insensitivity to ionic strength opens the door to applications in a wide range of salt concentrations. In contrast, oil seed proteins are usually minimally soluble at pH values of 5.5 to 6.5 and low ionic strengths ($I \leq 0.3$). Due to the strong influence of solubility behavior on the functional properties of a protein, this difference in the solubility behavior of microalgal protein extracts compared to the plant proteins can lead to unique techno-functional properties. For example, *tetraselmis*

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proteins exhibit stronger emulsifying behavior compared to the sunflower protein helianthinin (Hel), and the emulsifier-stabilizing abilities of the protease inhibitor protein isolated from potato juice (PIP) is comparable to that of whey protein isolate, the most important protein-containing emulsifier in food applications (Schwenzfeier, *et al*., 2011). Protein extracts from *Chlorella vulgaris* also show an excellent emulsifying capacity that is comparable to or higher than that of commercial proteins such as sodium caseinate and soy proteins (Ursu, *et al*., 2014). The protein isolate extracted from *Arthrospira platensis* (API) has relatively high oil- and water-absorption capacities. Moreover, API was able to form films when sorbitol (30% (w/w)) was used as plasticizer, and to form gels when the API concentration exceeded 12% (w/w) (Benelhadj, *et al*., 2016).

The functional properties of the proteins in the microalgae species we investigated suggest that such proteins have a high potential as additives in numerous food as well as non-food products, such as cosmetics. For example, microalgae proteins and their derivatives have moisture-retention properties and provide nutrients to skin and hair, making them good candidates for functional cosmetics (Samarakoon, *et al*., 2012). They can also serve as biological substitutes for commercial chemical emulsifiers and foaming agents in such personal care products as moisturizing creams, lotions, shampoos, soaps, hair foam, shaving foam, and many others. In addition, many biological activities of microalgae (eg., antioxidant, hypotensive, hepatoprotective, immunomodulatory, anti-cancer, and anti-coagulant) are associated with their proteins, protein hydrolyzates, or peptides (Karawita, *et al*., 2007; Morris, *et al*., 2007; Kang, *et al*., 2012; Buon, *et al*., 2014). Thus, extracting such proteins and other active compounds in tandem with phycocyanin, phycoerythrin, astaxanthin, lipids, and other primary active substances could open up additional revenue streams and add value to microalgae processing.

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Tall oil, its chemistries and applications

Bing Wang

Tall oil is a unique type of "oil" with properties that differ from those of common edible vegetable oils, such as canola, coconut, corn, olive, palm, peanut, safflower, sesame, soybean, and sunflower, as well as non-edible vegetable oils such as linseed oil and castor oil.

- **Tall oil, which is derived from sustainable and renewable sources of fatty acids and resins, has been produced commercially since the 1930s.**
- **Tall oil offers unique properties and a wide range of applications.**
- **The pine chemical industry has a big impact on the global economy and is evolving to find new applications.**

The term "tall oil" comes from the Swedish word for pine oil: "Tallolja." The term was anglicized to distinguish it from the essential oil that is produced from the steam-distillation of pine stumps, needles, twigs, and cones, and is referred to in English as pine oil.

Pine wood contains five major components, namely cellulose, hemicellulose, lignin, tall oil, and turpentine (Fig. 1). While cellulose fibers are mainly used for papermaking, the remaining components are considered to be by-products.

EXTRACTION PROCESS

For many years, tall oil was treated as waste or burned as fuel. Tall oil products were not made on a commercial scale until the 1930s, when the invention of the recovery boiler enabled recovery and reuse of organic chemicals in the Kraft wood-pulping process that separates tall oil from wood chips. (Fig. 2, page 28).

In the Kraft process, after the pine chips are digested and filtered, the filtrate, called "black liquor," is fed to an evaporator and skim tank for soap making. The soap is then acidulated to make crude tall oil (CTO). The CTO is then further fractionated at the refinery to get tall oil heads,

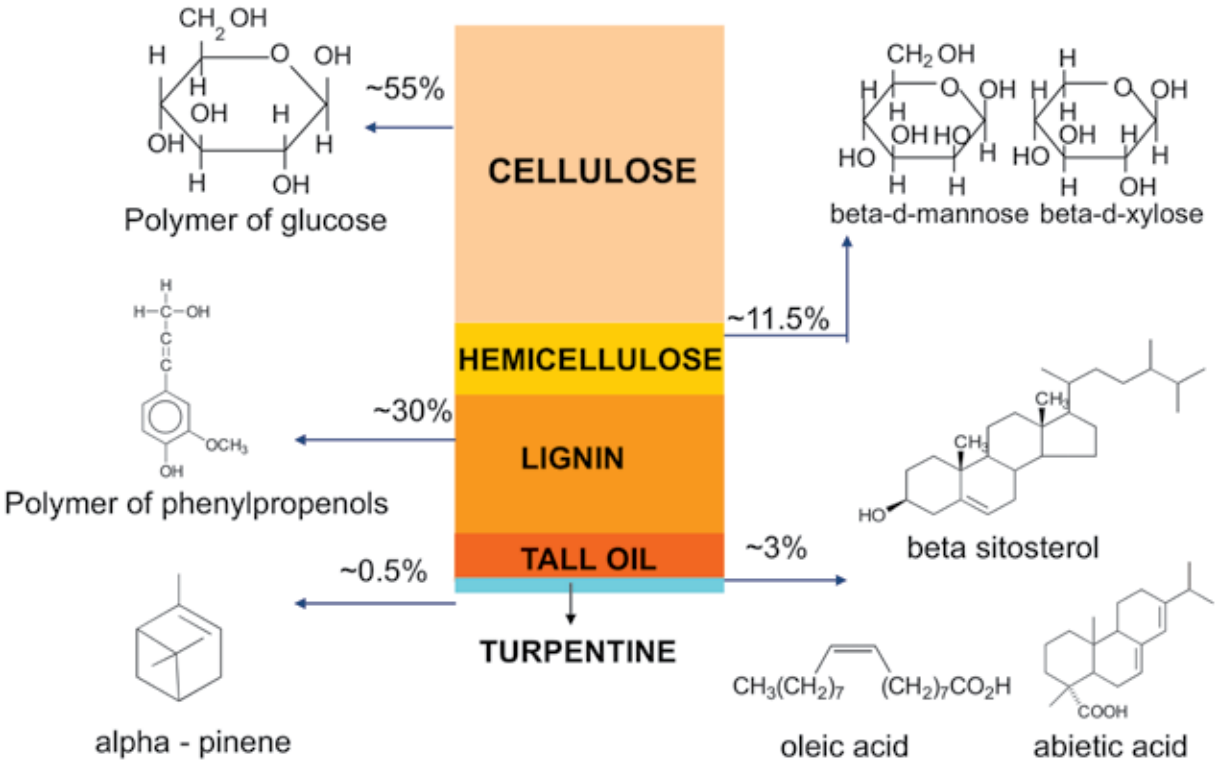


FIG. 1. Composition of a pine tree

tall oil fatty acids (TOFA), distilled tall oil fatty acids (DTO), tall oil rosin (TOR), and tall oil pitch (TOP) (Fig. 3, page 28).

The most important components in CTO are tall oil fatty acids (TOFA) and rosin acids (TOR). Unlike most vegetable oils and animal fats, tall oil is not produced as triglycerides but as straight fatty acids. Nevertheless, tall oil is considered to be from a renewable resource, just like vegetable oils.

With about 3% of total weight in pine wood chips, crude tall oil(CTO) is valued at $243 million in world exports, contributing to global revenues of $10 billion for the pine chemical industry ("Global impact of the modern pine chemical industry," Pine Chemical Association, 2016, "https://pinechemicals.site-ym.com/news/292194/GLOBAL-IMPACT-OF-THE-MODERN-PINE-CHEMICAL-INDUSTRY.htm).

TALL OIL COMPOSITIONS

With a composition similar to that of vegetable oils, TOFA is a mixture of fatty acids with various chain lengths and saturations. The most common components are oleic acid, linoleic acid, linolenic acid, palmitic acid, and stearic acid. The carbon chain distribution of tall oil is similar to that of sunflower and soybean oil, which have a higher prevalence of longer chains (C16 and higher) than coconut and palm kernel oil do.

A unique property of TOFA is that it contains various amount of rosin (represented here are abietic and pimaric acid). The presence of rosin creates physical properties that could not be obtained from vegetable and animal fats. For example, it reduces the bioactivity of TOFA in downstream for-

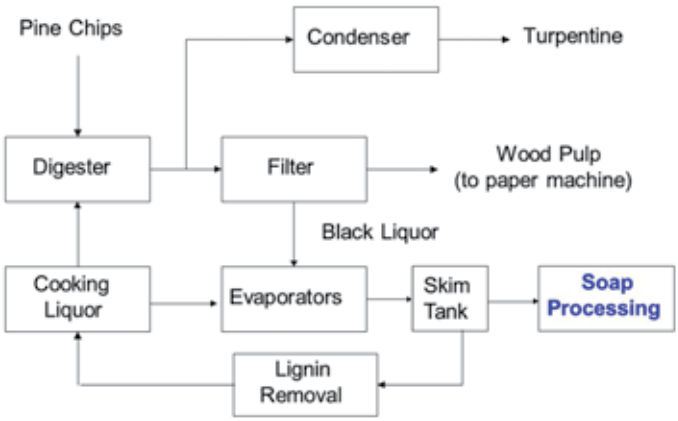


FIG. 2. Flow diagram of a typical Kraft pulping process

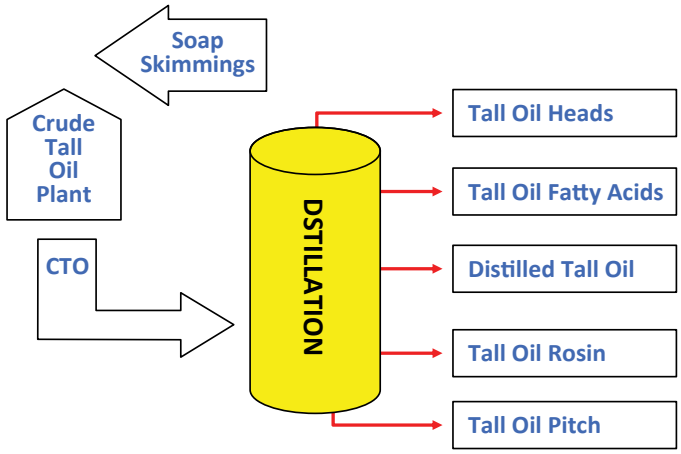


FIG.3. Components in tall oil fractionation

mulations, particularly in metalworking fluid and Household, Industrial, and Institutional (HI&I) products.

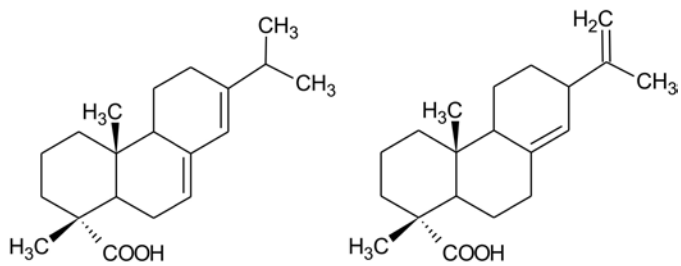
In addition to TOFA and rosin, there are other often-ignored components of tall oil processing—unsaponifiables. These are neutral compounds that do not have carboxylic functional groups and thus do not readily form soap when they react with caustic. The main components of unsaponifiables are hydrocarbons, alcohols, and sterols. Although such compounds appear in all five fractions of tall oil distillation, they are more dominant in tall oil heads and pitch. The extraction of sterols makes the unsaponifiables portion of tall oil more commercially attractive.

CHEMISTRIES AND APPLICATIONS

Derivatization of TOFA and rosin leads to their salts, esters, and resins. While C36 dimer acids and C-21 diacids are unique to TOFA, pitch can also be used to extract sterols for medical and fuel applications.

Current applications of TOFA include adhesive, inks, surfactants, painting and coatings, mining, and metalworking. Rosin is used in many applications, including adhesives, inks, tires, chewing gums, varnishes, electronics, papermaking, coating, and roadmaking.

Esters are one of the most common derivatives of TOFA due to the esterification of polyols (glycerol, pentaerythritol, and trimethylolpropane), short chain alcohols, and ethoxylates. Alkyd resins are a major application of TOFA esters. Short-chain alcohol esters have been used in biodiesel, synthetic lubricants, and as surfactants. An example of a new product based on C-21 diacids is Altalub 5300, which has shown promise in lubricant applications ("Performance lubricity additive for metalworking fluids," *Tribology & Lubrication Technology 72*: 76, 2016).



Abietic acid pimaric acid

FIG. 4. The molecular structures of two rosins found in tall oil fatty acids

TOFA amides are also being produced; applications include asphalt additives and mud drilling in oilfields.

TOFA in the forms of DTO, heads, and CTO or their mixtures, have been used as anionic collectors in mineral flotation. The presence of rosin acids in TOFA can sometimes help to improve the froth property of the collectors. In addition, TOFA amidoamines can also be used as cationic collectors in phosphate ore flotation (McSweeney, E., *et al.*, 1987).

The Diels-Alder reaction is a very commonly practiced reaction for both TOFA and rosin derivatization. For example, maleic anhydride would be used as a reactant with a conjugated portion of TOFA (conjugated linoleic acid) or rosin (abietic-type acids).

Another common reaction in tall oil derivatization is disproportionation—an isomerization reaction of TOFA or rosin under heat, usually with a catalyst. In TOFA, iodine has been used to catalyze disproportionation, thus converting non-conjugated linoleic acid to conjugated linoleic acid, and eventually to oleic acid.

Similarly, rosin can be disproportionated from its conjugated diene components, such as abietic and palustric acid, to its aromatic form as dehydroabietic acid, which is widely used in the rubber industry (Fig. 4).

Diene portions of rosin can be utilized for a Diels Alder reaction with maleic acid or anhydrides—or fumaric acids—to make tricarboxylic acids and further derivatizations for ink and adhesive applications.

NEW POTENTIAL APPLICATIONS

In addition to traditional applications in rubber, adhesives, and inks, new applications of tall oil products have been developed.

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Novel applications were recently discovered by making ionic liquids based on TOFA and rosin (Klejdsz, T., *et.al.*, 2016).

In addition, new potential applications for rosin-based chemistry related to flame retardants have been explored (Zhang, M., *et al.*, 2015, and Lei, *et al.*, 2015).

TOFA and rosin have also been explored as renewable hydrocarbon sources (Jenab, E., *et al.*, 2014).

Despite of its long history, the tall oil industry continues to evolve. As people pay more and more attention to green chemistry and sustainability, tall oil offers alternative raw materials and products to both petroleum oil and other natural oils.

Bing Wang is a senior principal scientist at Ingevity Corporation. He has broad experience in the chemical industry involving such areas as flame retardants, water treatment, mining, oilfields, and surfactants. His current research focuses on new applications of tall oil and its derivatives. He can be contacted at Bing.wang@ingevity.com.

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A conversation with Scott Bloomer

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

Laura Cassiday

In September 2017, AOCS welcomed Scott Bloomer as its new director of technical services, following the retirement of Richard Cantrill earlier in the year. Bloomer will lead AOCS technical products and services and represent the scientific interests of AOCS with key scientific and technical stakeholders in government, academia, and industry.

Bloomer has over 20 years of experience in the fats and oils industry. Most recently, he was a principal scientist and senior patent agent at Archer Daniels Midland Company. In that role, he assessed the value of new process technology and product development and prosecuted patents in the areas of food oil, biodiesel, and renewable chemicals from oils. He holds a doctorate in bioorganic chemistry from the University of Lund, Sweden.

I recently had a conversation with Bloomer about his background, goals, and vision for AOCS technical services.

Q: How did your previous experience in the fats and oils industry prepare you for your current role at AOCS?

I did research on many aspects of fats and oils processing at Cargill, including degumming, alkali refining, deodorization, and hydrogenation, as well as developing methods for biodiesel synthesis and emulsifier purification. I also worked at Land O'Lakes doing basic and applied research on modifying dairy fats and proteins with enzymes. Following that, I worked at Archer Daniels Midland as a patent agent, where I drafted and prosecuted patents on fats and oils processing and on replacing petroleum-based ingredients with bio-based feedstocks. I also was able to spend much of my time analyzing patents to identify opportunities for research and product development.

Q: What was your involvement with AOCS prior to accepting this position?

My first peer-reviewed paper was published in *JAOCS*. I was a peer reviewer and associate editor in the biotechnology area for many years and have been providing patents for the *Inform* patent column for about 15 years.

Q: In your mind, what are the strengths of AOCS Technical Services?

First, we have an outstanding team, dedicated to providing value to AOCS members. Our flagship production is the 7th Edition of the *Official Methods and Recommended Practices of the AOCS*, which contains more than 450 analytical testing methods used around the world. Our Laboratory Proficiency Program (formerly the Smalley Check Sample Program) is also broadly used to demonstrate laboratory accuracy and reliability. Our Certified Reference Materials are used to confirm the absence of GMO in oilseeds and other traded food commodities.

Q: Are there areas that need improvement?

We are working hard to obtain ISO certification for our Laboratory Proficiency Program. Because our program is 99 years old, it predates the ISO certification process by decades and requires a bit of custom tailoring.

Q: Do you have any specific plans for improving or advancing AOCS Technical Services?

Given the rapidly expanding consumer desire to see organic foodstuffs, we need to expand the offerings of our Certified Reference Material program to make more standards available to food industries around the world.

Q: Thus far, what do you like most about your job as director of technical services?

Without a doubt, the AOCS staff. They are smart, hard working, and genuinely invested in providing the best services to the AOCS membership and the broader fats and oils community.

Q: What activities to do you enjoy when not working?

I enjoy roasting my own coffee, driving my Triumph TR4A (the 50-year-old British sports car I rebuilt), and training in martial arts.

Olio is produced by Inform's associate editor, Laura Cassiday. She can be contacted at laura.cassiday@aocs.org.

Re-evaluation of **mono- and di-glycerides of fatty acids** (E 471) as food additives

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

European Food Safety Authority (EFSA) Panel on Food Additives and Nutrient Sources added to Food (ANS)

Mono- and di-glycerides of fatty acids (E 471) is authorized as a food additive in the European Union (EU) in accordance with Annex II and Annex III to Regulation (EC) No 1333/2008 on food additives and specific purity criteria have been defined in the Commission Regulation (EU) No 231/2012. The Scientific Committee on Food (SCF) concluded that the use of mono- and di-glycerides of fatty acids in nutrient preparations for use in infant formulae and follow-on formulae is acceptable within the direct additive limit of 4 g/L and for use in weaning foods within the direct additive limit of 5 g/kg. The Panel noted that this food additive has not been evaluated for its other authorized uses as a food additive in EU.

The Panel considered that it is very likely that hydrolysis of mono- and di-glycerides of fatty acids by lipases in the gastrointestinal tract would occur, resulting in the release of glycerol and fatty acids. Glycerol (E 422) and fatty acids (E 570) have been re-evaluated, and the Panel concluded that there was no safety concern regarding their use as food additives.

In rats, only traces of cottonseed oil monoglycerides were found in the feces, indicating that after hydrolysis, the components were well absorbed (97.8 ± 0.4%). In another study, the absorption of hydrolysis products from diglycerides of fatty acids was calculated to be 58.8 ± 14.3%.

The Panel noted that the diacylglycerol (diglyceride) used in several toxicity studies described below was intended to be used for nutritional purposes (as an edible oil substitute) and that it had a composition rich in unsaturated fatty acids (> 95%). The Panel further noted that its composition made this material acceptable with regard to the specifications of E 471. The Panel considered that the results of the toxicological studies with these diacylglycerols can be used for the assessment of E 471.

No study was available to evaluate the acute toxicity of E 471. No evidence for adverse effects were reported in short-term and subchronic studies in rats and hamsters even at the highest dose tested of 2,500 mg diacylglycerol/kg body weight (bw) per day in the rats and 7,500 mg glyceryl stearate/kg bw per day in hamsters.

The Panel considered that the available studies did not raise any concern with regard to genotoxicity.

No adverse effects were reported in chronic toxicity studies at doses as high as 7,800 and 2,000 mg diacylglycerol/kg bw per day in mice and rats, respectively. In mice and rats, diacylglycerol did neither show carcinogenic potential nor a promotion effect in initiation/promotion studies.

The refined estimates were based on 31 out of 84 food categories in which mono- and di-glycerides of fatty acids (E 471) is authorized. The Panel considered that the uncertainties identified would, in general, result in an overestimation of the exposure to mono- and di-glycerides of fatty acids (E 471) as a food additive in European countries for the refined sce-

nario as the food additive may not be used in food categories, for which no usage data have been provided.

However, the Panel noted that considering information from the Mintel's Global New Products Database (GNPD), mono- and di-glycerides of fatty acids (E 471) is used in food categories for which no use levels have been provided to the European Food Safety Authority (EFSA). The main food categories, in terms of amount consumed, for which no use levels reported were: unripened cheese; different kinds of pasta; processed fish and fishery products, including molluscs and crustaceans; processed eggs and egg products; and salads and savory-based sandwich spreads. The Panel further noted that the exposure to mono- and di-glycerides of fatty acids (E 471) from their use according the Annex III to Regulation (EC) No 1333/2008 (Parts 1, 2, 3, 4, and 5 A and B) was not considered in the exposure assessment. Therefore, the exposure to mono- and di-glycerides of fatty acids (E 471) may be underestimated in all scenarios.

The Panel noted that in Annex II of Regulation (EC) No 1333/2008, use levels of mono- and di-glycerides of fatty acids (E 471) in food for infants under the age of 12 weeks are included in category 13.1.1, 13.1.5.1 and 13.1.5.2. The Panel considered that these uses for infants under the age of 12 weeks would require a specific risk assessment in line with the recommendations given by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (1978), the SCF (1998) and EFSA (EFSA Scientific Committee, 2017). Therefore, the current re-evaluation of mono- and di-glycerides of fatty acids (E 471) as a food additive is not applicable for infants under the age of 12 weeks.

The Panel noted that no specific clinical data addressing the safety of use of mono- and di-glycerides of fatty acids (E 471) in "dietary foods for infants for special medical purposes and special formulae for infants" (food category 13.1.5.1) and in 'dietary foods for baby and young children for special medical purposes as defined in Directive 1999/21/EC' (food category 13.1.5.2) considering the defined maximum use levels were available to the Panel.

According to the conceptual framework for the risk assessment of certain food additives re-evaluated under Commission Regulation (EU) No 257/2010 (EFSA ANS Panel, 2014) and given that:

- in the current safety assessment carried out by the Panel, the uses and use levels reported by the food industry in 46 out of 84 food categories in which mono- and di-glycerides of fatty acids (E 471) is authorized were considered. However, only 31 food categories were taken into account for the refined exposure assessment;
- mono- and di-glycerides of fatty acids are subjected to hydrolysis by lipases in the gastrointestinal tract to liberate glycerol and fatty acids;
- data from the evaluation previously conducted for the food additives glycerol (E 422) and fatty acids (E 570) can be used for the evaluation of the food additive mono- and di-glycerides of fatty acids (E 471);
- there was no indication for a genotoxic, carcinogenic or reprotoxic potential from the available data; and
- the contribution of mono- and di-glycerides of fatty acids (E 471) to the daily diet represented at the mean only 0.8–3.5% of the recommended daily fat intake.

The Panel concluded that there was no need for a numerical acceptable daily intake (ADI) and that the food additive mono- and di-glycerides of fatty acids (E 471) was of no safety concern at the reported uses and use levels. The Panel recommended that:

- the European Commission considers lowering the current limits for toxic elements (arsenic, lead, mercury and cadmium) in the EU specifications for mono- and di-glycerides of fatty acids (E 471) in order to ensure that the food additive will not be a significant source of exposure to these toxic elements in food;
- the European Commission considers revising the EU specifications for mono- and di-glycerides of fatty acids (E 471) including maximum limits for impurities currently included in the EU specifications for glycerol (E 422) or recommended by the Panel in the re-evaluation of glycerol (E 422) (EFSA ANS Panel, 2017b);
- the European Commission considers revising the EU specifications for mono- and di-glycerides of fatty acids (E 471) including maximum limits for residual solvents which can be used when manufacturing mono- and di-glycerides of fatty acids (E 471), i.e. *tert*-butanol or *tert*-pentanol;
- the European Commission considers revising the EU specifications for mono- and di-glycerides of fatty acids (E 471) including maximum limits for trans fatty acids because mono- and di-glycerides of fatty acids (E 471) can be manufactured by glycerolysis of hydrogenated fats and/or oils, which contain significant amounts of trans fatty acids;
- the European Commission considers revising the EU specifications for mono- and di-glycerides of fatty acids (E 471) including maximum limits for glycidyl esters because refined vegetable oil, which can be used for manufacturing of mono- and di-glycerides of fatty acids (E 471) is the only identified source of glycidyl esters of fatty acids, which are formed during deodorization;
- the European Commission considers revising the EU specifications for mono- and di-glycerides of fatty acids (E 471) including maximum limits for erucic acid because erucic acid can be present among the fatty acids in edible oils which can be used for manufacturing of mono- and di-glycerides of fatty acids (E 471); and
- more data should be generated to decrease uncertainty arising from the occurrence of compounds of toxicological concern (e.g. 3-monochloropropane-1,2-diol (3-MCPD) or glycidyl esters), which can be produced under certain processing conditions from the food additive mono- and di-glycerides of fatty acids (E 471).

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Argentina: corn oil from the 6th worldwide producer of fats and oils

Leslie Kleiner

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

According to a recent article by the "Bolsa de Comercio de Rosario (Rosario Stock Market-Argentina)," Argentina's production during 2016/2017 would change the country's rank from 7th to 6th worldwide oil and fats producer (with "oil and fat" encompassing palm, soy, cotton, peanut, sunflower, corn, and others) [1]. A positive growth of 10.5% during 2016/2017 boosted the country's estimated total production to 10,231 thousand metric tons, pushing it into 6th place behind Indonesia, China, the European Union, Malaysia, and the United States, and ahead of Brazil, which was bumped to 7th place by negative growth during that period of-1.1%.

Since corn oil is one of the oils Argentina produces, I interviewed Licenciada Silvana Lisi, Jefa de Desarrollo de Agronegocios (Manager of Business Development- Agribusiness), Arcor Argentina, to learn more about this oil's production.

Q: In the United States, it is common to use soybean oil for daily applications, and canola oil for frying. What are common uses for corn oil in Argentina?

In Argentina, the most common uses of corn oil are for the preparation of salads and fried foods. Corn oil is also commonly used in the preparation of mayonnaise and preserves.

Q: What is the annual consumption of corn oil in Argentina?

Corn oil represents 2% of the oils consumed in Argentina, and has an annual volume of 4,200 metric tons. Arcor's corn oil (*aceite de maíz Arcor*) is leader in the field, with over 30% of the market segment. Figure 1 depicts the evolution of corn oil consumption per category (human consumption, or bioethanol and industrial feed combined).

Q: What does a characteristic fatty acid profile for corn oil look like?

Corn oil has a low saturated fatty acid content (15%), most of which (11%) is comprised of palmitic acid (C16:0). Instead, corn oil has a high percentage of unsaturated fatty acids (>80%), which are of

FIG. 1. Oil consumption per use. Y-Axis: kg/ person/year; dark blue indicates bioethanol and industrial feed combined; light blue indicates human consumption. Source: Ministerio de Agroindustria de la Nación – Subsecretaría de Mercados Agropecuarios (http://www.agroindustria.gob.ar/)

interest for their role in the reduction of cardiovascular diseases. Within the unsaturated fatty acids, linoleic acid (C18:2) comprises approximately 51% of the composition. This is followed by oleic acid (C18:1), which represents approximately 32% of the content. In addition, due to the mild processing conditions, Arcor corn oil has no trans fatty acids present in its composition.

Q: What additional benefits may arise from the consumption of corn oil?

Corn oil contains ~25 mg/100 g of vitamin E. Therefore, a 13 mL serving (this equates to 1.5 soup spoons) yields 30% of the recommended daily value currently established in Argentina. Vitamin E is an important component of the diet, since it has antioxidant properties that help prevent cell damage caused by the presence of free radicals.

In addition, corn oil has a larger content of phytosterols than olive and canola oil, respectively (0.77% phytosterols, by weight [2]). Phytosterols are plant-derived compounds that when consumed through diet, have been shown to reduce circulating LDL-cholesterol levels at a clinically significant level [3,4]. In particular, phytosterols from corn oil have been shown to substantially reduce cholesterol absorption in humans [2].

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Q: In general terms, how is corn oil produced?

Most of the corn oil is stored within the germ; therefore, corn oil production starts by removing the germ from the grain. This can be achieved by physical and chemical processes that lead to "wet milling," or by a physical process alone that instead leads to "dry milling."

From the corn germ, the oil extraction process is not much different than that used for soy and sunflower oil extraction: pressing and/or solvent extraction. These extraction processes first condition the germ by means of mills that break and laminate; then, a press extracts a large oil portion, and the remaining cake is further processed to recover trapped oil by means of solvent extraction. The resulting crude oil is degummed to eliminate hydratable phospholipids (Fig. 2), and the product is then refined (neutralized, winterized, washed, dried, and deodorized); see Figure 3. There are many variables that can be adjusted in the process, and these largely depend on the type and quality of the available germ.

FIG. 2. Process sequence to obtain crude and degummed corn oil

FIG. 3. Process sequence to obtain refined corn oil

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PATENTS

Milk-based alternative product and method for producing the same

Domazakis, *et al*., Creta Farm Societe Anonyme Industrial and Commercial, US9661863, May 30, 2017

The present invention concerns the production of a milk-based alternative product, using edible oil to substitute at least part of the milk fat. In particular, the present invention concerns the production of a cheese alternative product, an ice cream alternative product, a custard alternative product, or a chilled or frozen dessert alternative product, using an edible oil to substitute at least part of the milk fat. Further, a milk based alternative product, in particular a cheese alternative product, an ice cream alternative product, a custard alternative product, or a chilled or frozen dessert alternative product, and the use of an edible oil, in particular olive oil, for the production of the milk-based alternative product are disclosed.

Nanogel comprising water-soluble active ingredients

Ding, *et al*., DSM IP Assets B.V., US9661870, May 30, 2017

The present invention relates to a nanogel composition comprising at least one water-soluble active ingredient, one or more plant proteins, and one or more soy soluble polysaccharides. These compositions can be used for the enrichment, and/or fortification of food, beverages, animal feed, and/or cosmetics, and allow stabilization of the active ingredient. The present invention also refers to the process for the preparation of such nanogel compositions. The present invention furthermore refers to a process for the manufacture of a beverage by mixing the compositions with ingredients of beverages. The present invention also refers to beverages obtainable by this process.

Nutritional compositions containing structured fat globules and uses thereof

Banavara, *et al*., Mead Johnson Nutrition Company, US9661874, May 30, 2017

The present disclosure relates to a lipid source for nutritional compositions, comprising an enriched lipid fraction which comprises structured fat globules. The enriched lipid fraction provides fat globules having a desired size and fatty acid composition and may be stabilized by components such as phospholipids, cholesterol, milk-fat globule membrane protein, and combinations thereof. Additionally, the disclosure relates to methods of supporting lipid digestion in a pediatric subject by providing a nutritional composition comprising an enriched lipid fraction having structured fat globules that are more accessible to lipases. The chemical composition, size, and structure of the fat globules may improve digestion. The disclosed nutritional compositions may provide additive and or/synergistic beneficial health effects.

Botanical extract from the aqueous stream of the palm oil milling process for the prevention and inhibition of oxidative stress and hemolysis in human red blood cells

Balasundram, *et al*., Malaysian Palm Oil Board, US9669065, June 6, 2017

The invention provides a composition for the prevention and inhibition of oxidative stress and hemolysis in human red blood cell wherein said composition compounds obtained from the aqueous stream of palm oil milling (palm oil vegetation liquor), in particular from vegetative liquor from the milling of palm oil fruit.

Production of fatty acid alkyl esters

Nielsen, Novozymes A/S, US9670513, June 6, 2017

A method for producing fatty acid alkyl esters, wherein a solution comprising triglyceride, alcohol, water, and glycerol is contacted with a lipolytic enzyme.

Separation systems for dewatering of fog and biodiesel fuel production

Bell, *et al*., Smartflow Technologies, Inc., US9670429, June 6, 2017

The present invention provides for methods and systems that effectively separate dispersed FOG from emulsions and/or free-floating FOG from a waste stream to provide dewatered emulsions and/or separated fats, oils, and greases from emulsions thereby providing value added separated product while reducing disposal of solid or liquid waste matter into landfills or water treatment facilities.

Methods, compositions, and devices for supplying dietary fatty acid needs

Margolin, *et al*., Alcresta Therapeutics, Inc., US9668942, June 6, 2017

Nutritional formulas comprising long-chain polyunsaturated fatty acids (LC-PUFAs) are provided, along with methods and devices for preparing and/or administering nutritional formulas. In some embodiments, a percentage of the LC-PUFAs in the nutritional formula are in the form of monoglycerides and/or free fatty acids. In some embodiments, the nutritional formulas do not comprise added lipase. Also provided are methods for providing nutrition to a subject, methods for improving fat absorption, methods for improving cognitive ability, methods for preventing chronic lung disease, and methods for reducing the length of time a patient requires total parenteral nutrition.

Automatic frying machine

Kim, *et al.*, Kornic Automation Co., Ltd., US9668616, June 6, 2017

The present invention relates to an automatic frying machine comprising: a frying process part having divided spaces, wherein a plurality of module-type process units which carry out each of predetermined frying processes are detachably disposed in the divided spaces; and a transfer part which is in communication with the plurality of process units of the frying process part and which carries a basket having frying materials in and out of the plurality of process units and moves the basket, wherein the transfer part comprises: a basket which carries the frying material in and out through an opening formed on the plurality of process units; a transfer unit which raises and lowers the basket and slides it back and forth; and a horizontal moving part which moves the transfer unit horizontally.

Compositions and methods for producing elevated and sustained ketosis

D'Agostino, D.P., *et al.*, US9675577, University of South Florida, June 13, 2017

Beta-hydroxybutyrate mineral salts in combination with medium chain fatty acids or an ester thereof such as medium-chain triglycerides were used to induce ketosis, achieving blood ketone levels of (2-7 mmol/L), with or without dietary restriction. The combination results in substantial improvements in metabolic biomarkers related to insulin resistance, diabetes, weight loss, and physical performance in a short period of time. Further, use of these supplements to achieve ketosis yields a significant elevation of blood ketones and reduction of blood glucose levels. Use of these substances does not adversely affect lipid profiles. By initiating rapid ketosis and accelerating the rate of ketoadaptation, this invention is useful for the avoidance of glucose withdrawal symptoms commonly experienced by individuals initiating a ketogenic diet, and minimizes the loss of lean body mass during dietary restriction.

Cooking aid

Krauch, J., *et al.*, Nestec SA, US9675082, June 13, 2017

A cooking aid comprising a sheet of flexible burn-resistant material and a composition disposed on one face of the sheet, the composition comprising a mixture of vegetable or animal oil with a melting point below 20°C, vegetable or animal fat with a melting point above 20°C, and one or more herbs, spices, and flavor enhancers.

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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EXTRACTS & DISTILLATES

Seed development and hydroxy fatty acid biosynthesis in *Physaria lindheimeri*

Chen, G.O, *et al.*, *Ind. Crops. Prod. 108*: 410–415, 2017, https://doi.org/10.1016/j.indcrop.2017.06.065.

Hydroxy fatty acids (HFAs) are valuable industrial raw materials used in many industries. *Physaria lindheimeri* accumulates over 80% HFA, in the form of lesquerolic acid (20:1OH), in its seed oil. Understanding the seed development of *Physaria lindheimeri* is an important step to utilizing this unique wild species as a genetic source of HFAs biosynthesis. The changes of seed growth, lipid accumulation, and fatty acid composition during seed development of *P. lindheimeri* were examined from 14 days after pollination (DAP) to desiccation (56 DAP). The seed development could be divided into three periods. During the early period (14 and 21 DAP), seed rapidly increased in size and fresh weight. In mid-maturation period (28, 35, and 42 DAP), lipids and dry weights accumulated steadily. When seeds developed to late-maturation/desiccation stages (49 and 56 DAP), fresh weight dropped significantly due to water loss, and the dry weight and lipid accumulation reached their maximums. Seed color remained green up to 42 DAP and turned to orange-brown at 49 and 56 DAP. The major fatty acid 20:1OH started accumulation when seeds developed into mid-maturation stage (28 DAP) and the accumulation continued thereafter up to 56 DAP, eventually reaching up to 77% of the total seed oil. The HFA accumulation indicates embryonic storage tissue formation, thus 28 DAP defines a critical time point for seed development entering reserve synthesis and accumulation. The information and knowledge obtained from this study are essential to the success of HFA production using metabolic pathway engineering approaches in commodity oilseed crops.

Highly sensitive method for the quantification of trans-linolenic acid isomers in trilinolenin of edible oils using an ionic liquid capillary column

Guo, Q., *et al.*, *J. Sci. Food Agric. 97*: 4697–4703, https://doi.org/10.1002/jsfa.8337.

The polarities of linolenic acid isomers are very similar, and only a few studies to date have attempted to separate α-linolenic acid (ALA) isomers completely. The aim of this study was to fill this gap by developing and validating an accurate method for the analysis of ALA isomers in trilinolenin at 200, 220, and 240°C using a gas chromatograph–flame ionization detector equipped with an SLB-IL111 capillary column. Results showed that eight ALA isomer standards were separated effectively using these optimized gas chromatographic conditions. The coefficient of determination was r2 > 0.9994 in the linear range of each ALA isomer. The obtained limits of detection and limits of quantification of the ALA isomers were 0.02–0.08 ppm and 0.05–0.22 ppm, respectively. A high degree of reproducibility and percent recoveries between 96.2% and 106.5%, with coefficients of variation ranging from 0.82% to 0.97%, were achieved. The developed method has been successfully applied to the analysis of ALA isomers in heated pure trilinolenin as well as to trilinolenin in various edible oils, and the TALA isomerization pathways in heated trilinolenin were verified.

Economic feasibility analysis of soybean oil production by hexane extraction

Chenga, M.-H. and K.A. Rosentraterb, *Ind. Crops. Prod. 108*: 775–785, 2017, https://doi.org/10.1016/j.indcrop.2017.07.036.

Hexane extraction is the most common method used in the industry to produce soybean oil due to its high oil recovery and lower production cost. With the demands of soybean oil increasing either in food or industrial applications, expansion plans are considered by many companies to increase production capacity. Techno-economic analysis is performed to evaluate the economic feasibility of soybean oil production by hexane extraction based on historical scenarios from 1980 to 2015. Capital investment, operating costs, revenues, and profits are main parameters to consider when estimating profits, gross margin, return on investment (ROI), and payback time and are the indices used to evaluate the profitability of the process. As the plant capacity increases in scale to over 34.64 million kg of annual soybean oil production, the break-even is met and the producing stream is able to earn profits. Additionally, sensitivity analysis is also applied to examine which factor affects profit the most. In the hexane extraction process, material costs, especially for soybean prices, have the most significant effect on profit. However, soybean meal is the main driving force for soybean oil production due to its significant amount of productivity and revenues.

Production of seed-like storage lipids and increase in oil bodies in corn (maize; *Zea mays* l.) vegetative biomass

Alameldina, H., *et al.*, *Ind. Crops. Prod. 108*: 526–534, 2017, https://doi.org/10.1016/j.indcrop.2017.07.021.

Triacylglycerides (TAGs) are high energy density lipids with a $25 billion commodity at international level. Plant TAGs are produced via a series of chemical reactions catalyzed by certain enzymes including diacylglycerol acyltransferases (DGATs) and phospholipid diacylglycerol acyltransferases (PDATs). In Arabidopsis, certain transcription factors including Wrinkled 1 (Wri1) and Leafy Cotyledons2 (LEC2) supply the necessary substrates for synthesis of fatty acids and/or for packaging of the oil

bodies. TAGs will be stored as oil body structures which certain proteins such as oleosin can protect them from enzymatic degradation. In this study, we overexpressed three major genes involved in the TAG biosynthesis and accumulation; 1) dgat1 as a key enzyme in TAGs biosynthesis, 2) wri1 which is the major transcription factor involved in supplies of fatty acids for TAG biosynthesis, and 3) oleosin (Ole) gene which encodes for protein that protects TAGs from degradation. All three genes were integrated in maize genome under a constitutive promoter to allow the production of oil bodies and seed storage oil-like TAG in maize vegetative biomass. Our results indicated an increase in the total leaf oil contents by 79% in the metabolically engineered line. GC-MS analysis detected a total of 13 fatty acids in the leaf oil extract samples, representing ~99.99% of the total fatty acids. Overall, the percentage of the leaf total saturated (SFA) were decreased while the percentage of monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) were increased in metabolically engineered plant leaves. This is the first report of increasing TAG accumulation in maize vegetative biomass (stover) via metabolic engineering, which will open new dimension for creating new opportunities to complement and expedite the cellulosic biofuels applications.

Fatty acid metabolism and prospects for targeted therapy of cancer

Chen, T., *et al.*, *Eur. J. Lipid Sci. Technol. 119*: 1600366, 2017, https://doi.org/10.1002/ejlt.201600366.

Fatty acids are fundamental substrates required for energy storage, synthesis of membranes, generation of signaling molecules, and lipid droplet formation in cancer cells. High levels of fatty acid metabolic activity are one of the most aberrant metabolic alterations in cancer cells. The *de novo* fatty acid synthesis pathway is the primary source of fatty acids in cancer cells, but cancer cells can also acquire fatty acids through the lipolytic pathway, which helps cells survive and maintain their invasiveness. Key enzymes, including ATP-citrate lyase (ACLY), fatty acid synthase (FASN), acetyl-coenzyme A (CoA) carboxylase (ACC), stearoyl-CoA desaturase 1(SCD1), and monoacylglycerol lipase (MAGL), which are involved in fatty acid synthesis and degradation, are overexpressed in cancer cells. The alterations in fatty acid metabolomics in different cancers, at different stages of cancer, and in different tissues are clinically significant. This review focuses on current research into fatty acid metabolism to explore new targets against the fatty acid metabolic pathways for anticancer therapy.

The true methodology for rhamnolipid: various solvents affect rhamnolipid characteristics

Çakmak, H., *et al.*, *Eur. J. Lipid Sci. Technol. 119*: 1700002, 2017, https://doi.org/10.1002/ejlt.201700002.

Rhamnolipid, among the most effective biosurfactants, is a glycolipid-type biosurfactant primarily produced by *Pseudomonas aeruginosa*. In this study, rhamnolipid production was carried out using a strain of *P. aeruginosa* and it is aimed to compare rhamnolipid biopolymers obtained from various extraction methods using glycine (RG), hydrochloric acid (RH), diethyl ether (RD), ethyl acetate (RE). Comparison analyses were performed through NMR, FTIR techniques and viscosity, density measurements apart from determination of rhamnolipid yields. It can be concluded that rhamnolipid from diethyl ether for extraction is far from molecular structure to reference rhamnolipid molecule according to instrumental analyses performed. Besides, the yield of this rhamnolipid is much more than other rhamnolipids extracted through other methods but this is misleading because the value in there may be total sugar content apart from rhamnolipid. Therefore, RD extraction method can be said to be non-selective process for rhamnolipid obtained. In RH method, some functional group peaks belonging to rhamnolipid were not observed. NMR analysis showed that some CH groups were not observed in the RG method. However, especially NMR and FTIR analyses showed that rhamnolipid obtained from RE method represented more accurate rhamnolipid based on reference molecule.

Application of β-cyclodextrin, chitosan, and collagen on the stability of tocopherols and the oxidative stability in heated oils

Gim, S.Y., *et al.*, *Eur. J. Lipid Sci. Technol. 119*: 1700124, 2017, https://doi.org/10.1002/ejlt.201700124.

Effects of beta-cyclodextrin (β-CD), chitosan, and collagen on tocopherol and oxidative stability in heated oils were determined under moisture added condition at 180°C in this study. Collagen was added in the form of a mesh structure with different pore sizes (50, 100, 200, and 300 μm) whereas chitosan was added in the form of gel. Presence of 1% w/w β-CD significantly ($p < 0.05$) reduced the formation of *p*-anisidine compared to controls. Collagens also acted as antioxidants irrespective of pore sizes whereas chitosan gel failed to act as antioxidant or prooxidant. Collagen and β-CD significantly ($p < 0.05$) protected the decomposition of total tocopherols while chitosan failed to show such protection. Collagen with pore size of 300 μm significantly ($p < 0.05$) stabilized γ- and δ- tocopherols compared to controls and oils added with β-CD, chitosan, or collagen with pore size of 50 μm. The addition of β-CD, chitosan, and collagen significantly ($p < 0.05$) reduced the moisture content in heated oil compared to controls. β-CD or collagen mesh structure can be used in heated oils like frying condition to control the rates of lipid oxidation. Addition of biopolymers may extend the oxidative stability and shelf-life of heated oils and help to produce more food products.

Oryzanol modifies high-fat, diet-induced obesity, liver gene expression profile, and inflammation response in mice

Wang, L., *et al.*, *J. Agric. Food Chem. 65*: 8374–8385, 2017, https://doi.org/10.1021/acs.jafc.7b03230.

In Western countries and China, the dietary habit of high calories usually results in hyperlipidemia, which is closely asso-

ciated with cardiovascular diseases. In the study, we investigated the antihyperlipidemic effect of oryzanol and its molecular mechanism in the high-fat diet (HFD) mouse model. In total, 60 ICR mice were randomly divided into control group, HFD group, and HFD+Ory group. The mice from the HFD+Ory group were additionally fed with 100 mg/kg of oryzanol by intragastric administration. Our data indicated that oryzanol treatment for 10 weeks significantly reduced bodyweight, liver weight, and adipose tissues weight of the mice; lowered the contents of total cholesterol (TC), triglycerides (TG), and low density lipoprotein-cholesterol (LDL-C); and elevated high density lipoprotein-cholesterol (HDL-C) in the plasma of HFD mice. Compared with the HFD group, H&E staining showed that oryzanol treatment decreased the size of fat droplets of liver tissues and the size of adipocytes. Gene chip data found that oryzanol administration caused 32 genes to increase expressions while 60 genes had reduced expressions in the liver tissues of HFD mice. IPA software was used to analyze the protein interaction network and found that transcript factor NF-κB located in the central role of network, meaning NF-κB may have important function in the lipid-lowering effect of oryzanol. Western blotting and RT-qPCR confirmed that lipid metabolism-related gene expressions were obviously regulated by oryzanol administration. Oryzanol also inhibited expressions of inflammatory factor in the liver tissues of HDF mice. Taken together, our data indicate that oryzanol treatment can regulate lipid metabolism-related gene expressions and inhibit HDF-caused obesity in mice.

Plasma lipidomic profiles and cardiovascular events in a randomized intervention trial with the Mediterranean diet

Toledo, E., *et al., Am. J. Clin. Nutr. 106*: 973–983, 2017, https://doi.org/10.3945/ajcn.116.151159.

Lipid metabolites may partially explain the inverse association between the Mediterranean diet (MedDiet) and cardiovascular disease (CVD). We evaluated the associations between *1*) lipid species and the risk of CVD (myocardial infarction, stroke, or cardiovascular death); *2*) a MedDiet intervention [supplemented with extra virgin olive oil (EVOO) or nuts] and 1-y changes in these molecules; and *3*) 1-y changes in lipid species and subsequent CVD. With the use of a case-cohort design, we profiled 202 lipid species at baseline and after 1 y of intervention in the PREDIMED (PREvención con DIeta MEDiterránea) trial in 983 participants [230 cases and a random subcohort of 790 participants (37 overlapping cases)]. Baseline concentrations of cholesterol esters (CEs) were inversely associated with CVD. A shorter chain length and higher saturation of some lipids were directly associated with CVD. After adjusting for multiple testing, direct associations remained significant for 20 lipids, and inverse associations remained significant for six lipids. When lipid species were weighted by the number of carbon atoms and double bonds, the strongest inverse association was found for CEs [HR: 0.39 (95% CI: 0.22, 0.68)] between extreme quintiles (P-trend = 0.002). Participants in the MedDiet + EVOO and MedDiet + nut groups experienced significant ($P < 0.05$) 1-y changes in 20 and 17 lipids, respectively, compared with the control group. Of these changes, only those in CE(20:3) in the MedDiet + nuts group remained significant after correcting for multiple testing. None of the 1-y changes was significantly associated with CVD risk after correcting for multiple comparisons. Although the MedDiet interventions induced some significant 1-y changes in the lipidome, they were not significantly associated with subsequent CVD risk. Lipid metabolites with a longer acyl chain and higher number of double bonds at baseline were significantly and inversely associated with the risk of CVD.

Solvent-free biodiesel production catalyzed by crude lipase powder from seeds: effects of alcohol polarity, glycerol, and thermodynamic water activity

Kouteu, P.A.N., *et al., J. Agric. Food Chem. 65*: 8683–8690, 2017, https://doi.org/10.1021/acs.jafc.7b03094.

The aim of this work was to evaluate the potential of crude lipase powders made from *Adansonia grandidieri* and *Jatropha mahafalensis* seeds for the synthesis of fatty acid alkyl esters in a solvent-free system. The influence of the nature of the alcohol, the amount of glycerol, and hydration of the powder was investigated. Results showed that the activity of these crude lipase powders was inversely proportional to the alcohol polarity and the amount of the glycerol in the reaction medium. To ensure optimum activity, *A. grandidieri* and *J. mahafalensis* powders must be conditioned to a water activity of 0.33 and 0.66. To obtain a fatty acid ethyl ester yield greater than 95% with *A. grandidieri*, ethanol should be introduced at an amount corresponding to a triacylglycerol to ethanol molar ratio of 2:1 every 15 h for 96 h and use 25% of preconditioned crude lipase powders (2 additions of 12.5%).

They say coconut oil can aid weight loss, but can it really?

Clegg, M.E., *Eur. J. Clin. Nutr. 71*: 1139–1143, 2017, https://doi.org/10.1038/ejcn.2017.86.

There has in recent years, been much media speculation and consumer interest in the beneficial satiating properties of consuming coconut oil and its potential to aid weight loss. However, the media has primarily cited studies using medium-chain triglycerides (MCT) oil. The current perspective looks at the research that is available on coconut oil. It examines if and how MCT-related research can be applied to coconut oil and if there is potential for coconut oil to aid weight loss. The current report indicates a lack of consistent evidence on the topic of coconut oil, satiety, and weight loss. Given both the publicity and the increased consumption of coconut oil further research, particularly long-term clinical trials, in this area are warranted.

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Thinking outside the classical chain reaction box of lipid oxidation: evidence for alternate pathways and the importance of epoxides

Schaich, K.M., *et al.*, *Lipid Technol. 29*: 91–96, 2017, https://doi.org/10.1002/lite.201700025.

Lipid oxidation has always been viewed as a simple free radical chain reaction with straightforward sequence of radicals → hydroperoxides → products. The first paper in this series proposed that alternate reactions of lipid peroxyl and alkoxyl radicals compete with hydrogen abstraction to make the process much more complex. This article provides experimental evidence for formation of epoxides as major products and shows how monitoring a broad spectrum of products is critical for accurate assessment of the extent of lipid oxidation, elucidating reaction pathways, and anticipating potential toxicity.

trans-10,*cis*-12-conjugated linoleic acid affects expression of lipogenic genes in mammary glands of lactating dairy goats

Shi, H., *et al.*, *J. Agric. Food Chem. 65*: 9460–9467, https://doi.org/10.1021/acs.jafc.7b02377.

The molecular mechanisms on milk fat depression (MFD) in response to *trans*-10,*cis*-12-conjugated linoleic acid (*t*10,*c*12-CLA) supplementation in ruminants were elucidated in this research with dairy goats. A total of 30 2-year-old Xinong Saanen dairy goats [40 ± 5 days in milk (DIM)] at peak lactation stage were assigned to a 3 × 3 Latin square design (14-day treatment period, followed with 14-day washout). Three CLA treatments included (a) control, fed the basal diet only without CLA supplementation; (b) orally supplemented with 8 g/day of lipid-encapsulated CLA (low dose, CLA-1); and (c) orally supplemented with 16 g/day of lipid-encapsulated CLA (high dose, CLA-2). Expression levels of fatty acid metabolism genes in the mammary tissues were analyzed by real-time quantitative polymerase chain reaction (RT-qPCR) in three goats on day 1 and the other three goats on day 14 in each group after the discontinuation of CLA treatment in the third experimental period. Dietary supplementation of CLA led to a significant decrease of milk fat compared to the control ($p < 0.05$). Milk fat concentrations in CLA-1 and CLA-2 groups were 2.74 and 2.42%, respectively, while the milk fat concentration in the control group was 2.99%. Decreases in short- and medium-chain fatty acids (<16 carbons) and increases in unsaturated fatty acids were observed in the CLA-2 group ($p < 0.05$). The desaturation indexes of C16 and C18 fatty acids were obviously increased ($p < 0.01$). RT-qPCR results revealed decreases of the mRNA expression levels of *SREBF1*, *PPARG*, *LPL*, *CD36*, *FABP3*, *ACSL1*, *FASN*, *ACACA*, *DGAT2*, *TIP47*, *ADRP*, and *BTN1A1* genes in mammary glands ($p < 0.05$) and an increase of the *SCD* gene because of CLA supplementation ($p < 0.05$). In conclusion, *t*10,*c*12-CLA-induced MFD was possibly the result from the downregulation of genes involved in lipogenesis in goat mammary glands.

The physical state of emulsified edible oil modulates its *in vitro* digestion

Guo, Q., *et al.*, *J. Agric. Food Chem. 65*: 9120–9127, 2017, https://doi.org/10.1021/acs.jafc.7b03368.

Emulsified lipid digestion was tailored by manipulating the physical state of dispersed oil droplets in whey protein stabilized oil-in-water (O/W) emulsions, where the oil phase consisted of one of five ratios of soybean oil (SO) and fully hydrogenated soybean oil (FHSO). The evolution in particle size distribution, structural changes during oral, gastric, and intestinal digestion, and free fatty acid release during intestinal digestion were all investigated. Irrespective of the physical state and structure of the dispersed oil/fat, all emulsions were stable against droplet size increases during oral digestion. During gastric digestion, the 50:50 SO:FHSO emulsion was more stable against physical breakdown than any other emulsion. All emulsions underwent flocculation and coalescence or partial coalescence upon intestinal digestion, with the SO emulsion being hydrolyzed the most rapidly. The melting point of all emulsions containing FHSO was above 37°C, with the presence of solid fat within the dispersed oil droplets greatly limiting lipolysis. Fat crystal polymorph and nanoplatelet size did not play an important role in the rate and extent of lipid digestion. Free fatty acid release modeled by the Weibull distribution function showed that the rate of lipid digestion (κ) decreased with increasing solid fat content, and followed an exponential relationship ($R^2 = 0.95$). Overall, lipid digestion was heavily altered by the physical state of the dispersed oil phase within O/W emulsions.

Effects of different lipophilized ferulate esters in fish oil-enriched milk: partitioning, interaction, protein, and lipid oxidation

Qiu, X., *et al.*, *J. Agric. Food Chem. 65*: 9496–9505, 2017, https://doi.org/10.1021/acs.jafc.7b02994.

Antioxidant effects of ferulic acid and lipophilized ferulate esters were investigated in fish oil-enriched milk. Methyl ferulate (C1) and ethyl ferulate (C2) more efficiently prevented lipid oxidation than dodecyl ferulate (C12) did, followed by ferulic acid (C0). The combination of C1 or C2 with C12 could have a "synergistic" effect indicated by peroxide value, hexanal, and 1-penten-3-ol analysis results. These antioxidants also showed protein oxidation inhibition effects. The most effective antioxidants (C1 and C2) had the highest concentration in the precipitate phase but the lowest concentration in the aqueous phase, which was the opposite of the partitioning of C0. C12 had the highest concentration in the oil and emulsion phase. In particular, the interaction between ferulates esterified with short and medium alkyl chain lengths could lead to their "synergistic" effects in fish oil-enriched milk, which could be caused by the change in their partitioning or localization at the interface.

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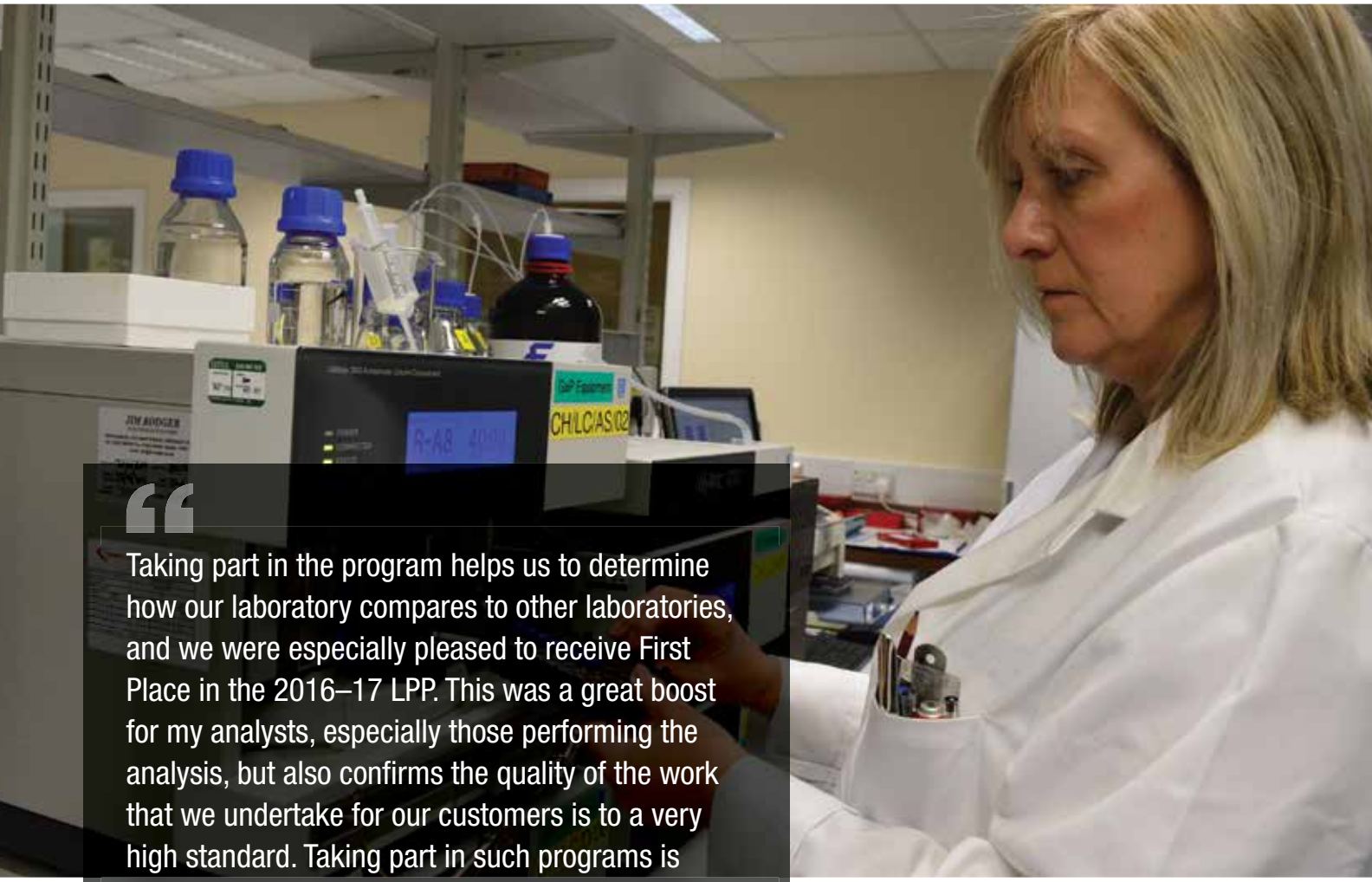

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Associations between fatty acids and low-grade inflammation in children from the LISAplus birth cohort study

Harris, C., *et al.*, *Eur. J Clin. Nutr. 71*: 1303–1311, 2017, https://doi.org/doi:10.1038/ejcn.2017.73.

Assessing fatty acid (FA) composition in relation to inflammatory markers can shed light on the role of different FA and their metabolism in low-grade inflammation. Existing exploratory studies in children are scarce, and findings inconsistent. We hence aim to analyze associations of FA with common inflammatory markers, high-sensitivity C-reactive protein (hs-CRP), and interleukin-6 (IL-6), in 10-year-old children. Complete data were available for 958 participants from the 10-year follow-up of the LISAplus (Influence of Lifestyle-Related Factors on the Immune System and the Development of Allergies in Childhood plus the Influence of Traffic Emissions and Genetics) birth cohort study. FA composition was assessed in serum glycerophospholipids. Hs-CRP and IL-6 were categorized into three levels. Associations of FA with inflammatory markers were assessed using multinomial logistic regression, adjusting for potential confounders. Additionally, sex-stratified analyses were carried out. FA exposures associated with significantly higher low-grade inflammation, as indicated by higher hs-CRP or IL-6 levels, included: palmitic acid (PA) (IL-6: $P<0.001$, 95% confidence interval: 1.30; 2.43), arachidonic acid (AA) (hs-CRP: $P=0.002$, 1.07; 1.31), n-6 highly unsaturated FA (HUFA) (hs-CRP: $P=0.002$, 1.06; 1.27), ratio of AA to linoleic acid (AA/LA) (hs-CRP: $P<0.001$, 1.16; 1.62) and total saturated FA (SFA) (IL-6: $P<0.001$, 1.77; 3.15). FA exposures associated with reduced levels of inflammatory markers included LA (hs-CRP: $P=0.001$, 0.84; 0.96; IL-6: $P<0.001$, 0.69; 0.90) and total polyunsaturated FA (PUFA) (IL-6: $P<0.001$, 0.57; 0.78). These findings suggest that higher SFA and minor n-6 HUFA, namely PA and AA, are associated with increased low-grade inflammation in children, whereas the major dietary n-6 PUFA and total PUFA are associated with reduced inflammation. Elevated desaturase activity, estimated by the ratio AA/LA, may be associated with higher inflammation, particularly in boys.

Adsorption removal of glycidyl esters from palm oil and oil model solution by using acid-washed oil palm wood-based activated carbon: kinetic and mechanism study

Cheng, W., *et al.*, *J. Agric. Food Chem. 65*: 9753–9762, https://doi.org/10.1021/acs.jafc.7b03121.

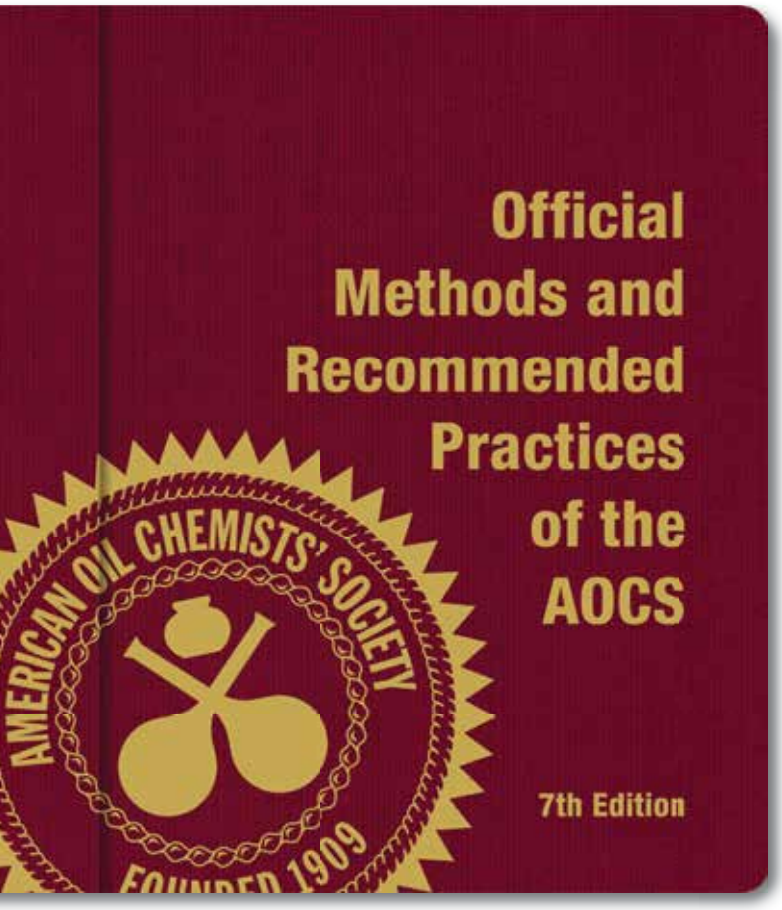
Acid-washed oil palm wood-based activated carbon (OPAC) has been investigated for its potential application as a promising adsorbent in the removal of glycidyl esters (GEs) from both palm oil and oil model (hexadecane) solution. It was observed that the removal rate of GEs in palm oil was up to >95%, which was significantly higher than other adsorbents used in this study. In batch adsorption system, the adsorption efficiency and performance of acid-washed OPAC were evaluated as a function of several experimental parameters such as contact time, initial glycidyl palmitate (PGE) concentration, adsorbent dose, and temperature. The Langmuir, Freundlich, and Dubinin–Radushkevich models were used to describe the adsorption equilibrium isotherm, and the equilibrium data were fitted best by the Langmuir model. The maximum adsorption capacity of acid-washed OPAC was found to be 36.23 mg/g by using the Langmuir model. The thermodynamic analysis indicated that the adsorption of PGE on acid-washed OPAC was an endothermic and physical process in nature. The experimental data were fitted by using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. It was found that the kinetic of PGE adsorption onto acid-washed OPAC followed well the pseudo-second-order model for various initial PGE concentrations and the adsorption process was controlled by both film diffusion and intra-particle diffusion. The desorption test indicated the removal of GEs from palm oil was attributed to not only the adsorption of GEs on acid-washed OPAC, but also the degradation of GEs adsorbed at activated sites with acidic character. Furthermore, no significant difference between before and after PGE adsorption in oil quality was observed.

Synthetic Biology

Microbial and genetically engineered oils as replacements for fish oil in aquaculture feeds

Sprague, M., *et al.*, *Biotechnol. Lett. 39*: 1599, https://doi.org/10.1007/s10529-017-2402-6.

As the global population grows, more of our fish and seafood are being farmed. Fish are the main dietary source of the omega-3 (n-3) long-chain polyunsaturated fatty acids (LC-PUFA), eicosapentaenoic (EPA) and docosahexaenoic (DHA) acids, but these cannot be produced in sufficient quantities as are now required for human health. Farmed fish have traditionally been fed a diet consisting of fishmeal and fish oil, rich in n-3 LC-PUFA. However, the increase in global aquaculture production has resulted in these finite and limited marine ingredients being replaced with sustainable alternatives of terrestrial origin that are devoid of n-3 LC-PUFA. Consequently, the nutritional value of the final product has been partially compromised with EPA and DHA levels both falling. Recent calls from the salmon industry for new sources of n-3 LC-PUFA have received significant commercial interest. Thus, this review explores the technologies being applied to produce *de novo* n-3 LC-PUFA sources, namely microalgae and genetically engineered oilseed crops, and how they may be used in aquafeeds to ensure that farmed fish remain a healthy component of the human diet.



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Recent developments on genetic engineering of microalgae for biofuels and bio-based chemicals

Ng, I.-S., *et al.*, *Biotechnol. J. 12*, October 2017, https://doi.org/10.1002/biot.201600644.

Microalgae serve as a promising source for the production of biofuels and bio-based chemicals. They are superior to terrestrial plants as feedstock in many aspects and their biomass is naturally rich in lipids, carbohydrates, proteins, pigments, and other valuable compounds. Due to the relatively slow growth rate and high cultivation cost of microalgae, to screen efficient and robust microalgal strains as well as genetic modifications of the available strains for further improvement are of urgent demand in the development of microalgae-based biorefinery. In genetic engineering of microalgae, transformation and selection methods are the key steps to accomplish the target gene modification. However, determination of the preferable type and dosage of antibiotics used for transformant selection is usually time-consuming and microalgal-strain-dependent. Therefore, more powerful and efficient techniques should be developed to meet this need. In this review, the conventional and emerging genome-editing tools (e.g., CRISPR-Cas9, TALEN, and ZFN) used in editing the genomes of nuclear, mitochondria, and chloroplast of microalgae are thoroughly surveyed. Although all the techniques mentioned above demonstrate their abilities to perform gene editing and desired phenotype screening, there still need to overcome higher production cost and lower biomass productivity, to achieve efficient production of the desired products in microalgal biorefineries.

Potential of commodity chemicals to become bio-based according to maximum yields and petrochemical prices

Straathof, A.J.J. and A. Bampouli, *Biofuel., Bioprod., Biorefin. 11*: 798–810, 2017,
https://doi.org/10.1002/bbb.1786

Carbohydrates are the prevailing biomass components available for bio-based production. The most direct way to convert carbohydrates into commodity chemicals is by one-step conversion at maximum theoretical yield, such as by anaerobic fermentation without side product formation. Considering these hypothetical yields and petrochemical prices in Europe in 2010–2014, a ranking of 58 commodity chemicals was made using a simple model with ethanol as a base case. It was concluded that base chemicals such as lower olefins and benzene-toluene-xylene (BTX) are too cheap and require too much carbohydrate to be produced competitively compared to bioethanol. However, more oxidized products that require multiple conversion steps in petrochemical production, such as adipic acid, acrylic acid, acrylate esters, and 1,4-butanediol, can be produced competitively from carbohydrates if theoretical yields are approached and if processing is efficient. Instead of carbohydrate fermentation, hypothetical photochemical production from CO_2 was also considered. Using again a simple model, the same commodity chemicals remained the most attractive ones.

Industrial Applications

Review of vegetable seeds oils as biolubricants

Kumar, D., et al., *Energy Environ. Focus*, *6*: 103–113, 2017, https://doi.org/10.1166/eef.2017.1251.

Vegetable oils are the best alternative source of lubricating oils used in automotive and industrial applications. Their high-oleic contents make vegetable oils environmentally friendly and cheaper than petroleum oils. The seeds of non-edible vegetable plants contain larger amounts of oils that can be converted into bio-lubricants and further used in engines and industrial applications. Bio-lubricants are renewable, nontoxic, and biodegradable. This research article reviews the fatty acid contents and friction behaviors of mahua, coconut, palm, sal, neem, olive, castor, canola, cashew nut, and jatropha oils.

Alternative oil extraction methods from *Echium plantagineum* L. seeds using advanced techniques and green solvents

Castejón, N., *et al.*, *Food Chem., 244*: 75-82, 2018, https://doi.org/10.1016/j.foodchem.2017.10.014.

The edible oil processing industry involves large losses of organic solvent into the atmosphere and long extraction times. In this work, fast and environmentally friendly alternatives for the production of echium oil using green solvents are proposed. Advanced extraction techniques such as Pressurized Liquid Extraction (PLE), Microwave Assisted Extraction (MAE) and Ultrasound Assisted Extraction (UAE) were evaluated to efficiently extract omega-3 rich oil from *Echium plantagineum* seeds. Extractions were performed with ethyl acetate, ethanol, water and ethanol:water to develop a hexane-free processing method. Optimal PLE conditions with ethanol at 150 °C during 10 min produced a very similar oil yield (31.2%) to Soxhlet using hexane for 8 h (31.3%). UAE optimized method with ethanol at mild conditions (55 °C) produced a high oil yield (29.1%). Consequently, advanced extraction techniques showed good lipid yields and furthermore, the produced echium oil had the same omega-3 fatty acid composition than traditionally extracted oil.

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