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UNCONVENTIONAL OILS

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Unconventional Oils

Laura Cassiday

Five vegetable oils dominate worldwide production: palm, soybean, canola (rapeseed), sunflower seed, and palm kernel (USDA, https://tinyurl.com/vegoils2018, 2018). Yet as the global demand for edible oils increases, the search for novel or unconventional oils accelerates. Particularly desirable are oil crops that flourish under conditions that most conventional oilseeds cannot, such as poor soil or drought. Many developing nations are seeking novel oil-producing plants that thrive in their native climate and soil, increasing the prosperity of farmers and reducing the nation's dependence on imported oils. In addition, investors, manufacturers, and consumers are looking for novel oils that have unique health-promoting properties or functional characteristics.

- Five vegetable oils dominate the world market: palm, soybean, canola, sunflower seed, and palm kernel.
- However, many new, unusual, or underutilized plant oils, including those from rice bran, pequi, pistachio, Allanblackia, and jatropha, are becoming more popular and helping to meet the increasing demand for edible oils.
- Unconventional oils are often harvested from wild plants, so domestication would likely enhance oil properties and production.

The five unconventional oils described herein represent promising new or underutilized oils that would expand the repertoire of vegetable oils available for food, cosmetic, or biodiesel applications. However, each unconventional oil has its own challenges that must be overcome to enable large-scale production and commercialization.

RICE BRAN OIL

Rice bran oil is produced from the outer coating, or bran, of rice (*Oryza sativa*). During the milling process, brown rice is polished to remove the bran and generate white rice. Because white rice is a staple food in many countries throughout the world, more than 60 million metric tons of rice bran is produced worldwide each year (Kahlon, T., https://tinyurl.com/ricebran-book, 2009). Most of this byproduct is currently sold as a low-cost animal feed. Rice bran has an oil content of about 20% (Shukla, H.S., and Pratap, A., https://doi.org/10.5650/jos.ess17067, 2017); however, untreated rice bran is unstable because it contains a lipase enzyme that rapidly degrades the oil. The lipase can be thermally inactivated, producing a stabilized rice bran with increased shelf life (Kahlon, T., https://tinyurl.com/ricebran-book, 2009).

Oil is typically extracted from stabilized rice bran by mechanical pressing or solvent extraction with hexane or isopropanol, although other methods such as supercritical CO_2 extraction and microwave-assisted extraction are under investigation (Shukla, H.S., and Pratap, A., https://doi.org/10.5650/jos.ess17067, 2017). Refining of rice bran oil involves degumming, neutralization, bleaching, dewaxing, and deodorization. Arawana, China's leading brand of edible oils (under Wilmar International), developed a low-temperature, enzymatic degumming process for rice bran oil to preserve the bioactive compounds γ-oryzanol and phytosterols (Wan, L., https://tinyurl.com/FoodNavArawana, 2018).

The fatty acid compositions of rice bran and other oils are shown in Table 1. Rice bran oil is approximately 19% saturated fatty acids, 39% monounsaturated, and 35% polyunsaturated fatty acids. The oil also con-

tains bioactive minor components such as γ-oryzanol, tocopherols, tocotrienols, and phytosterols. γ-oryzanol, which is a mixture of at least 10 steryl ferulates, has been shown to have antioxidant and LDL-cholesterol-lowering activities in animal models and humans (Friedman, M., https://doi.org/10.1021/jf403635v, 2013). Crude rice bran oil contains approximately 15 g/kg of γ-oryzanol. Tocopherols and tocotrienols, which are different forms of vitamin E, are also antioxidants, and phytosterols can lower LDL-cholesterol levels in humans.

Animal studies and several small clinical trials have indicated that rice bran oil and blends of rice bran oil with other oils can have modest but significant effects on LDL-cholesterol levels (Friedman, M., https://doi.org/10.1021/jf403635v, 2013). A systematic review and meta-analysis of 11 randomized controlled trials found that rice bran oil consumption decreased LDL-cholesterol levels by a mean of 6.91 mg/dL and total cholesterol levels by a mean of 12.65mg/dL (Jolfaie, N.R., *et al.*, https://doi.org/10.1055/s-0042-105748, 2016). In men only, rice bran oil also increased HDL-cholesterol concentrations by

TABLE 1. Fatty acid composition (% total lipids) of five unconventional and four conventional (palm, soybean, canola, and olive) edible oils

Oil	Linoleic 18:2 (*n*-6)	α-Linolenic 18:3 (*n*-3)	Oleic 18:1 (*n*-9)	Palmitic 16:0	Stearic 18:0	Other
Rice bran[1]	33.4	1.6	39.1	16.9	1.6	7.4
Pequi[2]	2.0	0.3	57.5	35.8	2.2	2.2
Pistachio[3]	29.7	0.8	55.5	11.3	1.0	1.7
Allanblackia[4]	0.4	--	39.4	3.2	56.8	0.2
Jatropha[5]	34.6	--	48.8	13.0	2.5	1.1
Palm[1]	9.1	0.2	36.6	43.5	4.3	6.3
Soybean[1]	51.0	6.8	22.6	10.5	4.4	4.7
Canola[1]	19.0	9.1	61.7	4.3	2.1	3.8
Olive[1]	9.8	0.8	71.3	11.3	2.0	4.8

[1]USDA-ARS Food Composition Database, Fats and Oils (https://tinyurl.com/USDAfood-data)
[2]Guedes, A.M.M., *et al.*, https://doi.org/10.5650/jos.ess16192, 2017
[3]Kerman variety; Ojeda-Amador, R.M., https://doi.org/10.1016/j.foodchem.2017.07.087, 2018
[4]Crockett, S.L., https://doi.org/10.3390/ijms160922333, 2015
[5]Mariod, A., *et al.*, https://doi.org/10.1016/B978-0-12-809435-8.00031-7, 2017

a mean of 6.65 mg/dL. It is currently uncertain whether the LDL-cholesterol-lowering effects of rice bran oil can be traced to its fatty acid composition or to minor components, such as γ-oryzanol or phytosterols.

With a mild flavor and high smoke point (232°C), rice bran oil is suitable for high-temperature cooking methods, such as deep frying. Because rice bran oil is relatively inexpensive, mixing it with more costly oils, such as sesame or olive, could produce blends with reduced prices and improved properties such as smoke point or fatty acid profile. Researchers have produced zero-trans-fat shortenings that contain bioactive components by using lipase-catalyzed interesterification of rice bran oil and palm stearin (reviewed in Friedman, M., https://doi.org/10.1021/jf403635v, 2013).

Rice bran is not a novel oil, but it is underutilized. Rice bran oil is fairly common as a cooking oil in Asian countries such as Japan, India, and China, but its popularity still lags far behind other oils such as palm and soybean. As a byproduct of rice milling, rice bran is inexpensive and readily available in many Asian countries. Increased production and consumption of rice bran oil could reduce these countries' heavy reliance on edible oil imports (for example, India imports 60% of its edible oils). Perhaps the biggest challenge facing rice bran oil lies in communicating its favorable properties to food companies, restaurants, and consumers amidst a plethora of competing oils.

PEQUI OIL

Pequi oil comes from the fruits of a perennial tree (genus *Caryocar*) native to Central and South America. The tree produces yellow-to-orange, strongly flavored fruits with spiny seeds (Guedes, A.M.M., https://tinyurl.com/lipid-library-pequi). Local people collect the fruits when they ripen and fall to the ground, selling the fruits and using them for traditional dishes, preserves, and oil (Fig. 1). The mesocarp of the pequi fruit contains between 36 and 66% dry weight of oil (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017).

The traditional method for making pequi oil involves boiling the peeled fruit in water with stirring. The oil that rises is skimmed off with a spoon and collected. Then, the oil is dried by heating and is filtered through a cotton cloth. The resulting oil is not very stable, but it does preserve many of the bioactive compounds. This traditional technique is time-consuming: The production of 6 L of oil takes up to 2 days (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017). In addition to the traditional method, pequi oil can be extracted with solvents such as acetone, ethanol, or hexane. Solvent extraction requires prior drying of the fruit pulp, and the solvents must be eliminated in the final stage of processing.

Oil can be produced form both the pulp of the pequi fruit and the seed kernel; both have similar fatty acid compositions. Pequi oil contains mainly palmitic acid (35–40%) and oleic

FIG. 1. Ripe pequi fruit nearly ready to fall to the ground, where it is harvested. Credit: Shutterstock

acid (54–60%). The high content of monounsaturated fatty acids (oleic acid) makes the oil attractive for food, cosmetic, and oleochemical applications (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017). In addition, the high content of palmitic acid makes pequi oil suitable for margarine and shortening applications. The major triacylglycerol in pequi oil is 2-oleo-dipalmitin (POP), which is also present in cocoa butter and is largely responsible for its functionality. The confectionery industry is interested in finding new sources of POP for use as cocoa butter equivalents (Guedes, A.M.M., https://tinyurl.com/lipid-library-pequi). The triacylglycerol composition of pequi oil depends to some extent on the location and species of the tree. Pequi oil contains up to 246 μg of carotenoids per gram, which act as antioxidants (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017).

Pequi oil has a similar fatty acid composition to palm oil (Table 1). "Although there are some similarities between palm oil and pequi oil, the flavor and odor are completely different," says Andréa M.M. Guedes, researcher at the Brazilian Agricultural Research Corporation in Rio de Janeiro, Brazil. "Pequi oil has a strong and sweet flavor caused by both natural volatiles and the extraction process. During the extraction, heat is applied, and new flavor components can be formed."

In tropical climates, pequi oil undergoes phase separation at room temperature because of the high levels of palmitic and oleic acids. Guedes and colleagues found that this undesirable property can be overcome by chemical interesterification, which produces a new, zero-trans fat with different crystallization and melting properties (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017). The interesterified oil has a broader range of functionality at room temperature and at cold temperatures. In addition, pequi oil can be enzymatically modified to incorporate stearic acid at the sn-1,3 position of triacylglycerols, producing a cocoa-butter-like fat. According to Guedes, the researchers are now working on fractionating pequi oil, or separating stearin from olein.

Animal studies have indicated that pequi oil may have antioxidant and anti-inflammatory properties (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017). However, more research on the effects of pequi oil on human health parameters is required, as well as a more compete characterization of bioactive compounds within the oil.

In 2011, an estimated 7,027 tons of pequi fruits were produced in Brazil from two major species (*Caryocur brasiliense* and *C. coriaceum*) (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017). Because the pequi tree has not yet been domesticated, production results mainly from trees growing naturally in the wild. Currently, the number of native pequi trees is not sufficient to meet the increasing demand (Guedes, A.M.M., https://doi.org/10.1051/ocl/2017040, 2017). Some communities have planted seedlings, and grafting and other agronomic practices are being investigated to boost productivity.

Currently, no large-scale facilities exist for producing or processing pequi oil, says Guedes. Small producers in Brazil form cooperatives to make and market the oil. "The large-scale industry has not shown interest in processing it," says Guedes.

"However, the cosmetics industry has purchased and processed crude pequi oil for use in hair products, for instance."

PISTACHIO OIL

Pistachio oil comes from the nuts of the *Pistacia vera* tree, which originated in the Middle East and Asia. Pistachios have been cultivated in these regions for millennia, and more recently in California. In 2014, Iran was the world's largest producer of pistachio nuts (415,000 tons), followed by the United States (230,000 tons) (Ojeda-Amador, R.M., https://doi.org/10.1016/j.foodchem.2017.07.087, 2018). Pistachios are popular snacks and components of foods such as ice cream and confections. The nuts are rich in oil, with an oil content of about 50%. Virgin pistachio oil is yellow-green in color and has a strong but pleasant flavor (Fig. 2).

In some Middle Eastern and European countries, pistachio oil is used primarily as a salad dressing or gourmet oil. Pistachio oil is also used in cosmetic applications. Because many consumers desire lightly processed oils, particularly within the gourmet market, mechanical pressing is more common than solvent extraction for producing virgin pistachio oils (Ojeda-Amador, R.M., https://doi.org/10.1016/j.foodchem.2017.07.087, 2018).

Virgin pistachio oil is rich in oleic acid, and linoleic acid is the second-most prevalent fatty acid (Table 1). The oil is approximately 12% saturated fatty acids, 56% monounsaturated fatty acids, and 31% polyunsaturated fatty acids. There are substantial differences among varieties of pistachio oil, with the more common Kerman variety having higher linoleic acid (29.7%) and lower oleic acid (55.5%) compared with other varieties, for example, Larnaka (12.8% linoleic and 73.6% oleic acid) (Ojeda-Amador, R.M., https://doi.org/10.1016/j.foodchem.2017.07.087, 2018).

Phytosterol content also varies significantly among pistachio varieties (3,200–7,600 mg/kg), but is higher than that of olive oil (1,100–2,100 mg/kg) (Ojeda-Amador, R.M., https://doi.org/10.1016/j.foodchem.2017.07.087, 2018). Pistachio oil is rich in γ-tocopherol (550–720 mg/kg), a vitamin E isoform that appears to be a more efficient antioxidant than α-tocopherol for food lipids. Pistachio oil is also a good source of other antioxidants, such as phenolic compounds and carotenoids. Pistachio oil has a characteristic aroma contributed by volatile compounds such as terpenes (predominantly α-pinene).

Pistachios, like several nuts, have shown beneficial health effects when consumed by humans, such as reduced LDL-cholesterol. However, pistachio oil had not been well studied in the clinic. Pistachio oil's high content of oleic acid, similar to olive oil, as well its antioxidant and anti-inflammatory components, warrant investigation for potential cardioprotective and other benefits.

A trained sensory panel described the attributes of pistachio oil as having an intense green appearance; a marked pistachio aroma and flavor; a sweet flavor, neither bitter nor pungent; and an oily-in-mouth sensation (Ojeda-Amador, R.M., https://doi.org/10.1016/j.foodchem.2017.07.087, 2018). Although not unpleasant, the strong flavor of pistachio oil may limit its use for some applications. As such, pistachio oil is likely to remain a niche oil, produced in small quantities by artisanal mills and sold primarily in gourmet and health food markets.

FIG. 2. Pistachio oil and nuts Credit: Shutterstock

ALLANBLACKIA OIL

Allanblackia oil is produced from the seeds of the Allanblackia tree (typically *Allanblackia parviflora, A. floribunda*, or *A. stuhlmannii*). This tree grows in the tropical rain belt of Africa, from Guinea in the west to Tanzania in the east. Named in honor of Scottish botanist Allan Black (1832–1865), Allanblackia is an evergreen tree that produces large brown fruits weighing up to 15 pounds (7 kg) and containing 40–50 seeds. The tree begins fruiting at about 8 years of age and continues for longer than 50 years. A single Allanblackia tree can produce up to 300 fruits per year, with 100–150 being average. Dehulled and dried seeds contain up to 70% oil.

In the late nineteenth century, many alternative oil seeds were identified and studied by French, Belgian, and Italian colonists in Africa (Crockett, S.L., https://doi.org/10.3390/ijms160922333, 2015). Later, during World War I, Allanblackia oil was used as a substitute for cocoa butter in chocolate. During the 1970s and 1980s, Allanblackia oil was exported to Europe in small quantities, but the supply was never sufficient to meet demand. Local people use the oil for cooking and soap-making.

Allanblackia seeds are predominantly harvested from trees growing in the wild. When fruits are ripe, they fall to the ground. Harvesters collect the fruits and manually extract and clean the seeds. Prior to oil extraction, the seeds must be dried in the sun for 1–2 weeks. After transport to a mill, such as the Allanblackia

Oil Mill in Tanga, Tanzania, the seeds are crushed with a press, and the crude oil is filtered and stored at 40-45°C so that it remains liquid. The remaining cake, which contains fibers and residual oil, can be used as a renewable energy source in the mill. After reaching its manufacturing destination, the crude oil can be refined to remove free fatty acids and off-flavors.

Allanblackia oil contains a unique blend of fatty acids that make it an excellent structuring fat in foods such as margarines. The oil has an unusually high stearic acid content—above 50% (Table 1), causing it to be solid at room temperature. Allanblackia oil is composed of only a few triglycerides derived from palmitic, oleic, and stearic acids. The oil has a melting point of 34°C and very steep melting behavior, which makes it useful for foods such as margarine without further modification or fractionation. Minor bioactive compounds remain to be fully characterized; however, crude Allanblackia oil contains tocopherols, benzophenone derivatives, and xanthones (Crockett, S.L., https://doi.org/10.3390/ijms160922333, 2015). Health effects of Allanblackia oil have not been studied yet, but stearic acid does not raise levels of LDL-cholesterol like other saturated fatty acids, such as palmitic acid, do.

In 2002, Unilever, several African research agencies, farmers, and non-governmental organizations partnered to establish the Novella Africa Project to increase production of Allanblackia oil. Unilever has estimated that the market demand for Allanblackia oil could exceed 100,000 tons per year, yet in 2013 only about 210 tons of oil were produced (Ofori, D., *et al.*, https://doi.org/10.17660/ActaHortic.2013.979.32, 2013). An insufficient number of wild trees, combined with erratic flowering and fruiting behavior, underlie the deficit.

The Novella partnership promotes the widespread planting and domestication of Allanblackia trees to meet worldwide demand for the oil. A commitment from Unilever to purchase Allanblackia oil ensures a stable supply chain, which encourages local farmers to plant seedlings. Also under the Novella Africa Project, research efforts are focused on analyzing *Allanblackia* genetic diversity, selecting superior plants, establishing gene banks, and determining the best tree propagation and cultivation practices (Ofori, D., *et al.*, https://doi.org/10.17660/ActaHortic.2013.979.32, 2013).

In 2007, the European Food Safety Authority declared that Allanblackia oil is acceptable for human consumption in "yellow fat and cream-based spreads." (Crockett, S.L., https://doi.org/10.3390/ijms160922333, 2015). In September 2014, Unilever launched the "Becel Gold" brand of margarine in Sweden, which contains Allanblackia oil.

JATROPHA OIL

Jatropha curcas is a small flowering tree native to Mexico and Central America. The shrub is now grown throughout the world in tropical and subtropical areas. Jatropha seeds from within pods that contain three seeds, with an average oil content of 46.4% (Mariod, A., *et al.*, https://doi.org/10.1016/B978-0-12-809435-8.00031-7, 2017) (Fig. 3). Jatropha oil is not edible due to the presence of toxic phorbol esters, but it can be processed into high-quality biodiesel.

J. curcas trees start yielding at about 1 year of age and have a life expectancy of 40 years. The plant is resistant to aridity and can grow in almost any soil, making it invasive in many areas. Jatropha's apparent ability to thrive on marginal land made the plant very attractive for biodiesel applications, as the crop would not compete with food crops for arable land. Under optimal conditions, *J. curcas* has an estimated yield of 2,270 L of high-quality biodiesel per hectare, compared with 540 L per hectare for soybean oil and 7,130 L per hectare for palm oil (Bayer CropScience, *Inform*, 2008).

Jatropha oil contains oleic (44.8%), linoleic (34.6%), palmitic (13%), and stearic (2.5%) acids (Mariod, A., *et al.*, https://doi.org/10.1016/B978-0-12-809435-8.00031-7, 2017) (Table 1). The oil also contains a protein called curcin, which is similar to ricin from castor beans but much less toxic (King, A.J., *et al.*, https://doi.org/10.1093/jxb/erp025, 2009). The toxicity of jatropha oil has been linked primarily to phorbol esters, which are purgatives, skin toxins, and possible tumor promoters. The presence of phorbol esters and other potential toxins in the seed meal obtained from oil extraction precludes its use for animal feed, although the protein quality is comparable to soy. No cost-effective approaches to detoxifying the meal have yet been identified. However, naturally occurring, edible varieties of jatropha exist in Mexico.

The oil has favorable parameters for biodiesel performance, including viscosity, density, flash point, cloud point, and cetane number. In the production of biodiesel, jatropha oil is transesterified with ethanol to produce fatty acid methyl esters. In 2004, a modified Mercedes Benz automobile that was powered by jatropha biodiesel toured 5,900 km (3,666

FIG. 3. *Jatropha curcas*, also known as Barbados nut
Credit: Shutterstock

miles) in India, with much publicity (Bayer CropScience, *Inform*, 2008). In 2008, researchers at Daimler Chrysler, Archer Daniels Midland, and Bayer CropScience undertook a joint project to explore jatropha fuel for automobile use. And in 2008–2011, airlines in New Zealand, the United States, Mexico, and China flew successful test flights using blends of jatropha oil with conventional jet fuel in one engine.

In the 2000s, jatropha was widely promoted as a "wonder crop" that could flourish on wastelands with very little water and bring prosperity to impoverished farmers in developing nations. As a result, in 2009 2.5 million hectares of jatropha were planted in India and China (King, A.J., *et al.*, https://doi.org/10.1093/jxb/erp025, 2009). However, since 2011, skepticism has prevailed. Farmers discovered that although jatropha will grow on marginal land with little water, oil yields are very poor (5-fold or less than optimal conditions). Therefore, jatropha competes with edible crops for water, land, and other resources, reigniting the "food versus fuel" debate. In addition, a life cycle analysis predicted that clearing tropical woodlands for jatropha cultivation would actually result in a net *increase* in greenhouse gas emissions over a 20-year period compared with the production and use of fossil fuels (Romijn, H.A., https://doi.org/10.1016/j.enpol.2010.07.041, 2011).

According to Promode Kant, director of the Institute of Green Economy in New Delhi, India, the governments of China and India have withdrawn all support from jatropha as a biofuel. "The jatropha plantations raised in the first decade of this century have been more or less abandoned," he says. "A very few do survive in isolated areas in India, more out of inertia than anything else. Facilities for oil extraction that were specif-

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ically set up for jatropha seeds also stand abandoned or have been converted to use for other oilseeds."

In a viewpoint published in *Environmental Science & Technology* entitled, "The extraordinary collapse of jatropha as a global biofuel," Kant and Shuirong Wu of the Chinese Academy of Forestry (Beijing, China) describe the "massive planting program of unprecedented scale" for jatropha in India, China, Tanzania, and other developing countries (Kant, P., and Wu, S., https://doi.org/10.1021/es201943v, 2011). When seed production fell far short of expectations, and petroleum prices dropped, the jatropha market collapsed, "bringing misery to millions of poorest people across the world," the authors write. "It appears to be an extreme case of a well-intentioned, top-down climate mitigation approach, undertaken without adequate preparation and ignoring conflict of interest ... "

Jatropha may best serve as a cautionary tale about the dangers of hyping and heavily investing in a novel oil without proper research and due diligence. However, the case for jatropha as a biofuel is not completely hopeless. Already, people in isolated communities in southern and eastern Africa use the oil to power their homes. And with research and time, jatropha could be optimized, like conventional crops, through selective breeding, genetic modification, or gene editing. Using these tools, seed yield and oil content could be improved. To enable the use of jatropha press cakes in animal feed, genes in the phorbol ester pathway could be disrupted, or naturally non-toxic varieties of jatropha could be further explored.

TAMING NEW OIL CROPS

Although unconventional oil crops offer exciting new properties and functionalities, they lack the years of research, improvements, and experience that have been invested in conventional oilseeds. Only time will tell if an unusual oil will displace one of the tried-and-true conventional oils, or if the oil will simply expand the repertoire of edible oils for different locations, price points, or purposes. Large-scale production of any new oil will almost certainly require its domestication from wild plants.

Interestingly, scientists at the University of Copenhagen and Bayer CropScience recently modified mustard, a close relative of canola, so that it no longer produces the bitter defense proteins that give mustard (and mustard oil) its strong flavor (Nour-Eldin, H.H., *et al.*, https://doi.org/10.1038/nbt.3823, 2017). Through targeted genetic modification, the researchers made mustard plants that lack these compounds in seeds but express them in the rest of the plant so that it can defend itself against herbivores and pathogens. The modified mustard plant can grow in warmer, drier climates than canola, enabling cultivation in areas not suitable for the conventional oilseed crop. Large field trials have already been conducted. A similar approach could perhaps be taken with other unconventional oil crops around the globe.

Laura Cassiday is a former associate editor of Inform.