# Industrial oil crops when will they finally deliver on their promise?

#### Denis J. Murphy

Most *inform* readers are aware of the large number of articles over the past few decades that have highlighted the promise of new types of industrial oils from crop plants. As a researcher in this area since the 1970s, I am one of many who have regularly pointed out the vast range of possible industrial oils that could be obtained from plants. Indeed it is now more than 15 years since I edited a book, optimistically entitled *Designer Oil Crops* (VCH Publishing, Weinheim, Germany, 1994), that described the brave new world of customized oil MMT) is used for nonfuel industrial applications as oleochemicals. However, the recent interest in supposedly carbon-neutral cropderived biofuels has started to divert significant amounts of vegetable oil feedstocks away from food or oleochemicals and toward the large-scale production of biodiesel.

## CONVENTIONAL BREEDING

Due to the unusual and exotic nature of many industrially useful fatty acids (FA), conventional breeding approaches have been less useful in manipulating the FA profiles of edible oil crops to produce industrial oils. This is because most crop plants do not already contain genes allowing them to accumulate such exotic FA and therefore a transgenic (genetically modified) approach is normally required.

One important exception is oleic acid, which can be used as either a premium edible oil or a high-grade industrial feedstock.



crops that could be bred or engineered for dozens of nonfood applications, from polymers to highvalue cosmetics. However, as we approach the second decade of the 21st century, only a very few of these new oils have achieved any significant commercialization. The purpose of this article is to briefly survey the near- to medium-term prospects for the industrial oil crops sector.

In 2008, worldwide-traded oil production from crop plants was almost 130 million metric tons (MMT), mostly used as edible vegetable oil. The proportion of plant oils used for nonedible or industrial purposes has fluctuated as petroleum and coal feedstocks increasingly competed with plant oils as sources of hydrocarbon-based products such as polymers, lubricants, fine chemicals, and fuels. Currently, only about 20% of global vegetable oil (25 Existing uses of high-oleic soybean oil include lubricating oils, greases, printing inks, plasticizers, electrical insulation, detergents, soaps, shampoos, and disinfectants. Oleic acid is a major component of all plants and is often abundant in seed and fruit oils, which means that many plant oils have the potential to act as feedstocks for some of the uses listed above for soybean oil. However, the value of oleate-rich oils as industrial feedstocks is often severely limited by the additional presence of oxidation-prone polyunsaturates, especially linoleic and  $\alpha$ -linolenic acids. These FA reduce the thermal performance and oxidative stability of many plant oils and therefore restrict their industrial uses. A major challenge for breeders has therefore been to reduce polyunsaturate levels in seed oils.

This challenge has been addressed with considerable success by breeders in several major oil crops. For example, breeders in the former Soviet Union developed high-oleic (75%) sunflower varieties. Sunflower and safflower lines are now available with 75% oleate and <1%  $\alpha$ -linolenate. More recently, breeders in the United States and Europe have developed high oleate/low polyunsaturate lines of soybean and rapeseed/canola, which may have potential industrial applications and are now being marketed by major seed companies. By 2004, high-oleic rapeseed/canola was already being planted on about 250,000 hectares (ha) in Canada, which is 5% of the total area of canola cultivation. Some of these new high-oleate oils have already been used as biodegradable lubricating fluids: Their characteristics include relatively long working lives and low susceptibility to oxidation at high temperatures.

Efforts are also under way to produce very high-oleate varieties of oil palm. This is especially challenging owing to the slow growth and long generation time of oil palm trees, which take 5–7 years to flower and produce oil and 10–15 years to reach full commercial productivity. Over the past decade, several promising lines of the two oil palm species, *Elaeis guineensis* and *E. oleifera*, that can contain up to 65% oleate in the mesocarp oil have been identified in Africa and South America. By using DNA-based molecular markers, breeders now hope to cross high-oleate lines into existing commercial lines; this is unlikely to produce commercial amounts of high-oleic palm oil, though, until well after 2020.

# TRANSGENIC OIL CROPS

In theory, it is possible to express almost any FA in a plant oil by genetic engineering. However, despite 20 years of intensive research, most novel FA still only accumulate at relatively low levels in transgenic species, as shown in Table 1. The main reason is that simply transferring the relevant acyl modification gene into a plant does not necessarily mean that the corresponding FA will accumulate at high levels in the storage oil of the recipient plant. Indeed, despite more than 20 years of sometimes ingenious efforts by molecular biologists, yields of novel FA in most transgenic plants remain stubbornly low.

Sometimes novel FA levels can be increased by transferring additional genes, such as acyltransferases. But the additional

# *inform*ation

# For further reading:

- Cahoon, E.B., J.M. Shockey, C.R. Dietrich, S.K. Gidda, R.T. Mullen, and J.M. Dyer, Engineering oilseeds for sustainable production of industrial and nutritional feedstocks: solving bottlenecks in fatty acid flux, *Current Biology* 10:236–244 (2007).
- Dyer, J.M., S. Stymne, A.G. Green, and A.S. Carlsson, High-value oils from plants, The Plant Journal 54:640–655 (2008).
- Gunstone F.D., J.L. Harwood, and A.J. Dijkstra (eds.), The Lipid Handbook, 3rd edn., Taylor & Francis, Oxford, United Kingdom, 2007.
- Metzger, J.O. and U. Bornscheuer, Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification, Applied Microbiology and Biotechnology 71:13–22 (2006).
- Murphy, D.J., Future prospects for biofuels, Chemistry Today 26:44–48 (2008).
- van Beilen, J.B., and Y. Poirier, Prospects for biopolymer production in plants, Advances in Biochemical Engineering and Biotechnology 107:133–151 (2007).

enzymes/genes required to accumulate a given novel FA are not always predictable. A further problem in obtaining high levels of novel FA is that in some crop species, such as rapeseed/canola, not all of the novel acyl groups are necessarily channeled to storage lipids. Some of the exotic FA may accumulate instead in membrane lipids. This is one reason why some transgenic plants are unable to accumulate high levels of novel FA. It is also an important reminder of the complexity of metabolic regulation in plants and the difficulties of manipulating this process via the insertion of one, or a few, transgenes.

Although transgenic approaches to oil modification have mainly focused on the introduction of exotic FA, they have also been used to downregulate existing genes in order to reduce levels of unwanted FA. For example, linoleate desaturase genes have been suppressed to reduce levels of  $\alpha$ -linolenate in seed oils. This approach has been used by several companies to complement conventional breeding programs aimed at developing high-oleate, lowpolyunsaturate oils. The following high-oleate transgenic lines have been developed, but not necessarily commercialized, to date: rapeseed/canola with 89% oleate; soybean with 90% oleate; and cottonseed with 78% oleate.

# CHEMICAL AND BIOTECHNOLOGICAL TRANS-FORMATIONS OF BASIC INDUSTRIAL OILS

Even relatively homogeneous oils, such as 95% triricinolein, still often require downstream chemical and/or biotechnological conversions to generate specific oleochemical products at the required degree of purity. Less pure oils will require even more processing, and therefore research and development (R&D) into appropriate technologies will still be necessary, whatever the success of breeders in producing new crop-based oils. Downstream conversion and diversification transformations sometimes require biotechnological procedures such as lipase-catalyzed interesterification or transesterification. Alternatively, they may involve strictly chemical processes such as epoxidation or hydroxylation.

After a relatively slow start, novel oils from several new crops are also becoming industrially available, although not as yet in large quantities. Examples include petroselinic acid from coriander, calendic acid from Calendula officinalis, α-eleostearic acid from tung oil, santalbic acid from Santalum album, and vernolic acid from Vernonia galamensis. Useful new products include environmentally friendly industrial fluids and lubricants, insulating fluids for electric utilities, and additives to asphalt. In addition to modern methods of synthetic organic chemistry, enzymatic and microbial transformations can be used for the selective functionalization of alkyl chains. Some of the products of such syntheses include long-chain di-acids,  $\omega$ -hydroxy FA, and  $\omega$ -unsaturated FA. It is also possible to open up C=C bonds via chemical epoxidation to produce such advanced intermediates as polyetherpolyols. Finally, the purification of biologically produced (and therefore enantiomerically pure) FA from oil crops provides the basis for the synthesis of high-value nonracemic building blocks in the manufacture of fine chemicals.

# KEY TARGETS FOR FUTURE INDUSTRIAL OIL CROPS

One of the prerequisites for the commercial viability of future industrial oil crops is that they should accumulate single FA

FA⁵	Donor species	% FA in donor species	Recipient species	% FA in recipient species
Lauric 12:0	California bay	65	Rapeseed	60 <sup>c</sup>
Petroselinic 18:1 6c	Coriander	80	Arabidopsis	< °
Ricinoleic 18:1-OH	Castor bean	90	Arabidopsis	<b>26</b> <sup>d</sup>
Vernolic 18:1 9c,12OH	Crepis palaestina	60	Arabidopsis	۱5 <sup>۲</sup>
Crepylinic 18:2 9c,12trp	Crepis alpina	70	Arabidopsis	25 <sup>c</sup>
α-Eleostearic 18:3 9c,11t,13t	Momordica charantia	65	Soybean	۱ <b>7</b> ۵
Calendic 18:3 8t,10t,12c	Calendula officinalis	60	Arabidopsis	20°

TABLE I. Selected examples of transgenic plants modified to produce potential industrial oils<sup>a</sup>

<sup>*a*</sup>In the vast majority of cases, which are not shown here, only very low levels (<5%) of novel fatty acids were produced.

<sup>b</sup>FA, fatty acid; *c*, *cis* double bond; *t*, *trans* double bond; trp, triple bond.

Jaworski, J., and E.B. Cahoon, Industrial oils from transgenic plants, *Current Opinion in Plant Biology* 6:178–184 (2003).

<sup>d</sup>Burgal, J., J. Shockey, C. Lu, J. Dyer, T. Larson, I. Graham, and J. Browse, Metabolic engineering of hydroxy fatty acid production in plants: RcDGAT2 drives dramatic increases in ricinoleate levels in seed oil, *Plant Biotechnology Journal* 6:819–831 (2008).

<sup>e</sup>Cahoon, E.B., C.R. Dietrich, K. Meyer, H.G. Damude, J.M. Dyer, and A.J. Kinney, Conjugated fatty acids accumulate to high levels in phospholipids of metabolically engineered soybean and *Arabidopsis* seeds, *Phytochemistry* 67:1166–1176 (2006).

species, or very specific FA mixtures, or other lipid-derived feedstocks (such as polyhydroxyalkanoates) at the highest possible yields and purity. This needs to be achieved without compromising other important agronomic characteristics of the crop. It will also be necessary to ensure that such industrial crops can be grown, harvested, and processed on a large scale without affecting adjacent crops that might be destined for animal feed or for the human food chain. A list of some key targets for developers of industrial oil crops is given below.

- *Tailored oil composition*: The chosen FA for a particular end use should make up the vast bulk of the triacylglycerol oil of a crop, ideally at least 80–90%, in order to reduce downstream costs. This goal has been difficult to achieve due to the genetic and biochemical complexities underlying storage lipid composition in plants. Further progress here will depend on more information about the identity of target genes to be selected by breeders.
- *High oil yield*: An industrial oil should be accumulated at the highest possible yields by the crop in question; for example, simply increasing the proportion of oil in seeds of a crop like meadowfoam from its current low levels of 20% to a value of 30% would result in an increased crop oil yield of 50%, without affecting any other production costs. This could significantly increase the market uptake of such minor crops and

stimulate further efforts to improve them to supply renewable oleochemicals.

- Use of co-products: The commercial viability of any industrial oil can be considerably increased if co-products of the crop are also exploited for profit, rather than being an additional expense for separation and disposal. Examples include the protein "cake" in oilseeds, which can often be processed to make animal feed. In other crops the vegetative parts of the plant, such as fibers, stems, and trunks, can be used.
- Management and processing of industrial oil crops: To date there has been relatively little research into the kinds of management and processing systems that will be required for many new industrial oil crops. Most of these crops have been developed separately on a piecemeal and rather empirical basis, with relatively little dissemination of useful methodologies or best practice. Among the novel challenges that might face the grower and user of completely new crops are differing requirements for

the sowing, cultivation, harvesting, oil extraction, and downstream processing of such crops. This might entail the purchase or hire of new kinds of equipment on-farm. Cultivation of the new crops might also affect the management of existing crops being grown on the same farm.

# FUTURE PROSPECTS

For the foreseeable future, oil crops will continue to serve primarily as sources of edible vegetable oils for a global population that is projected to rise to more than 9 billion people by 2050. The recent diversion of plant oils towards the biodiesel sector is likely to be transient as second generation biofuels are developed. In the much longer term, as fossil-derived hydrocarbons inevitably become depleted and therefore more expensive, plant oils will gradually begin to replace them in more and more applications. However, and unlike the picture a few decades ago, it now appears that this process will take many decades and the speed of the transition from petrochemicals to oleochemicals will depend crucially on factors such as the health of the global economy, progress in R&D into new plant oils, and wider political developments. Examples of the latter include government policies such as carbon taxes or renewables obligations that might encourage use of plant oils and stimulate a more rapid rate of R&D into industrial plant oils.

## INDUSTRIAL OIL CROPS (CONTINUED FROM PAGE 751)

Although it is unlikely that there will be a sudden surge in industrial demand for plant oils over the next few years, it is virtually certain that the coming decades will see a gradual but steady increase in the use of oleochemical feedstocks across all sectors.

This developmental timescale—measured in decades rather than months or years—is ideal for a series of new programs to develop improved industrial oil crops using the many new biotechnologies now at our disposal. It may take another decade or so to resolve the problem of producing transgenic crops with 70–90% levels of a given FA. Recent progress in this area of research has been encouraging, but we still have a long way to go from typical current best levels of 25–30%.

Increasing oil yields will be equally challenging. The best temperate oilseed crops currently yield about 1 metric ton (MT)/ha, but that figure is based on a seed oil content of 40%, which could be increased toward values of 60–70% already found in some nuts. Oil yields of the major global crop, oil palm, are currently about 4 MT/ha, but trees are available that can yield more than 10 MT/ha. If we can increase global oil yields by 50% and improve FA purity in plant oils, there will be sufficient production to meet demand for edible oils and also to sustain a significant growth in price-competitive feedstocks for a widening range of industrial uses. To meet these aspirations, it will be desirable to make use of all available plant breeding methods, as well as to continue with efforts to understand the biochemical and cellular processes that underlie oil accumulation, and related aspects of nonstorage lipid metabolism in plant tissues. As we have learned over the past two decades, none of our current breeding or engineering methods are particularly rapid, but neither is the required timescale for commercializing the new generation of industrial oil crops. By investing relatively modest sums now in applied breeding R&D for new oil crops and in basic lipid metabolism studies, we could lay the groundwork for the development of sustainable and environmentally friendly plant-based hydrocarbon feedstocks. Such feedstocks will surely become increasingly needed as fossil carbon resources become depleted during the rest of the 21st century.

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quality of co-products. As these process modifications are validated and commercially implemented, improvements in the generated co-products will be realized, and unique materials (such as high-protein, low-fat, and/or low-fiber distillers grains) will be produced as well.

## CONCLUSION

Ethanol is not the entire solution to our energy needs, but it is a key component to the bigger picture of energy independence. Support for ethanol has been growing over the years, and the industry has been rapidly expanding in response to increased demand. This means there will be many opportunities for those involved in process and product development to help add value to the process-ing residues—the co-products known as distillers grains.

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#### A PHOSPHOLIPIDS PRIMER (CONTINUED FROM PAGE 795)

stabilizing and regenerating effects on the skin-lipid barrier. PC helps to maintain or restore normal barrier function in dry or sensitive skin. Further, incorporation of PC containing saturated fatty acids into organic sunscreens improves their water resistance.

#### SUMMARY

Every phospholipid has its own specific application profile. Extensive scientific studies have demonstrated the effects on the human body that can result from the nutritional action of phospholipids, such as PS as a brain cell nutrient, PC for liver cell regeneration, soy phospholipids for lipid-reducing effect, and hydrogenated phospholipids as a basis for production of stable liposomes. Further tailor-made products produced from natural phospholipids, in combination with other active substances, are offering new potential markets.

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