The third product area currently served by the PCI and OCI is that of linear short-chain fatty acids. Production of linear fatty acids by the PCI in the United States is limited to C_5, C_7 and C_9 chain lengths. They amounted to ca. 20% of the total US linear acids produced in this range in 1980. Ca. 15% of world production, excluding the Eastern Block, is estimated to be from synthetic sources, as shown in Figure 11. The extent to which demand evolves for the specific properties of narrow cut synthetic acids will determine their future competitive position. Growth of the synthetic lubricant market is believed to be the most important key to overall demand growth for these products. Until such high performance demand materializes, the outlook remains more favorable for the oleochemical industry where these acids can be produced economically in the modest volumes needed and in an acceptable balance with other coproducts.

Closely linked to the fatty acid market are the detergent-range (C_{12}-C_{18}) fatty amines. In 1980 in the USA, ca. 80% of the C_{12}-C_{18} fatty amines produced came from fatty acids. The remainder were manufactured from petrochemical-based detergent alcohols and α-olefins. World production is similarly more heavily based on OCI sources as shown in Figure 11. Unless demand for the fatty amines expands faster in the future than anticipated, we believe this ratio of PCI and OCI supply sources will not change significantly. As in the previous cases, products based on petrochemicals are preferred in applications where precise control of hydrophobe chain lengths and purity are critical.

Thus, in those product areas where opportunities exist for significant substitution, factors other than feedstock prices are important. In the areas which have been discussed, it seems unlikely, however, that products from the PCI will capture significantly greater market share than they have today. The petrochemical industry will continue to provide a stabilizing influence in supply-demand balances. In addition, should accelerated demand occur in any of these markets, technology and resources available in the PCI will allow it to meet the demand without coproduct burdens. Thus, end users can depend on the availability of these products on a large scale and therefore plan for the long term.

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Development of New Crops for Industrial Raw Materials

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ABSTRACT

Commercial fats and oils are still used extensively in chemical manufacturing processes, but their fatty acid compositions are limited in variety. An extensive screening program for potential new oilseed crops has led to the discovery of many good sources of new lipid classes and fatty acids. Among them are long-chain acids (*Crambe, Limnanthes, Lunaria*), medium-chain acids (*Cuphea, Umbelliferae, Lauraceae*), hydroxy acids (*Lesquerella*), epoxy acids (*Vernonia, Stokesia*), acids with special unsaturation (conjugated; acetylenic; Δ3, Δ5, Δ6, Δ17 monoenes) and liquid wax esters (Simmondsia). Many of these plant species have received further attention in terms of germplasm collection and evaluation; breeding and agronomic studies; and processing and utilization research on oil and byproduct meal. Some have been developed sufficiently for early commercialization. Recent history has shown this last step to be the most difficult. No satisfactory mechanism has been devised as yet to simplify the process of transferring research information on a developed new crop to reach the ultimate goal of sustained, large-scale commercial production. Close cooperation between governments and private sector institutions, with some financial support, may be required for the first few years to achieve successful commercialization.

INTRODUCTION

Earlier reviews on USDA's long-term research program in the search for and development of new industrial oilseed crops have centered around the screening of uncultivated plant species, and plant breeding and agronomic efforts to upgrade wild germplasm to manageable crops (1-4). Other aspects of this program include chemical and engineering research necessary to convert harvested seed crops to high-quality commodities, in this case oil and meal; and research to identify prospective users or to adapt new oils or derivatives to existing raw material streams. The latter areas involve research, exploring the feasibility of new bulk products and studies on the often unique chemical and physical properties of unusual lipids that reside in the botanical store house.

Existing processing technology was developed for a select few commercially produced oilseeds, principally: soybean, sunflower, cottonseed, peanut, linseed, rapeseed and palm species. Processing parameters are well established to reduce these crops to high-quality oils and valuable by-products. All of the commercial oils are made up of the glycerides of a select few fatty acids (Table I); and their stability during processing is sufficiently understood to guard against hydrolysis, oxidation or other detrimental deterioration. For new oilseed crops, existing equipment and processes can be useful, but often proper parameters have to be established to produce acceptable products.

Similarly, new seed oils that can be produced domestically need testing to prove their merit as replacements for

TABLE I

Major Industrial Fatty Acids and Their Commercial Sources

Class	Acid	Most common sources
Saturated	C_{12} (lauric)	Coconut
	C_{16} (palmitric)	Oil palm
	C_{18} (stearic)	Tallow, hydrogenated oils
Monounsaturated	C_{18} (oleic)	Olive, tall oils
	C_{22} (erucic)	Rapeseed
Diunsaturated	C_{18} (linoleic)	Sunflower, soybean
Multiunsaturated	C_{18} (18:3, etc.)	Linseed, tung, fish
Hydroxy	C_{18} (ricinoleic)	Castor

imported oils from other plant species or nonbotanical sources. Again, it has to be determined if such replacements can be effected without changes in conditions or parameters.

Different oils and derivatives that are potentially available from new oilseed crops (Table II) require research to show that they could lead to new product lines; such as, engineering polymers, lubricants, coatings and adhesives. Of course, new oilseed fatty acids are often so different from traditional commercial types that little is known about their basic physical and chemical properties; these need exploration as well.

It is the purpose of this paper to review some of the chemical research that has been carried out at the Northern Regional Research Center of the Agricultural Research Service (NRRC) on new oilseed crops.

LONG-CHAIN FATTY ACIDS

With the development of and gradual worldwide change to low erucic acid-containing rapeseed, chemical industries are losing reliable and economical supplies of long-chain fatty acids. Accordingly, the USDA has placed much research emphasis on the development of new crops to produce such acids. Although several candidates were identified from early screening programs, most attention was given to *Crambe abyssinica, Limnanthes* species, and high-erucic, low-glucosinolate rapeseed. *Lunaria annua,* another excellent candidate, has not received the attention it should have. Typical oil compositions are presented in Table III. NRRC's research on the developmental chemistry of these oils was essentially restricted to crambe and meadow foam.

Crambe

This species, native to countries around the Mediterranean, has long been known to produce high levels of erucic acid. An extended research program. conducted mainly at Purdue University, led to development of improved seed lines and cultivars. Early field trials generated sufficient seed quantities to start chemical studies at NRRC. They included processing studies to arrive at high-quality oil and nutritious meal, to evaluate the oil in uses that traditionally required rapeseed oil, to develop new products from the oil, and to run animal feeding trials with the meal so that FDA approval could be obtained for its disposal in a profitable manner.

Crambe seed processing. Plant species of the family Cruciferae, including many vegetables we consume regularly, contain one or more glucosinolates in all of their underground and aboveground parts. These glucosinolates, or

TABLE II

Some Examples of Fatty Acids and Unusual Lipids Discovered in NRRC Screening Program

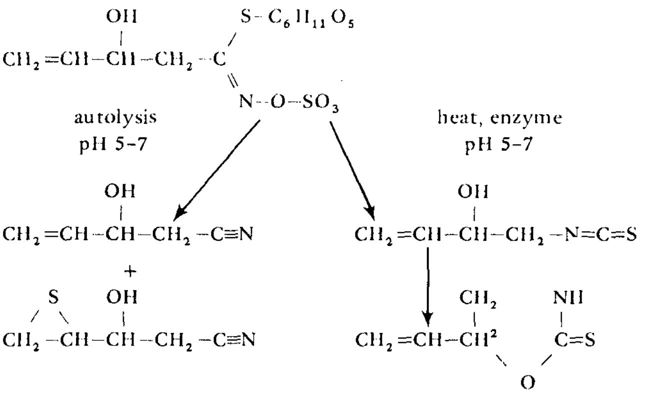
Class	Examples
Fatty acids	
Monounsaturated	Δ3, Δ5, Δ6, Δ11, Δ17
Diunsaturated	Δ5-Δ13, allenic (–C=C=C–)
Multiunsaturated	Conjugated tri- and tetraenes
Acetylenic	Δ6, Δ9, ene-yne
Hydroxy (C_{18} and C_{20})	α-OH, diene-OH, di- and tri-OH, 9-OH-Δ12C_{18}
Epoxy (C_{18} and C_{20})	Monoene-epoxy
Keto (C_{18}–C_{29})	Monoene through tetraene + keto
Unusual chain length	C_{18}–C_{12}, C_{20}–C_{28}
Cyclic	Propane, propene, pentanyl
Other	Anacardic acid analogs
Lipids	
Cyanolipids	1 or 2 fatty acids esterified to mono- or dihydroxy derivatives of 3-methyl-2(or 3)-butenoic acid nitrile
Acetoglycerides	1 or 2 regular fatty acids replaced by acetic acid in triglyceride
Glycolipids	1 fatty acid in triglyceride replaced by mono- or disaccharide by means of ether bond.
Tetra- and pentaacyl glycerides	1 or 2 additional fatty acids through ester linkage with hydroxy fatty acids in triglyceride
Terpenoid esters	Mainly saturated fatty acids esterified to terpenoid moieties

TABLE III

Typical Oil Compositions of Crambe, Meadowfoam, Honesty and High Erucic-Low Glucosinolate Rapeseed

Species	Oil content in seed (%)	Typical fatty acid composition		
Crambe (*C. abyssinica*)	30–45	18:1	17%	
		18:2	9%	
		18:3	6%	
		20:1	5%	
		22:1	55%	
		Other	8%	
Meadowfoam (*Limnanthes alba*)	25–35	$20{:}1^{5c}$	60%	95%
		$22{:}1^{5c}$ }		
		$22{:}1^{13c}$ }	20%	
		$22{:}2^{5,\,13c}$	15%	
		Other	5%	
Honesty (*Lunaria annua*)	30–40	$18{:}1^{9c}$	18%	90%
		$22{:}1^{13c}$	48%	
		24:1	24%	
		Other	10%	
Rapeseed, 0.7% glucosinolate (*Brassica napus*)	40–45	18:1	13%	
		18:2	11%	
		18:3	5%	
		20:1	10%	
		$22{:}1^{13c}$	55%	
		Other	6%	

their breakdown products, are known to be toxic and are often concentrated in the seed. Ca. 80 different glucosinolates are now known. In crambe, *epi*-progoitrin is the most prominent, and its formula and breakdown pathways are as follows:



Glucosinolates and their aglucon breakdown products are known to affect humans and animals in various detrimental ways. They have been linked with thyroid disturbances, liver damage, throat abscesses, appetite depression, tongue swelling and abortion (in cattle). Whereas traditional cole crops, such as cabbage, brussel sprouts, cauliflower, rutabaga, turnip and radish contain glucosinolates at levels up to 1200 ppm in the vegetative and root parts, these metabolites are often concentrated in the seeds as high as 8%. An additional problem with utilization of such seed meals as feed, is that animal diet is often fed continuously for long periods of time; whereas humans generally encounter diets containing raw cruciferous vegetables only on occasion.

In the USA, essentially no glucosinolate-containing seed meals were used in animal feeds before the advent of crambe development. Therefore, use of crambe meal required approval by the Food and Drug Administration (FDA). The FDA required proof that feeding a ration containing crambe meal to beef cattle over a period of 150–180 days would (a) be as beneficial to the animal as soybean meal in terms of weight gain, weight gain/feed ratio and general health, and (b) result in final products in which muscle tissue, fat, liver and kidney would not contain more than 1 ppm of glucosinolates or known breakdown products.

Early research had shown that intact glucosinolates were tolerated well by cattle; and that crambe meals could be prepared with most of the glucosinolates intact by inactivation of the enzyme myrosinase (thioglucosidase, ED 3.2.3.1) early in processing. It thus became necessary to scale up seed production in order to test processing in commercial equipment and produce sufficient meal quantities for large-scale animal feeding trials. Each year for ca. 7 years, contracts were let for production of up to 300 tons of crambe seed for processing in direct solvent extraction or prepress solvent extraction facilities for beef cattle feeding experiments. No serious problems were encountered with meal levels as high as 15% of total diet in beef cattle. However, the FDA granted clearance for use at a maximum of 4.2% (5). Details of feeding trials and tissue analyses are published elsewhere (6–8). A review of all processing research and trials is also available (9).

Oil utilization research. Typical industrial rapeseed oil contains 40–55% erucic acid by weight; crambe oil has as much as 55–60%. Rapeseed oil was used (as is) as a lubricant in steel manufacturing. Erucic acid or its derivatives (especially erucamide and behenylamine) were used in plastics, foam suppressants, and lubricants. Use of crambe oil in all these applications has been quite satisfactory or superior, and no technical barriers have ever been indicated that would preempt direct substitution of crambe oil for high-erucic rapeseed oil. In addition to evaluation for the purpose of direct substitution, NRRC research explored prospects for new products from crambe oil. This research led to experimental production of hydrogenated crambe oil (a solid harder than beeswax), brassylic acid (by oxidative ozonolysis of erucic acid, with pelargonic acid as coproduct), numerous brassylic acid esters, various engineering nylons including nylon 1313 and liquid wax esters, which were successfully evaluated in high-pressure lubricant applications. Detailed information is provided in a following section and in other publications (10–18).

Crop status of crambe. Upon assurance of FDA approval for the use of crambe meal in animal rations, large-scale planting was initiated in 1979 and 1980. In 1981, one chemical company contracted with farmers to plant 1,000 acres in western Kentucky. Extraordinarily warm weather in March that year resulted in an aphid epidemic at the time of seedling emergence, and the crambe fields, as well as those of other sensitive crops in the region, were severely attacked before effective countermeasures could be used. Damage was sufficient enough to abandon 800 acres, but reduced stands from the remaining acreage furnished planting seed for the following year. A fire at the storage facility during the winter resulted in a disastrous loss, and 1982–83 had to be devoted again to increasing the planting seed for eventual commercial production.

Such events, although unfortunate and time-consuming, are not atypical of farming. They are not expected to deter ultimate acceptance of crambe as a domestic crop for erucic acid oil. In addition to the fact that there will soon be no other convenient source of erucic acid, economic evaluation of crambe indicates that it can be profitable for farmers and chemical producers alike (19).

Limnanthes

Limnanthes species in North America are endemic to the Pacific Coast. Several have been evaluated agronomically for crop potential. Most impressive and desirable seems to be Meadowfoam (*L. alba*), which lately has received much attention, especially at Oregon State University. Up to 35 acres of Meadowfoam have been farmed for several years in Oregon, and industrial interest is increasing. As shown in Table III, typical *Limnanthes* seed oil is unusual in its fatty acid composition (20, 21). The combination of C_{20} and C_{22} fatty acids (>95% of total) is primarily monoenoic, and even the principal dienoic acid has unsaturated bonds far removed from each other ($\Delta5$, $\Delta13$). This results in a potentially greater stability than is found in conjugated or methylene-interrupted acids. The unsaturation in *Limnanthes* acids provides for an unusual mixture of mono- and dibasic acids. Oxidative ozonolysis, analogous to that conducted with erucic from crambe, would produce a 1:4 mole mixture of 9- and 15-carbon monoenic acids and a dibasic acid mixture of 5-, 11- and 13-carbon chainlengths. By the same process, dodecadienoic acid in *Limnanthes,* enriched substantially in selected cultivars, would also contribute the C_8 dibasic acid, suberic. With further crop improvement and an economical conversion process, *Limnanthes* might thus provide a source of commercial suberic acid, which historically has been generated from either cork or castor oil. However, prospects are dim for suberic acid at prices that would be competitive to shorter- or longer-chain dibasic acids.

Clearly, *Limnanthes* could benefit from research to exploit the combination of unusual fatty acid structures and nutritious protein in its seed. Data from such investigations are meager. Studies at the NRRC have explored certain lubricant uses with emphasis on preparation and evaluation of liquid wax esters (15, 17, 18, 20, 21) and use of sulfurized wax esters is beneficial because the unaltered triglyceride oil reacts with sulfur under traditional sulfurization conditions to yield factice, solid chemical rubber. Evaluation of sulfurized wax esters form three different preparations, at 5% in base oil, is summarized in Table IV in comparison with sperm whale oil and two commercial replacements.

The first preparation had good lubricating properties, but it corroded copper, foamed badly, and thickened excessively under in-use conditions in a hot gear box.

With the second preparation, different synthesis conditions decreased copper corrosion and maintained lubricating properties but produced more foam. This sample did not merit a thermal stability test.

On the third try, techniques were developed for fractionating *Limnanthes* acids; and wax esters were prepared from enriched monoene and diene acids. The diene wax (made from monoenoic acids) resulted in an increased wear scar, but other important properties were excellent. Additional time and material would probably have allowed a compromise between wear scar and foaming. Significantly, the weld point remained comparable to that of sperm oil throughout all variations. The tetraene wax accepted up to ca. 12% sulfur without solidifying, but tended to polymerize at higher levels.

From the data shown, it appears that suitable wax ester sperm oil replacements can be made from *Limnanthes* acids, and that oil with high monoene content would be preferred as starting material. It is doubtful, however, that diene acids need be excluded entirely. Cultivars with 10–15% diene will probably be adequate. Much additional testing, particularly in-use testing, is needed to ensure valid estimates of the performance of *Limnanthes*-derived products in fully formulated lubricants.

To enable these tests, a process for enriching C_{20} and C_{22} acids by fractionation at low temperature was developed (22). Eicosenoic acid could be enriched to 74% in the precipitated fraction, and docosadienoic acid to 70% in the supernatant in acetone at −50 C.

Both *Limnanthes* oil and liquid wax ester prepared therefrom have been hydrogenated to solid waxes. The triglyceride wax melts at 78–85 C and the hydrogenated wax ester at 66–68 C. These figures compare well with carnauba (83–86 C) and candelilla (65–69 C).

TABLE IV

Limnanthes Sulfurized Liquid Wax Esters in Lubricant Testing

Sulfurized material	Copper corrosion	Wear scar (mm)	Weld point (kg)	Foam test (mL)	Thermal stability (% viscosity increase)
Limnanthes A	3C	0.538	240	240/20/330	421
Limnanthes B	1B	0.545	220	530/75/490	–
Limnanthes C	1A	0.675	220	5/2/5	52
Sperm oil	1A–2A	0.558–0.597	220–230	250/20/80	108
Commercial replacement I	1B	0.606	220	220/20/100	101
Commercial replacement II	1B	0.596	230	280/30/100	171

Seed processing and meal utilization. Several small processing runs (up to 7 tons each) have been completed by solvent extraction, with no major problems identified. The resulting oil is more colored than crambe or rapeseed oil, but can be cleaned up easily by routine procedures. The genus *Limnanthes* is closely related to the Cruciferae family, and the seed also contains glucosinolates (23). Because it can be expected that FDA approval may be also required for the utilization of *Limnanthes* meal in animal feed, a study for its use in broiler chicks and rabbits has already been carried out (24), and is now being extended to beef cattle, goats and horses.

Lunaria

Whereas *Limnanthes* seed oils provide a blend of C_{20} and C_{22} acids, *Lunaria annua* oil is composed of high levels of C_{22} and C_{24} acids. *Lunaria annua* also has the advantage that over 90% of the acids are monounsaturated (Table III). Annual lines of *Lunaria* became available through mutation breeding (25) and appear promising in view of high seed yield potential, high oil content, favorable oil composition and the opportunity to bypass the biennial cropping required earlier. Dr. Wellensiek, developer of annual *Lunaria* lines, has retired and donated his seed samples to Wayne Craig of Saskatchewan Research Council, Canada, for further research.

Because *Lunaria annua* is a member of the Cruciferae family, it is anticipated that glucosinolates are the only antinutritional compounds in the seed meal, and that no special processing will be required for quality oil and meal, above that described earlier for crambe. No processing or utilization research has been attempted.

High-Erucic, Low-Glucosinolate Rapeseed

After the development of low-erucic, low-glucosinolare rapeseed lines and their successful commercial deployment, we felt that it might also be possible to create high-erucic, low-glucosinolate lines to satisfy the continuing industrial need for erucic acid. In cooperation with Oregon State University such rapeseeds have indeed been developed (26). Typical oil composition is shown in Table III. The variety 'Indore' has been registered and is available (27).

Glucosinolate content of the defatted meal has been reduced from typically 5-7% to 0.7%, and it is expected that the meal can be used in animal feed without need for special precautions during seed processing. Acceptance of this rapeseed as an industrial source of erucic acid probably hinges more on additional work in agronomy and seed handling (to prevent comingling of high- and low-erucic species) than on the need for chemical, processing, or nutrition studies.

SHORT- TO MEDIUM-CHAIN FATTY ACIDS

The principal commercial botanical source for lauric and shorter-chain saturated fatty acids has been coconut oil, the main supplier being the Philippines (28). Much of the coconut oil production is used in the chemical industry for surfactants and lubricants, where the main interest is in the free fatty acids and their derivatives. Coconut oil contains ca. 50% C_8–C_{12} acids. Early in the NRRC screening program, plant species from the genus *Cuphea* in the family Lythraceae were identified as potential sources for such acids (29, 30). During the past 6 years there has been a strong interest in that early discovery. A research program was started at the University of Göttingen in Germany by Röbbelen with Hirsinger (31), and has now grown to international research cooperation. Many additional species have been collected and evaluated. Recent studies include elucidation of biosynthetic pathways; genetic manipulation through selection, mutation, and hybridization; agronomy, to develop production practices; and engineering, to design the harvesting equipment for these unique plants.

Although oils from the different species are well characterized and protein content and composition are known for many species, there is no information on the existence of antinutritional factors or toxicants in the meal. At present, the first meal-feeding studies in mice are under way to gain such information. If any detrimental effects are noted, the factors will have to be identified, and processing research will be conducted to improve meal quality.

Extraction of oil from small quantities of seed from various *Cuphea* species did not reveal any problems in terms of oil quality; and since most of the oil will likely be converted to fatty acids in commercial operations, we anticipate no processing problems beyond those associated with the possible presence of toxicants in the meal. Likewise, there will be no special need for utilization research with the oils, because a ready market for such oils is already established. Elevation of *Cuphea* species to crop status will depend mainly on harvestable yields and oil price.

Other Approaches to Increased Lauric Acid Supply

The Lauraceae family has long been known for high levels of lauric acid in the seed oils of many of its species. Some oils contain as much as 90% lauric acid, meaning that such products are almost pure trilaurin. Unfortunately, the family is made up only of trees and shrubs, and the general misgivings of agricultural interests about using perennials for other than edible fruits and nuts so far has precluded any serious consideration. Table V indicates some excellent candidates (32).

Another pathway to lauric acid could be its production via oxidative ozonolysis of petroselinic acid (C_{18}-$\Delta 6$-monoene), which is preferably formed in seeds of many plants in the family Umbelliflorae (33):

$$\mathrm{CH_2{-}(CH_2)_{10}{-}CH{=}CH{-}(CH_2)_4{-}COOH} \xrightarrow{\text{oxidative ozonolysis}} \underset{\text{lauric acid}}{\mathrm{CH_3{-}(CH_2)_{10}{-}COOH}} + \underset{\text{adipic acid}}{\mathrm{HOOC{-}(CH_2)_4{-}COOH}}$$

Both the process and products are already commercial, adipic acid being a time-honored monomer in the synthesis of certain nylons. Since many species of Umbelliferae have been domesticated for use as vegetables, garnishes and condiments (carrot, celery, dill, fennel, cumin, parsley, parsnip), it may be expected that additional species might likewise be amenable to cropping. Whereas fennel (*Foeniculum vulgare*) is now produced for essential oil, additional processing for the triglyceride oil could serve as one source of petroselinic acid.

Except for the identification of potential plant species as sources for lauric acid from the NRRC screening programs, no development programs are underway or planned outside of the *Cuphea* program.

HYDROXY FATTY ACIDS

Castor oil has been the sole commercial source of hydroxy fatty acids (ricinoleic acid). At present, all castor oil is imported, although castor beans could be produced in the USA and many other parts of the world. Since production of castor brings with it the danger of seed toxicity, allergic reactions of field workers and the liability of disposing of the toxic meal after extraction of the oil, many potential

TABLE V

Some Examples of Lauraceae Rich in Lauric Acid

Species	% Oil in seed	% Lauric acid in oil
Actinodaphne hookeri	71	90
Lindera benzoin	61	47 (+42% C_{10})
Litsea cubeba	62	83
Litsea umbrosa	68	59
Umbellularia californica	64	58 (+33% C_{10})

production areas have shunned the crop.

Again, the NRRC screening program has revealed many other candidate plant species throughout the plant kingdom that could be used for the production of hydroxy fatty acids. Although ricinoleic acid was found to be present in other species, no plants were discovered with levels comparable to that in castor oil. However, many other hydroxy acids were found in copious amounts that could function as direct substitutes or that may have advantageous properties over the materials used now. Some examples are:

$$CH_3-(CH_2)_5-\underset{OH}{CH}-CH_2-CH=CH-(CH_2)_9-COOH$$

lesquerolic acid

$$CH_3-CH_2-CH=CH-(CH_2)_2-\underset{OH}{CH}-CH_2-CH=CH-(CH_2)_7-COOH$$

densipolic acid

$$CH_3-CH_2-CH=CH-(CH_2)_2-\underset{OH}{CH}-CH_2-CH=CH-(CH_2)_9-COOH$$

auricolic acid

$$CH_3-(CH_2)_4-CH\overset{t}{=}CH-CH\overset{t}{=}CH-\underset{OH}{CH}-(CH_2)_7-COOH$$

dimorphecolic acid

$$CH_3-(CH_2)_4-\underset{OH}{CH}-CH\overset{t}{=}CH-CH\overset{c}{=}CH-(CH_2)_7-COOH$$

coriolic acid

Also, good sources for di- and trihydroxy fatty acids have been identified (3). The genus *Lesquerella* in the Cruciferae family has been especially noteworthy for high levels of hydroxy fatty acids in its seed oils. Its taxonomic position appears to indicate that glucosinolates will be the only problem in meal quality (34), thus giving it a major advantage over castor oil. Another advantage would be that many species of this genus are native to dry areas from Oklahoma to Mexico, and often produce dense stands in the wild. Some botanical evaluation, selection and agronomic work was conducted and showed favorable results, but little interest has been generated so far in promoting a vigorous research program for *Lesquerella* or any other hydroxy fatty acid-bearing plant species.

Evaluation work on hydroxy acids at NRRC has been confined to characterization of the physical properties of lesquerolic acid and its simple derivatives relative to those of similar compounds from ricinoleic. Thus far in terms of preliminary thermal behavior data, lesquerolic acid continues to look quite good as a replacement for ricinoleic derived from castor oil.

EPOXY FATTY ACIDS

In addition to large quantities of petrochemically derived epoxy compounds, there is a solid market for epoxidized vegetable oils and fatty acids. Ca. 100-180 million lb of linseed and soybean oil are converted annually to various levels of epoxidation.

Many plant species have been identified from the NRRC screening program that produce high levels of epoxy fatty acids. The most common is vernolic acid:

$$CH_3-(CH_2)_4-\overset{O}{\overbrace{CH-CH}}-CH_2-CH=CH-(CH_2)_7-COOH$$

Vernolic acid makes up ca. 80% of the fatty acids in trigylceride oils from wild plants. Through careful selection and breeding, the levels can probably be increased. So far, most attention has been given to three species, *Vernonia anthelmintica*, *V. galamensis* and *Stokesia laevis*, which are all part of the Compositae family and contain similar amounts of oil (ca. 40%) in the seed and epoxy acids (75-80%) in the oil. Most processing work and product evaluation has been carried out on *V. galamensis* oil, although early agronomic studies concerned *V. anthelmintica* and similar studies are still being pursued on *S. laevis*.

Laboratory extraction trials and oil analyses showed that (a) most of the vernolic acid is present in the form of tri- and divernolin; (b) lipase activity in the seed meal or flakes can result in high levels of free fatty acids (FFA); (c) simple extraction leaves the epoxy moiety intact; (d) the pappi and setae (fibers and bristles attached to seed) need to be and can be removed to arrive at efficient oil extraction and a meal of acceptable fiber content. Tempering at 95-100 C and moisture level of 14-15% for 90 min resulted in lipase inactivation and low FFA levels. It also freed the seed from most fibrous material, therefore seed and fibers could be effectively separated by aspiration. The seed can then be flaked and extracted with hexane. Various degrees of refined oil were obtained by treatments with charcoal and/or bleaching earth, degumming and alkali refining (35).

Whereas the high oxirane levels of commercial epoxy oils make such products mostly suitable for incorporation in plastics; natural epoxy oils, such as obtained from *Vernonia* and *Stokesia*, are more likely to attain a role in coatings and adhesives technology. Our preliminary evaluation showed that clear and TiO_2-pigmented films baked from neat or solvent-containing *Vernonia* oil on cold rolled steel panels were promising in terms of color, adhesion, toughness, hardness and resistance to acid, alkali and solvents.

Although an antinutritional agent, vernolepin, is known to be present in *Vernonia* seed meals, limited trials with rats showed normal growth rates at 20% feeding levels for 90 days. Since industrial interest in the natural epoxy oils has been increasing, the *Vernonia* development program would benefit greatly from a systematic approach of additional germplasm collection, selection and breeding, and intensive agronomical studies. Until now, all production efforts have been attempted with seed stock from wild collections. *Stokesia* is receiving a continuing, although low-level, effort in the USDA to arrive at strains with improved seedling vigor and initial stand development of this perennial aster (36).

WAX ESTERS

Jojoba oil, the subject of additional evaluation research at NRRC, already is the principal focus for fledgling industry engendered during the past decade in the worldwide search for alternatives to sperm whale oil. Commercial activity associated with jojoba oil, which promises a technology as diverse as that associated with the material it replaces, has generated new interest in synthetic wax esters (37) and other sources of natural liquid wax esters (38).

Currently, jojoba oil satisfies many needs in cosmetics earlier met by sperm whale oil. As jojoba production increases, reportedly to ca. 50 million lb during the next decade, the oil should not find additional uses among those to which approximately that amount of sperm oil was devoted annually in the USA prior to 1972. World consumption of sperm oil was, of course, much larger at that time, ca. 250-300 million lb annually.

Before US imports of sperm oil were banned in 1971, ca. 25 million lb were consumed annually in extreme pressure (EP) lubricants. NRRC evaluations of jojoba concentrated logically on this potential volume use. Throughout evaluations consisting of bench-scale and simulated in-use tests (17, 18, 39), jojoba oil generally performed as well as or better than sperm whale oil or similar wax esters derived via chemical means from long-chain triglyceride oils. Table VI compares the performance in certain crucial tests of several sulfurized preparations of jojoba oil, or synthetic wax esters from crambe oil, with that of sulfurized sperm oil. Similar results for synthetic wax esters from *Limnanthes* oil were given in a preceding section. These data demonstrate that effective EP agents can be derived from seed oils that are rich in long-chain monoenoic acids. Industry may thus currently choose to prepare wax esters from relatively cheap triglyceride oils via moderately expensive synthetic processes, or to collect them directly from a relatively expensive seed via a cheap process. A third source, the orange roughy fish (*Hoplostethus atlanticus*), appears limited to ca. 5 million lb of oil annually by commercial fishing regulations (38).

Our experience indicates that either route to lubricants from plant seeds can involve uncertainties, because many factors that influence the performance of botanicals in such fluids remain unknown. Oilseed processing and product formulation variables undoubtedly will require careful adjustment to achieve balanced performance. Just how difficult such adjustments might be remains to be seen. For example, the various jojoba samples in Table VI exhibit a wide range of viscosity increase, 34–457%, which reflects different purification treatments. Interestingly, those purified to improve thermal stability, i.e., reduced viscosity increase, generally lower, less desirable weld points. The treatment to stabilize viscosity also reduced steel-on-steel wear dependably, but at the same time they produced erratic, sometimes detrimental changes in lead and copper corrosion.

When these sulfurized wax esters from jojoba and crambe were carried further, into simulated in-use tests, both performed better overall than sulfurized sperm oil. At 1% in crankcase oil, sulfurized jojoba and crambe wax esters reduced the viscosity increase sustained with sulfurized sperm oil by 24 and 61%, respectively. But, as might have been anticipated from lead corrosion results, the particular jojoba preparation that was used in fullscale tests allowed greater rod bearing erosion. It also increased oil ring band deposits. Both are undesirable characteristics that probably depend on the extent to which break materials are removed from the oil.

In a transmission test fluid that was not fully formulated, all candidates, as well as sulfurized sperm oil, foamed badly enough to interrupt the tests. Significantly, sulfurized jojoba oil performed satisfactorily under the same conditions for 4-5 times longer than either sulfurized sperm oil or the crambe oil derivatives.

Foaming, viscosity changes, varnish formation and compatibility with nonferrous metals or plastics are but a few of the performance problems with which the lubricants industry deals routinely. The isolated problems that we encountered seem insignificant in such a context and by comparison to the overall quality performances that we found. Thus, seed-based wax esters, either from the perennial jojoba or from annual plants such as *Crambe* or *Limnanthes* offer excellent opportunity for proprietary advantage to companies that know how to deal with their

TABLE VI

Lubricant Performance of Sulfurized Wax Esters

Preparation	Wear test scar (ASTM D-2266-67) 5% (10%) in base oil	Weld point load (ASTM D-2783) 5% (10%) in base oil	Lead corrosion (FTM 5321.1)	Thermal stability (FTM 2504)	
				Viscosity increase	Copper loss
	(mm)	(kg)	(mg/sq in.)	(%)	(%)
Jojoba					
I	0.620	260	10	457	0.14
II	0.650	250	1	169	0.09
III	0.500	240	9	34	0.06
IV	0.645	240	11	36	0.12
V	0.465	240	19	68	0.24
VI	0.590	240	–	72	0.05
	(0.505)	(280)			
Crambe					
I	0.495	280	20	–	–
II	0.493	250	22	32	0.05
III	0.672	240	0	127	0.03
	(0.495)	(280)			
IV	0.510	240	–	54	0.08
	(0.575)	(260)			
Sperm oil					
I	0.558	230	13	108	–0.06[a]
	(0.623)	(300)			

[a]Weight increased.

subtle idiosyncrasies.

Hydrogenation of jojoba oil and similar wax esters prepared from the trigylcerides of *Crambe, Limnanthes* and *Lunaria* produces brittle crystalline white solids that melt at 66-70 C, near beeswax (62-70 C) and lower than carnauba (83-86 C) (40). In terms of increasing hardness (indicated by Brinell Hardness Number), these waxes rank as follows: limnanthes (0.16), lunaria (0.28), crambe (0.28), beeswax (0.38), jojoba (0.48) and carnauba (2.6) (40).

Interestingly, hydrogenated jojoba oil, even though a mixture of chain lengths, is quite similar crystallographically to polyethylene (41). This probably accounts for its ability to mix in all proportions with polyethylene and polypropylene. This ability allows for the preparation of a variety of solid mixtures that generally melt lower than the pure plastic and yet apparently retain the tensile strength of the plastic (42). Mixtures of hydrogenated jojoba oil and low-density polyethylene exhibit an added benefit; they are all harder than either component alone (43). Such synergism adds new dimension to possible uses for hydrogenated jojoba oil.

DISCUSSION

Considering the extent of research and development accomplishments in the various new crops programs described here, one cannot help being anxious about the historically lethargic pace at which the world has adopted new crops. Our experiences during the past 25-30 years have gained much more than just scientific and technical knowledge. Some of our perceptions on new crop development may be especially pertinent in the contemporary context of heightening international interest in botanicals; and increased support for new crops studies to provide oils, pharmaceuticals, fiber, rubber and other hydrocarbons.

Certainly, novel technical or economic advantages are compelling features that every potential new crop must possess to merit development effort. Thus, crambe is an easily segregated dependable source of erucic acid; jojoba looks promising to a country denied sperm whale oil; cuphea might provide cheap short-chain acids; domestic lesquerella could reduce castor oil imports; and limnanthes offers a cattle feed supplement for a protein-deficient Pacific Northwest in the USA. The list of plants with recognized benefits could be much longer. But even when the benefits are clear, additional elements must be in place for new crop development to occur.

Plant Screening

Often minimal quantities of seed or other plant parts are satisfactory for preliminary chemical screening, especially now that sensitive analytical equipment and methods are commonplace. It is advisable, however, to start with enough extra propagative material so that plants can be generated for follow-up studies. We have encountered situations where additional collections could not be made, or where such collections resulted in shipment of a different plant species due to misidentifications. For this latter reason, voucher specimens should always be deposited and preserved for correct identification and future reference.

Although random screening can be a good initial approach, when patterns become obvious or suspected, it may be more fruitful to direct further work to specific families or genera; or even to collections of the same species from different habitats and locations for the purpose of evaluating genetic variability.

Organized Research Approach

Once a desirable species has been identified for potential crop development, a multidisciplinary research approach will be required: botanists for germplasm acquisition, plant identifications and preliminary botanical evaluation; geneticists, plant breeders and tissue culturists for cultivar selection, breeding, hybridizing and propagation; agronomists and agricultural engineers to develop production and harvesting parameters; chemists and chemical engineers to work on processing, storage, handling and utilization of the crop and its intended main products; chemists and animal nutritionists to study utilization of byproducts, preferentially in animal feed; economists to evaluate economic feasibilities; furthermore, biochemists and molecular biologists may be needed, should it prove necessary to transfer desired traits to better hosts via molecular mechanisms.

Even if the expertise were available to carry out all the required tasks for a particular new crop species, it cannot be stressed enough that leadership and authority to synchronize these tasks are critical. Past history has often shown a lack of central planning in terms of priorities, funding levels, interdisciplinary cooperation and integrated time tables. An example of good coordination has been the development of kenaf (*Hibiscus cannabinus*) as an annual fiber crop for paper production. Scientists of many disciplines worked well together, and periodic overviews of progress and planning sessions for additional work were held regularly. This systematic approach to development of new oilseed crops has often been lacking. A notable exception has been the planning of *Cuphea* research, for which specific needs were established jointly by all principals and which is monitored regularly for progress.

The Need for Champions

It is true that every cause needs a champion and championing has certainly been beneficial to new crops. It has been our experience that those potential new crops in which single individuals or special interest groups registered interest fared best in research progress or acceptance for development and commercialization. For example, only after kenaf was brought to the attention of the American Newspaper Publishers Association (ANPA), the ultimate user of the new product (newsprint), did it become a viable candidate for domestic newsprint production. Until then, American pulp and paper manufacturers has shown little interest in changing from wood to an annual fiber source.

Two examples of new oilseeds that gained from championing are jojoba and cuphea, although support came from opposite camps. Jojoba started its climb to commercial success only after environmentalists and protectors of endangered wildlife made strong pleas for saving whales. This expanded the awareness of jojoba as an excellent source of liquid wax esters. For cuphea, it was the international community of lauric acid-using chemical manufacturers who felt threatened by a possible precarious supply of coconut oil. Their pressure and financial support resulted in rapid escalation of research and development, albeit many years after the initial discovery of the genus *Cuphea* as a source for medium-chain fatty acids. Unfortunately, champions for new oilseed crops do not emerge via standard plan. Obviously, erucic and other long-chain acids still need advocates. One would expect greater interest in view of the decrease in availability of such acids due to concern over their presence in foods.

Time Needed to Fruition

Initially, people in new crops research or commercialization often have misconceptions about the length of time it takes to reach success. Proposals for research funding usually minimize the time and resources required to develop a plant species to crop status. This paper has shown by examples that many aspects need to be explored by researchers of many disciplines before all problems can be resolved. Many entrepreneurs do not foresee all the problems that remain in commercialization of a new crop, even after no researchable issues remain. It behooves the research organization to postpone attempts at commercialization until it has been established that there is good reason to expect success. Feeble attempts at early crambe production failed regularly for involved farmers, because no system was in place for processing or marketing of the products.

Government-Private Sector Cooperation

Even if a new crop reaches some point of success where the private sector can make informed decisions on commercial production, our experiences have shown that the financial burden may be too severe to be borne by a single organization. Marketing channels and standards must be established. Also, efforts to transfer the knowledge gained (from contracting with farmers, planting regimens, harvesting, storing, and processing and on through ultimate utilization) needs to be extensive, requiring close cooperation between research organizations and the private sector. Even then, disasters such as the aphid epidemic or the fire described for crambe, make the first few years sufficiently haphazard to warrant a joint venture with government backing to help overcome such financial setbacks. Development grants, guaranteed loans or tax incentives could ease crop commercialization during initial stages.

At this moment, neither the USDA nor any other governmental organization appears to have funded programs now in place for the concerted development of new botanical resources. Obviously, the extent and type of support, as well as the period for which it is needed, will vary depending on circumstances relating to each particular new crop. Only after federal-private cooperation has expanded opportunities and established feasibility should the free market be expected to sustain production levels and prices.

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