NATIONAL CENTER FOR AGRICULTURAL UTILIZATION RESEARCH
New Crop and Processing Technology Research

Steven C. Cermak
Research Chemist - Lead Scientist

Ph.D. Chemistry, The University of Iowa
B.S. Chemistry, Bowling Green State University

New Crops and Processing Technology Research Unit
National Center for Agricultural Utilization Research
United States Department of Agriculture
Peoria, IL 61604

Tel: (309)-681-6233
Fax: (309)-681-6524
E-mail: Steven.Cermak@ars.usda.gov

Research

The research that I conduct involves both field work and laboratory research. We work with new crops such as cuphea and lesquerella. In many cases we are responsible for growing these new plants to produce seed for oil. This requires us "Chemists" to act as farmers to produce seed. The harvested seed is processed in our facility to produce a new crop oil. With oil in hand, I am able to express my true scientific interests – organic chemistry. I am interested in the modification and/or transformation of fatty acids and oils into useful industrial products such as biodegradable lubricants and cosmetics.

Laboratory - Estolides

Consumers today are demanding more from their automobile lubricants than ever before. The use of renewable lubricants can meet these demands and at the same time lessen the demand for foreign oil. A new functional fluid, estolides, has shown great promise as cosmetics, coatings, and biodegradable lubricants. Estolides and their co-products compare favorably with commercially available industrial products, such as petroleum-based hydraulic fluids, soybean-based fluids, and petroleum oils, and usually outperform the competition.

Estolides are a class of esters, based on vegetable oils, which form when the carboxylic acid functionality of one fatty acid reacts at the site of unsaturation, or double bond, of another fatty acid to form an ester linkage. These linkages are used to help characterize the structure of the estolide since the estolide number (EN) is defined as the average number of fatty acids added to a base fatty acid. The secondary ester linkages of the estolide are more resistant to hydrolysis than triglycerides, and the unique structure of the estolide results in materials that have physical properties far superior to those of vegetable and mineral oils for certain applications. Vegetable oil-based lubricants and derivatives have excellent lubricity and biodegradability properties, for which they are being more closely examined as a base stock for lubricants and functional fluids. Two major problems with vegetable oils as functional fluids are their low resistance to thermal oxidative stability and poor low-temperature properties such as pour points. Pour points are defined as the lowest temperature at which a material is still fluid before freezing. However, with the addition of additives, these properties can sometimes be improved, but only at the sacrifice of biodegradability, toxicity, and cost.

The goal of the estolide project was to construct a molecule that would not need 40–60% additives to be acceptable, like most commercial soybean lubricants. Two different estolide 2-ethylhexyl esters were synthesized, one from oleic acid and another from oleic and coconut fatty acids with 0.05 mole equivalents of perchloric acid at 60°C under vacuum followed by direct conversion to the corresponding ester by the addition of 2-ethylhexanol at 60°C for 3 h under vacuum. The two different estolide 2-ethylhexyl esters were vacuum distilled to remove any excess 2-ethylhexanol, while the coconut-oleic estolide 2-ethylhexyl ester underwent additional vacuum distillation to remove any excess fatty acids, thus improving the cold-temperature properties of the estolide.

RPVOT times (a measure of oxidative stability) on the coconut-oleic estolide 2-ethylhexyl ester were determined at 150°C while varying the amounts of Lubrizol 7652 (biodegradable oxidative stability package). The unformulated coconut-oleic estolide 2-ethylhexyl ester showed an expected low RPVOT time of 17 min. In this case, the coconut-oleic estolide had RPVOT values almost twice that of the oleic estolides. This could be accounted for in terms of iodine value (IV). The simple oleic estolide had an IV of about 40, whereas the coconut-oleic estolide had an IV of about 15. The IV is really a measurement of the amount of unsaturation in the molecule. Oxidative stability is known to be directly dependent on the amount of unsaturation in a molecule.

Lubrizol 7652 was added in 0.5 wt% units to the coconut-oleic estolide 2-ethylhexyl ester. As 0.5% of the oxidative stability package was added, there was a 6.5-fold improvement in the RPVOT value to 113 min. By adding a 1.0% oxidative stability package, the RPVOT time was increased to 245 min, which exceeded the times for the petroleum crankcase oils. Therefore, an RPVOT time of 200 min, common for most petroleum crankcase oils, could be achieved easily with less than 1.0% of the oxidative stability package. Synthesis of the coconut-oleic estolide showed that it could be easily and inexpensively formulated into a crankcase formulation. After adding a 2.0% oxidative stability package, the reported RPVOT values were comparable to those of premium hydraulic fluids. The RPVOT values reached a maximum with the addition of about 3.0%

oxidative stability package, which produced an RPVOT time of 504 min. This time compares favorably with aviation oil for single-engine propeller planes. This is an improvement of more than 30 times over the original.

Overall direct comparison between the oleic estolide 2-ethylhexyl ester and the coconut-oleic estolide 2-ethylhexyl ester showed a noticeable difference between the two estolides, as the coconut-oleic estolide 2-ethylhexyl ester gave much better RPVOT values. The most noticeable case was with the 1.5% oxidative stability package, where the coconut-oleic estolide 2-ethylhexyl ester had almost twice the RPVOT value of the oleic estolide 2-ethylhexyl ester. In both cases, the RPVOT values peaked at 2.5 and 3.0%, respectively, and held somewhat steady as the times started to decline with an increased oxidative stability package.

The estolide project is unique in that we designed a molecule to perform under the required functional fluid conditions rather than trying to formulate an unacceptable material into more acceptable material. Recently, this material has been licensed by Peaks and Prairies and we are working on developing new industrial uses with them.

Field Work - Cuphea

Cuphea (Lythraceae) is an annual that produces a seed oil rich in saturated medium-chain triglycerides (MCT). Approximately 260 species of Cuphea are native to the Americas. Among these species, a good diversity for saturated fatty acid classes (caprylic, capric, lauric, myristic and palmitic) is present where each MCT is represented in high concentration within the oilseed. The obvious desire to produce an annual renewable source of MCT that would supplement supplies of coconut and palm kernel oils has driven research to develop varieties that are suitable for agricultural production. Initial oil characterization of a number of Cuphea species by the United States Department of Agriculture (USDA) Research Center in Peoria, Illinois, described oil contents that ranged from 16 to 42% which were rich in lauric and capric acids. Breeding work has been developed by our collaborators which have yielded promising crosses, ie PSR-23 (partial seed retention). These new varieties have been mechanically harvested by researchers at USDA in Morris, Minnesota, and Peoria, Illinois. We have also worked on drying this green crop as well different swathing techniques..

Cuphea is unique in the diversity among its species to produce high levels of individual MCT. High levels of each MCT class (C10:0 to C16:0) are available, however, most of these species are not suitable for cultivation and harvesting for agronomic reasons. Several species have seen intense breeding efforts towards domestication. Among these species C. lanceolata, C. wrightii and C. viscosissima have shown the greatest likelihood for cultivation.

Cuphea suffers from many problems normally encountered in a developing crop. Seed shattering has been a particularly difficult problem in Cuphea. However, recent crosses have provided partial seed retentive varieties that resulted from a cross of C. lanceolata with C. viscosissima (PSR-23). PSR-23 is high in capric acid with an oil content of 30%. One of the most notable characteristics of Cuphea is a sticky substance found on the leaves and stems of the plant. This sticky material appears to function as a means of protection against some insect damage. Unfortunately, this stickiness does pose major problems for some harvesting equipment. However, USDA researchers at both Morris Minnesota, and Peoria, Illinois, have reported successful mechanical planting and harvesting of a sticky Cuphea variety with conventional farm equipment found in the Midwest. We have also studied planting dates and seeding rates and found an optimum planting date and seeding rate for our geographical location.

Selected Publications

Cermak, S.C., Skender, A.L., Deppe, A.B., and Isbell, T.A. Synthesis and Physical Properties of Tallow-Oleic Estolide 2-Ethylhexyl Esters. *J. Am. Oil Chem. Soc.* (accepted)

Cermak, S.C., John, A.L., and Evangelista, R.L., Enrichment of Decanoic Acid in Cuphea Fatty Acids by Molecular Distillation. *Ind. Crops Prod. 26*:93-99, 2007.

Cermak, S.C., Brandon, K.B., and Isbell, T.A. Synthesis and Physical Properties from Lesquerella and Castor Fatty Ester. *Ind. Crops Prod. 23*:54-64. 2006.

Cermak, **S.C.**, Isbell, T.A., Isbell, J.E., Akerman, G.G., Lowery, B.A., and Deppe, A.B. Batch Drying of Cuphea Seeds. *Ind. Crops Prod. 21*:353-359. 2005.

Cermak, **S.C.** and Isbell, T.A. Estolides - The Next Bio-Based Functional Fluid. *Inform*. *15*:515-517. 2004.

Cermak, S.C. and Isbell, T.A. Synthesis and Physical Properties of Cuphea-Oleic Estolides and Esters. *J. Am. Oil Chem. Soc. 81*:297-303. 2004.

Cermak, **S.C.** and Isbell, T.A. Synthesis and Physical Properties of Estolide-Based Functional Fluids. *Ind. Crops Prod. 18*:183-196. 2003.

Cermak, **S.C.** and Isbell, T.A. Improved Oxidative Stability of Estolide Esters. *Ind. Crops Prod. 18*:223-230. 2003.

Cermak, **S.C.** and Isbell, T.A. Pilot Plant Distillation of Meadowfoam Fatty Acids. *Ind. Crops Prod. 15*:145-154. 2002.

Cermak, **S.C.** and Isbell, T.A. Physical Properties of Saturated Estolides and Their 2-Ethylhexyl Esters. *Ind. Crops Prod. 16*:119-127. 2002.

Cermak, **S.C.** and Isbell, T.A. Biodegradable Oleic Estolide Ester Having Saturated Fatty Acid End Group Useful as Lubricant Base Stock. U.S. Patent 6,316,649 B1. November 12, 2001.

Cermak, **S.C.** and Isbell, T.A. Synthesis of Estolides from Oleic and Saturated Fatty Acids. *J. Am. Oil Chem. Soc*. *78*:557-565. 2001.