

Chemistry and physical properties of estolides

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RESUMEN

Propiedades físicas y químicas de los estólidos

Los estólidos son una familia de compuestos sintetizados a partir de aceites hidroxilados como los de ricino o lesquerella o mediante la condensación de ácidos grasos sobre el doble enlace de un segundo ácido graso insaturado. Los estólidos de ricino y lesquerella se derivan tanto de sus triglicéridos como de sus ácidos grasos libres empleándose el residuo hidroxilo para formar los ésteres estólidos de los mismos. Los triglicéridos estólidos tienen puntos de fluidez crítica de entre 9 y -36°C y baja estabilidad, con tiempos de oxidación en recipiente vacío a presión (RPVOT) de entre 29 y 52 minutos incluso con la adición de un 1% de una mezcla antioxidante a las muestras. Estas propiedades contrastan con las de los estólidos de ácido lesquerólico y ricinoleico, que poseen puntos críticos de fluidez mucho más bajos (de -36 a -54). Los estólidos derivados mediante la condensación de ácido oleico con otros ácidos grasos por catálisis ácida pueden realizarse con buen rendimiento y presentan un rango bastante amplio de propiedades físicas. A este respecto son de bastante interés los estólidos de ácido oleico esterificados con ácidos grasos saturados los cuales presentan tanto buen comportamiento a bajas temperaturas (puntos de fluidez crítica de -5° a -39°C) como buena estabilidad oxidativa. Los estólidos de los ácidos grasos del aceite de prado (*Limnanthes alba*) no presentan buenas propiedades de lubricación a baja temperatura pero su uso está muy extendido en cosmética, donde muestran buenas propiedades como agente hidratante.

PALABRAS-CLAVE: Ácido oleico – Lesquerella – Propiedades físicas – Ricino – Síntesis.

SUMMARY

Chemistry and physical properties of estolides

Estolides are a developing class of natural and synthetic compounds that have been synthesized from hydroxy oils like castor and lesquerella or by the condensation of fatty acids across the olefin of a second fatty acid. Castor and lesquerella estolides are derived from either their triglycerides or their free fatty acids utilizing their hydroxyl moiety to establish the estolide bond. The triglyceride estolides have pour points of 9 to -36°C but suffer poor oxidative stability with RPVOT times of 29 – 52 minutes even with 1% of an anti-oxidant package incorporated into the samples. In contrast to the triglyceride estolides of castor and lesquerella, the estolides from lesquerolic and ricinoleic acids have very good pour points of -36 to -54°C. Estolides derived from the acid catalyzed condensation of oleic acid with a variety of fatty acids can be made in good yield and possess a wide range of physical properties. Of particular interest are the saturated

capped estolides of oleic that have both good low temperature properties (pour point -5 to -39°C) and good oxidative stability. Estolides from meadowfoam fatty acids do not have good low temperature properties but have been extensively used in cosmetics where they provide good moisturizing properties.

KEY-WORDS: Castor – Estolide – Lesquerella – Oleic acid – Physical Properties – Synthesis.

1. INTRODUCTION

Estolides are natural and synthetic compounds derived from fats and oils. The estolide structure is identified by the secondary ester linkage of one fatty acyl molecule to the alkyl backbone of another fatty acid fragment. Figure 1 describes the general nomenclature of an estolide where the internal ester linkage is the estolide bond position. The Estolide Number (EN) is defined as $n + 1$ indicating the extent of oligomerization of the molecule. Estolides can be free acids, esters or found within a triglyceride structure. The later form of estolide occurs naturally in the genus lesquerella where the species *lesquerella auriculata* produces up to 96% of its seed oil as estolides (Hayes *et al.*, 1995a). Triglyceride estolides have been synthesized from castor and lesquerella oils and used in a wide range of lubricant applications and when the estolide is dehydrated the resulting product is a drying oil (Penoyer *et al.*, 1954). Estolides synthesized from unsaturated fatty acids have introduced a wide range of new estolide structures based on the position of the original olefin of the starting fatty acid (Isbell *et al.*, 2001). Estolides based on these sources have been used in cosmetics and industrial applications. This review will discuss the synthesis and physical properties of this unique class of fatty acid derivative.

2. GLYCERIDE ESTOLIDES

2.1. Natural estolides

Although glyceride estolides, polyacyl glycerides, are not unexpected components from hydroxy and epoxy containing oils their natural presence are not

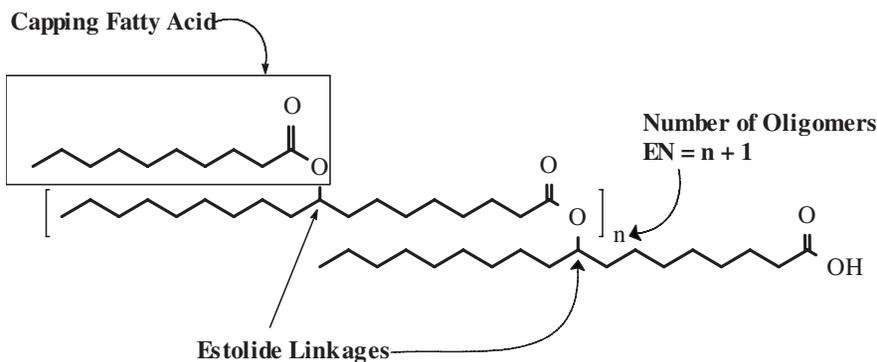


Figure 1.
Estolide Nomenclature: Free acid estolide capped with a C10 saturated fatty acid with an estolide number of 2 (EN = 2).

widely described in the literature and none of these unique oils has ever reached a commercial scale. The literature reports estolides from eleven different plant genus: *Cardamine*, *Chamaepeuce*, *Dimorphotheca*, *Heliophila*, *Holarrhena*, *Lesquerella*, *Monnina*, *Nerium*, *Sapium*, *Sebastiana* and *Trewia*. Of this list a few unique and promising seed oils should be discussed. *Heliophila amplexicaulis* (Platner *et al.*, 1979) is a member of the mustard family collected in Spain and produces a seed oil rich in lesquerolic acid (30%) where all of the hydroxy groups are found esterified into estolides. Interestingly, the *Heliophila amplexicaulis* estolide capping fatty acid group is erucic acid where the other seed oil estolides mentioned in the group above all have fatty acid groups of 18 carbons or less as the predominant capping fatty acid. Recent interest in the utilization of the invasive shrub *Sapium sebiferum* (Chinese tallow) may provide a source for an allenic estolide, 8-(2(*E*), 4(*Z*)-decadienoyl)-5(*E*), 6-(*E*)-octadecadienoic acid, (Aitzetmuller *et al.*, 1992; Payne-Wahl and Kleiman 1983). The last member of this unique group of seed oils are the estolides derived from *lesquerella auriculata*. This seed contains 32% oil of which 96% of the oil is found as an estolide (Hayes *et al.* 1995a; Kleiman *et al.*, 1972). Unfortunately, the availability of these natural estolides has limited the quantity of oil and physical properties of these novel materials have not been reported.

2.2. Synthetic glyceride estolides

The hydroxy functionality of castor and lesquerella oil provides a useful site to conduct esterification reactions where the resulting product is an estolide. The hydroxyl moiety being a relative reactive species can be easily esterified on the intact triglyceride without degradation of the glyceride molecule. Early work by Penoyer *et al.*, (1954) demonstrated the feasibility of synthesizing estolides via a high temperature esterification reaction at 250°C under a CO₂ sparge. This estolide was then directly dehydrated under vacuum at 260°C into a conjugated oil that was used for making drying films. In this case the estolides were not characterized or their physical properties determined. Erciyes *et al.*, (1991) provided additional details to the

synthesis of triglyceride estolides where they explored the rates of estolide formation from castor oil when condensed with oleic acid between 200°C to 250°C. Erdem *et al.*, (1994 and 1995) explored the use of Lewis acid catalysts like tin chloride and cobalt chloride in reactions of castor oil with oleic acid but the high reaction temperatures (200°C to 250°C) studied for the cobalt catalyzed reaction provided no real advantage to those reactions performed in the absence of catalyst. However, Erdem's work did provide insight into the reaction mechanism. Later work on the kinetics of the esterification reaction of castor with lauric acid in the presence of various Lewis acid catalysts by Kulkarni *et al.*, (2003) demonstrated that *n*-butyl titanate was an effective catalyst for the formation of estolide. When 4% catalyst was employed, at 185°C, a 68% conversion to triglyceride estolide was obtained in 6 hours. The reaction was first order in both fatty acid and hydroxy oil.

A patent by Lawate (1995) describes the synthesis of triglyceride estolides for castor and lesquerella with heptanoic, isostearic, adipic and fumaric acids as the capping fatty acid using *p*-toluenesulfonic acid as the catalyst (Figure 2). A reaction temperature of 150°C was used to azeotropically remove the water of esterification. All of the estolide products synthesized were run at stoichiometry such that the triglyceride hydroxyl groups would all be esterified to estolide. The lesquerella triglyceride estolide products were then evaluated for their thickening performance by the change in viscosity in admixtures with a high oleic vegetable oil (80% Oleic). Figure 3 graphs the percent increase in viscosity of the high oleic vegetable oil when 5, 20 and 30% triglyceride estolide was added. Fumaric acid, a diacid, had the largest impact under the conditions studied where a 5% incorporation of estolide produced a 23% increase in the solution viscosity. The other diacid reported, adipic, had similar thickening capabilities where a 5% mixture gave a 17% increase in viscosity at 40°C. The monoacid, isostearic, provided no apparent increase in viscosity beyond simple thickening by mixing two fluids, one of low viscosity with one of high viscosity (5% mixture gave a 5% increase in viscosity).

Later Isbell and Cermak (2002) synthesized a series of triglyceride estolides from both castor

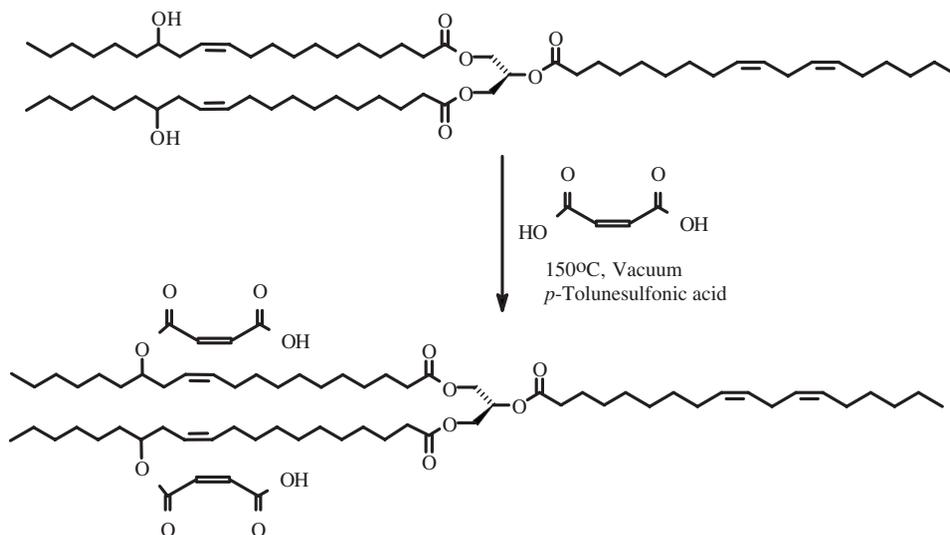


Figure 2
Synthesis of lesquerella triglyceride estolides (Lawate 1995).

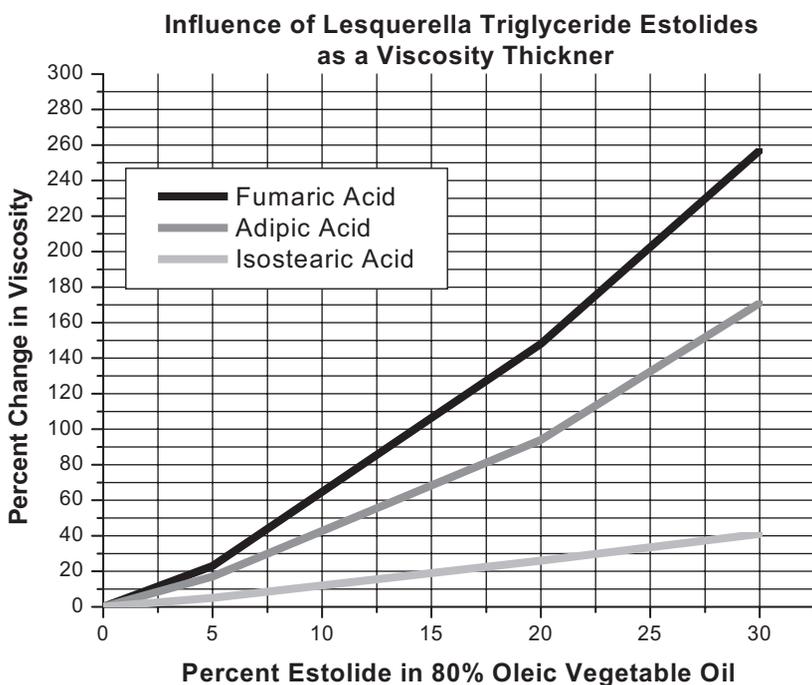


Figure 3
Influence of lesquerella triglyceride estolide on high oleic vegetable oil viscosity. Data summarized from Lawate (1995).

and lesquerella oils and compared their physical properties (Isbell *et. al.*, 2006). Their work demonstrated (Figure 4) that mono-, di- and fully-capped triglyceride estolides could be synthesized from both castor and lesquerella oils with oleic acid as the capping fatty acid. Table 1 outlines the general reaction conditions explored where all reactions were run neat. The bulk of the reactions used vacuum to remove the water of esterification but the reaction could also be performed under nitrogen (Entry L-C, Table 1). Although reactions

can be performed at lower temperature (100°C) the reaction nears completion in 24 hours when the reaction exceeds 175°C (Entry L-D, Table 1). If the temperature is pushed to 250°C increase in the undesirable dehydration product, diene, is observed (Entry L-E, Table 1). Stoichiometry of the capping fatty acid with respect to the oil dictates the extent of estolide formation and capping of individual hydroxyl groups on the triglyceride is observed (Entries C-A, C-B and C-D, Table 1). For lesquerella oil, a fully capped estolide has an

Table 1
 Synthesis of estolides from oleic acid with Lesquerella and Castor oils

Entry ¹	FA Equiv. ²	Atmosphere	Temp. (°C)	Time (h)	Conversion (%) to estolide	EN ³ Crude (NMR)	Diene (mole %) ⁴
L-A	1	Vacuum	200	24	56	1.06	0.0
L-B	3	Vacuum	200	24	100	1.89	0.0
L-C	2	Nitrogen	200	24	77	1.45	0.0
L-D	2	Vacuum	175	24	97	1.84	0.0
L-E	2	Vacuum	250	24	100	1.89	3.5
L-F	2	Vacuum	200	12	100	1.89	0.0
C-A	1	Vacuum	200	24	37	0.98	0.9
C-B	2	Vacuum	200	24	59	1.58	0.0
C-C	3	Vacuum	200	24	92	2.46	3.2
C-D	4	Vacuum	200	24	100	2.67	0.3

Data from Isbell and Cermak (2002). ¹L is Reactions run with lesquerella oil and C are reactions run with castor oil. ²Mole equivalents of oleic acid based on the moles of lesquerella. ³EN values were determined by NMR. A fully capped lesquerella estolide has an EN of 1.89 and a fully capped castor estolide has an EN of 2.67. ⁴Mole percent determined by GC.

EN = 1.89 and for castor oil a fully capped estolide has an EN = 2.67. These theoretical EN values are based on 60% hydroxy fatty acid concentration in lesquerella and 90% hydroxy fatty acids in castor oil. Castor oil full-capped estolides require additional excess equivalents of capping fatty acid to fully esterify the hydroxy moieties probably due to the developing steric hindrance of the triglyceride molecule once two estolide groups are already formed. When smaller fatty acid groups are used to

form the triglyceride estolides (C2-C4), anhydrides must be employed along with reduced temperature (60°C). When mid chain (C6-C12) fatty acid groups are used for capping, tin(II) 2-ethylhexanoate catalyst and intermediate temperatures of 130°C are used to avoid boiling off of the capping fatty acid during the course of the reaction (Isbell *et al.*, 2006). When fatty acid capping groups longer than C12 are used the reactions can be run neat under vacuum at 200°C.

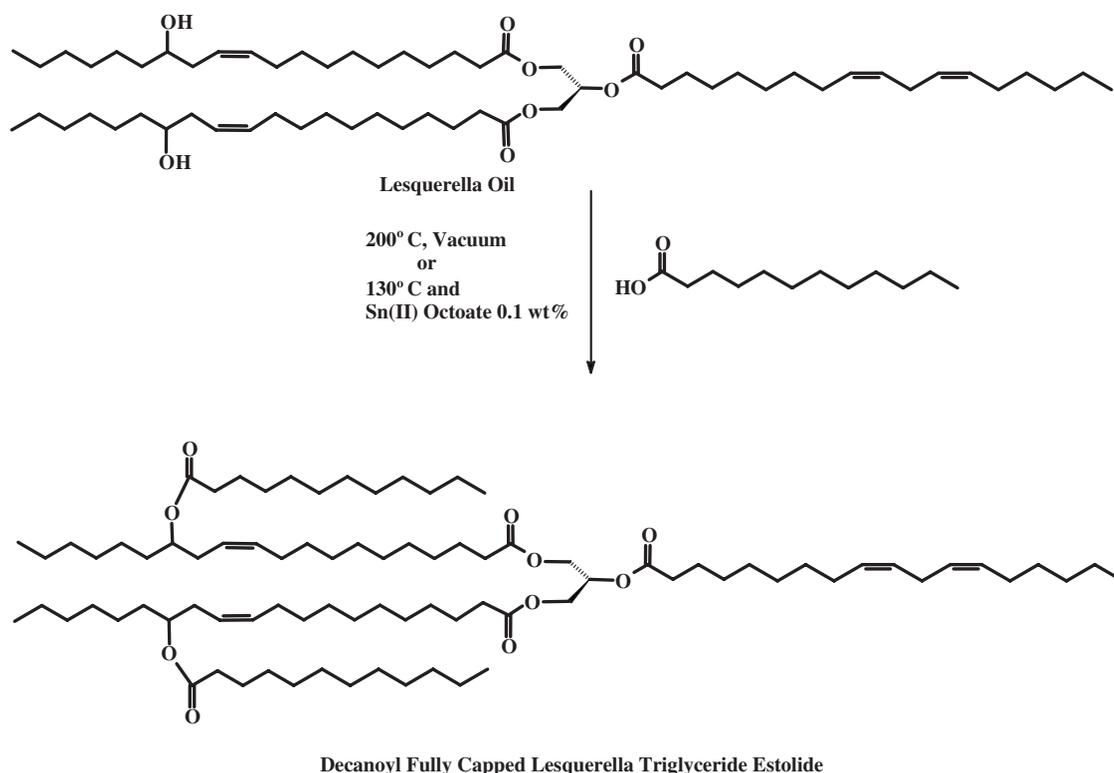


Figure 4
 Synthesis of triglyceride estolides from lesquerella under vacuum (Isbell *et al.*, 2002).

A series of saturated C2 to C18 and 18:1 capping fatty acids were used to mono- and fully-cap castor and lesquerella oils and their physical properties are reported in Tables 2 and 3 (Isbell *et. al.*, 2006). The starting hydroxy oils, lesquerella and castor, have pour points of -21°C and -15°C , respectively. Because of the hydroxy group in these oils and the resultant hydrogen bonding, both of these oils have high viscosities at 40°C , 127.7 cSt for lesquerella and 260.4 cSt for castor oil. This high viscosity limits their use in many lubricant and fuel applications. When estolides are formed at the hydroxyl positions the pour point as well as the viscosity can be improved. The fully capped estolides C2-C10 for lesquerella and C2-C12 for castor gave lower pour points than the corresponding mono-capped triglyceride estolide. The larger saturated capping groups (C12–C18 for lesquerella and C14–C18 for castor) gave lower pour points for the mono-capped series than the full-capped estolides. The longer chain capping fatty acids apparently have sufficient alkyl stacking interactions due to the unhindered exposure of the alkyl portion of the capping fatty acid to increase cloud and pour points. The shorter chain fatty acid capping groups improved the pour points for the underivatized oils by disrupting alkyl stacking

interaction of the triglyceride itself. This effect is not observed in the acetate estolides indicating that the very short chain length is not capable of providing disruption of the alkyl stacking interactions. The acetate group would not be of sufficient length to sweep the entire length of the alkyl chain beyond the hydroxy functionality. Of particular note is the fact that the hexanoic capping group gave the lowest pour points in all the estolides series where the length of the hexanoyl chain would be capable of completely sweeping the alkyl chain but not of sufficient length to expose its own backbone to alkyl stacking interactions. As a result, the minimum pour points observed were -36°C for hexanoic fully-capped lesquerella and -45°C for hexanoic capped castor triglyceride estolides.

The two main factors in this series of homologous compounds that impact viscosity are hydrogen bonding by the hydroxyl groups and the steric bulk of the molecules. Intermolecular hydrogen bonding between the hydroxy triglycerides increases the steric bulk of the solution by creating weakly associated dimers, trimers, etc. of the original triglycerides, therefore increasing the viscosity of the oil. In all cases, the full-capped triglyceride estolides have lower viscosities for all chain-lengths than the mono-capped estolides

Table 2
Physical Properties of Lesquerella triglyceride estolides

Capping Fatty Acid	Capping Extent	Estolide Number	Pour Point ($^{\circ}\text{C}$)	Cloud Point ($^{\circ}\text{C}$)	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)
None	NA	NA	-21	-22	127.7	15.2
C2:0	Mono	0.90	-21	>r.t.	92.8	14.6
C2:0	Full	1.70	-30	-18	79.7	14.2
C4:0	Mono	0.88	-27	<-27	86.7	14.4
C4:0	Full	1.50	-33	-30	74.7	13.9
C6:0	Mono	0.78	-33	>r.t.	103.0	15.9
C6:0	Full	1.23	-36	>r.t.	87.9	15.2
C8:0	Mono	0.75	-27	-25	115.7	15.1
C8:0	Full	1.41	-33	-27	76.0	14.8
C10:0	Mono	0.66	-27	-26	118.5	17.2
C10:0	Full	1.51	-30	-17	99.9	16.7
C12:0	Mono	1.00	-27	-23	110.8	17.4
C12:0	Full	1.60	-18	-28	101.0	17.2
C14:0	Mono	1.29	-18	1	129.9	19.2
C14:0	Full	1.46	3	21	118.6	18.4
C16:0	Mono	0.83	0	15	135.2	20.5
C16:0	Full	1.75	6	27	114.2	18.7
C18:0	Mono	1.46	9	28	137.4	20.5
C18:0	Full	1.75	24	45	Solid	34.3
C18:1	Mono	0.97	-27	-16	119.6	18.7
C18:1	Full	1.56	-27	-16	95.1	17.0

Data from Isbell *et. al.*, (2006).

Table 3
Physical properties of castor triglyceride estolides

Capping Fatty Acid	Capping Extent	Estolide Number	Pour Point (°C)	Cloud Point (°C)	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)
None	NA	NA	-15	-34	260.4	20.1
C2:0	Mono	0.82	-24	<-24	147.4	16.8
C2:0	Full	2.59	-27	<-27	110.0	15.6
C4:0	Mono	0.93	-27	<-27	117.4	15.4
C4:0	Full	2.70	-33	-30	82.2	14.0
C6:0	Mono	0.80	-36	<-36	133.0	19.4
C6:0	Full	1.67	-45	<-45	79.0	17.0
C8:0	Mono	0.98	-21	<-21	203.0	21.1
C8:0	Full	2.54	-36	<-36	105.9	16.8
C10:0	Mono	1.04	-27	<-27	183.8	21.0
C10:0	Full	2.34	-36	<-36	91.8	16.2
C12:0	Mono	0.92	-27	<-27	193.1	21.4
C12:0	Full	2.36	-33	<-33	120.0	19.1
C14:0	Mono	1.11	-24	-17	223.4	25.6
C14:0	Full	2.69	-18	-7	155.9	23.2
C16:0	Mono	0.81	-18	-3	220.6	24.1
C16:0	Full	2.69	3	21	177.8	26.1
C18:0	Mono	2.10	9	27	226.8	26.6
C18:0	Full	2.42	18	24	174.5	25.7
C18:1	Mono	1.55	-33	<-50	186.9	23.5
C18:1	Full	2.69	-27	-27	131.8	21.9

Data from Isbell *et al.*, (2006).

even though the size of the molecule is much larger. Capping of the hydroxyl moiety reduces or eliminates the hydrogen bonding and consequently reduces the viscosity of the oil. The viscosity trend across the chain-length series follows a relationship where increasing viscosity is correlated to increasing chain length.

The oxidative stability of these estolides is poor due to the inherent unsaturation remaining in the triglyceride molecule even after the estolide is formed. As a result, Rotating Pressure Vessel Oxygen Testing (RPVOT) of the original oils and the series of estolides from both castor and lesquerella gave poor results (RPVOT times ~ 15 minutes). Even when oxidative stability agents were added RPVOT times could only be improved to about 100 minutes with 2% additive (Isbell *et al.*, 2006).

3. ESTOLIDES FROM FATTY ACIDS

3.1. Estolides from hydroxy fatty acids

The potential to synthesize estolides from the hydroxy oils is not limited to the triglyceride structure only. The fatty acids from the hydrolyzed oils provide

even greater opportunity to develop industrial materials with enhanced performance properties. The ability to modify the fatty acid functionality with esters of various chain lengths and branching, along with the potential to build up incremental molecular weights through homo-polymerization, provides a good route to making molecules with targeted physical properties. Estolides have been reported in the literature from castor oil for quite some time (Meyer 1897) and the homopolymerization extensively studied by a variety of wet chemical means (Modak and Kane 1965). Modak and Kane's work clearly demonstrated the formation of polyestolide from castor oil fatty acids by the homo-polymerization reaction at 202°C gave an acid value of 38 mg KOH/g Oil. Based on the molecular weight of ricinoleic acid this molecule would have contained 5 ricinoleate groups thus EN = 4 and a molecular weight of 1,476 g/mole. Modak and Kane's work was most interested in the decomposition of estolide into conjugated dienes unfortunately; the estolide fraction was not characterized for its physical properties. However, work by Teeter *et al.*, (1953) describes the synthesis of estolide esters from hydroxystearic

acid obtained by the hydrogenation of ricinoleic acid. Hydroxystearic acid was first esterified with various alcohols and the resulting esters reacted with an acid anhydride or acid chloride to form the corresponding estolide. Teeter reports both viscosity and pour point data on these estolides with an acetyl capped estolide 2-ethylhexyl ester providing the lowest pour point of -63°C (Table 4).

Lipases have been used to synthesize estolides and esters from lesquerolic acid (Hayes and Kleiman 1995b) and estolide yields reached 62% after 65 hours using *Pseudomonas sp.* lipase where the estolide formed was $>80\%$ monoestolide. Subsequent conversion to oleyl and decyl esters was readily accomplished and melting points of -19°C was reported for both of these derivatives along with viscosity indices of 150-302. Hayes went on to write a review for the use of lipase catalysis (Hayes 1996) with a few examples of estolides formed from lesquerella and castor fatty acids. Kiatsimkul *et al.*, (2008) used *C. rugosa* or *C. antartica* lipases to synthesize homo-oligomeric estolides of ricinoleic acid both under vacuum and atmospheric pressures at 60°C . The reaction required 5 days to yield $\sim 50\%$ estolide which consisted of dimmers and trimers. These estolides were later used to open epoxidized soybean oils to make polyols.

Lesquerella and castor free acid estolides were also produced (Figure 5) from a variety of capping fatty acids and their physical properties compared (Cermak *et al.*, 2006). The estolides were synthesized from castor and lesquerella oils corresponding hydroxy 2-ethylhexyl esters and capped with saturated, branch chain or unsaturated fatty acids as shown in Table 4. Both the simple oleic and the branched 2-ethylhexyl capping groups gave excellent pour points of -54°C for both lesquerolic and ricinoleic estolides as their 2-ethylhexyl esters. The viscosities of these estolides are sufficiently low enough to meet many lubricating

applications that the triglyceride estolides from these parent oils could not meet.

Estolides have also been synthesized from 17-hydroxy stearic acid (Zerkowski *et al.*, 2008) utilizing a protection, deprotection sequence to yield structured estolides. These estolides have exact estolide linkages in terms of both number of oligomers and position. The process will not produce large quantities of material but may shed some insight into the role of linkage position and oligomerization on the resulting physical properties of these novel fluids.

3.2. Estolides from unsaturated fatty acids

The next class of estolides is derived from the condensation of a fatty acid across the double bond of a second fatty acid as depicted in Figure 6. Estolides were first identified as minor by-products in the synthesis of dimmer acids using montmorillonite clays as catalysts (Burg and Kleiman 1991) and later synthesized in modest yield (14%) using a modified version of this batch procedure (Erhan and Kleiman *et al.*, 1993 and Erhan and Isbell 1997), 250°C under a 60 psi nitrogen atmosphere over a Montmorillonite K-10 clay catalyst. This work led to a detailed investigation by Isbell *et al.*, (1994a) and a mechanism for the formation of estolides was explored. Estolides from unsaturated fatty acids were shown to arise from protonation of the double bond to form a carbocation which was subsequently captured by a second fatty acid molecule. Stronger acids with weak nucleophilic conjugate bases gave faster rates of formation and higher yield of estolide. Weak acids like clay only provide 0.04-0.08 mmoles of H^+ /g of clay. In addition, the clay limited the reaction to the formation of monoestolide due to the small intra-spacial dimensions of the layers within the clay which prohibited penetration of estolide

Table 4
Physical properties of lesquerolic and ricinoleic estolide 2-Ethylhexyl esters

Hydroxy Fatty Acids	Capping Fatty Acids	Pour Point ($^{\circ}\text{C}$)	Cloud Point ($^{\circ}\text{C}$)	Viscosity @ 40°C	Viscosity @ 100°C
Hydroxystearic	Acetic	-63	NA	NA	NA
Hydroxystearic	Propanoic	-62	NA	NA	NA
Hydroxystearic	Butanoic	-31	NA	NA	NA
Ricinoleic	Oleic	-54	<-54	34.5	7.6
Ricinoleic	Stearic	3	23	41.7	8.6
Ricinoleic	Coconut Fatty Acids	-36	-30	29.0	6.5
Ricinoleic	2-Ethylhexanoic	-51	<-51	70.6	11.8
Lesquerolic	Oleic	-48	-35	35.4	7.8
Lesquerolic	Stearic	3	12	38.6	8.2
Lesquerolic	Coconut Fatty Acids	-24	<-24	40.4	8.4
Lesquerolic	2-Ethylhexanoic	-54	<-54	51.1	10.1

Estolides synthesized from either castor fatty acids or lesquerella fatty acids as their 2-ethylhexyl ester. Data summarized from Cermak *et al.*, (2006) and Teeter *et al.*, (1953).

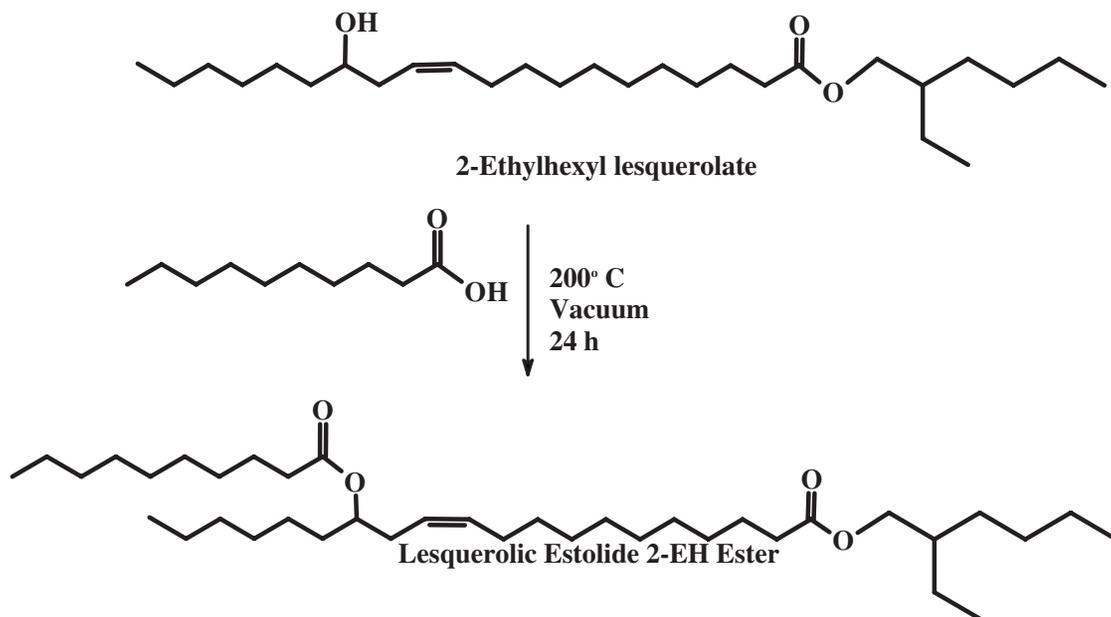


Figure 5
Synthesis of estolides from hydroxy fatty acids.

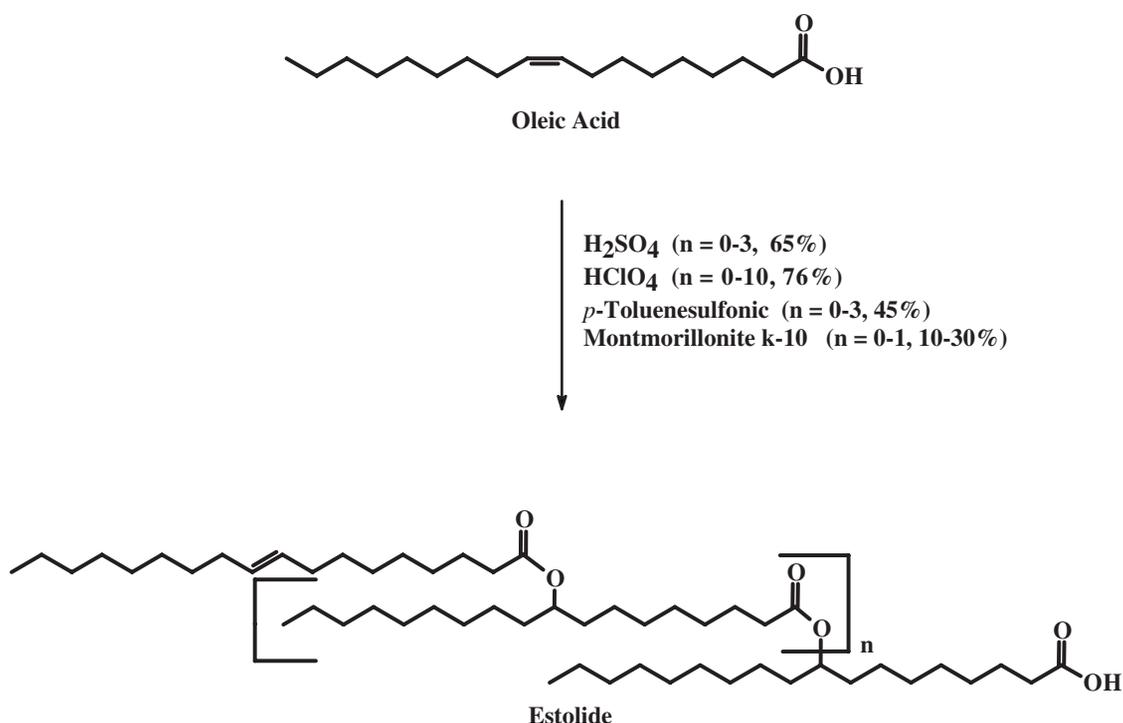


Figure 6
Synthesis of estolides from oleic acid.

and subsequent formation of higher oligomers. In the best cases, activated clays with increased H⁺ activity could produce estolide yields up to 41%.

Stronger mineral acids like sulfuric and perchloric with relatively weak nucleophilic conjugate bases gave rapid rates of estolide formation in high yield (76%) with considerable formation of polyestolide (Isbell *et al.*, 1994a and Isbell and Kleiman 1994b). These acid catalyzed reactions had EN values of

2.65 with oligomers as high as 11. Weaker acids like *p*-toluenesulfonic acid had EN values up to 4. The stronger acids clearly stabilize the carbocation on the fatty acid molecule and provide an opportunity for the condensation reaction into estolide to proceed. Side products of the reaction are lactones, positionally and geometrically isomerized monounsaturated fatty acids. Table 5 outlines a few of many reactions that produced estolide. Sulfuric acid reactions (Isbell *et*.

Table 5
Synthesis of estolides from oleic acid

Acid Catalyst	Catalyst Equiv.	Temperature (°C)	Reaction Time (h)	Yield (%)
HClO ₄	1.0	50	2	70
HClO ₄	0.05	60	24	78
H ₂ SO ₄	1.0	50	6	60
H ₂ SO ₄	3.3	55	24	80
<i>p</i> -Toluene sulfonic acid	1.0	100	24	45
BF ₃ -Et ₂ O	1.4 wt%	50	168	71
Montmorillonite K-10 Clay	20 wt%	150	118	41

Data summarized from Isbell *et al.*, (1994).

al., 1997) gave good yields of estolide but require higher acid equivalents to achieve good reaction rates. Unfortunately, small amounts of sulfonated fatty acids remain unquenched in the estolide products and their decomposition in the product over time can generate very acidic species that are detrimental to estolide performance. The perchloric acid catalyzed reaction can be run at extremely low equivalents, yet maintain reasonable reaction rates with good estolide yield. These estolides do not suffer from catalyst addition products and remain stable over very long periods of time.

The formation of estolides has been demonstrated in other monounsaturated fatty acids as well; meadowfoam, crambe and oleic acids (Isbell and Kleiman 1996; Isbell *et al.*, 2001). The synthesis of meadowfoam estolide was challenged by the

formation of the ring closure product δ -Lactone, which is a very competitive reaction path due to the close proximity of the carboxylic functionality of the 5-eicosenoic acid found in this seed oil. Low equivalents of perchloric acid and lower temperatures favored estolide formation where higher acid equivalents and temperature favor lactone formation. These estolides have found a number of uses in the area of cosmetics (Awang *et al.*, 2007b; Isbell *et al.*, 2000).

The melting point, pour points and viscosity data are reported by Isbell *et al.* (2001) for a series of estolide esters from crambe, meadowfoam and oleic acids. A subset of this data is shown in Table 6. The oleic estolide series had the best melting points of all those studied and the branched alkyl esters of the estolide further improved upon these

Table 6
Physical properties of estolide esters

Estolide	Melting Point (°C)	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)
Crambe estolide	0	679.0	58.6
Crambe estolide 2-ethylhexyl ester	-12	184.4	26.1
Meadowfoam estolide	6	229.8	27.4
Meadowfoam estolide 2-ethylhexyl ester	-1	104.2	16.5
Oleic estolide	-31	404.9	40.0
Oleic estolide methyl ester	-27	169.1	23.7
Oleic estolide butyl ester	-27	238.4	30.3
Oleic estolide decyl ester	-10	149.0	21.4
Oleic estolide oleyl ester	-22	187.2	26.8
Oleic estolide 2-methylpropyl ester	-32	200.7	26.7
Oleic estolide 2-ethylhexyl ester	-34	161.2	22.5
Oleic estolide C18 Guerbet ester	-43	206.6	27.4
Oleic estolide C24 Guerbet ester	-32	169.4	24.3

Data summarized from Isbell *et al.*, (2001).

low temperature properties. Oleic estolide had a melting point of -31°C and upon esterification with a C18 Guerbet alcohol was improved to -43°C . Although the Guerbet esters had better low temperature properties the cost associated with production of these alcohols makes this a very expensive ester. In light of these cost issues, the inexpensive 2-ethylhexyl ester provided good low temperature properties and was later used to make a variety of esters from estolides for use in lubricant applications.

The position of the estolide has a pronounced effect on its physical properties. Crambe estolide positions are centered around the original $\Delta 13$ olefin, meadowfoam around $\Delta 5$ and oleic around $\Delta 9$ with melting points of 0°C , 6°C and -31°C respectively. This melting point trend suggests that estolides with mid-chain linkages will provide better low temperature properties. As expected, molecular weight also impacts low temperature properties with higher molecular weight molecules yielding higher pour points. Table 7 reports this effect where estolides of increasing estolide number showed an increase in pour point temperatures and monoestolide gave the lowest pour point of -42°C for an oleic estolide 2-ethylhexyl ester. However, when these molecules iodine values were

set equal by hydrogenation the impact on pour point was greatly diminished suggesting the composition of the last fatty group to form the estolide may be the most important on the overall physical properties of the molecule.

The capping fatty acid of the estolide was evaluated for the impact of chain length on pour points (Cermak and Isbell 2001; Cermak and Isbell 2002; Cermak and Isbell 2009). Table 8 provides a summary of the work by Cermak and Isbell (2002) which demonstrated that a decanoyl capping group for the estolide provided the lowest pour points within this series. This would be consistent with the concept that the length of the fatty acid capping group should completely reach the terminus of the oleic estolide but not extend beyond the end or fall significantly short of the methyl terminus. When these chain-length requirements are met, intermolecular stacking interactions are prevented and crystal formation inhibited. These molecules have very low iodine values yet have excellent pour point values thereby contradicting the general trend observed for fats that correlate low iodine values with high pour points. As a result of reducing the unsaturation in the molecule, estolides and particularly saturate capped estolides have

Table 7
Effect of oleic estolide oligomerization on physical properties

Estolide	EN #	Pour Point ($^{\circ}\text{C}$)	Viscosity @ 40°C (cSt)	Iodine Value
#1 2-EH ester	3.0	-3	292.8	16.2
#2 2-EH ester	2.3	-27	133.2	30.5
#3 2-EH ester	1.1	-42	43.1	52.5
Hydrogenated #1 2-EH ester	3.0	6	285.6	2.4
Hydrogenated #2 2-EH ester	2.3	-15	139.9	3.6
Hydrogenated #3 2-EH ester	1.1	-9	48.8	2.2

Data summarized from Isbell *et. al.*, (2001).

Table 8
Effect of capping fatty acid chain length on oleic estolide physical properties

Capping Fatty Acid	Pour Point ($^{\circ}\text{C}$)	Cloud Point($^{\circ}\text{C}$)	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)
4	-30	-36	125.5	19.3
6	-30	-34	114.5	17.9
8	-36	-41	104.4	16.8
10	-39	NA	93.8	15.5
12	-36	-32	73.9	13.0
14	-25	-22	80.5	13.9
16	-12	-13	81.6	13.5
18	-5	-4	81.8	14.0

Data summarized from Cermak and Isbell (2002).

good oxidative stability (Cermak and Isbell 2003b; Biresaw *et al.*, 2007; Cermak *et al.*, 2008). Table 9 summarizes the oxidative performance of oleic estolide 2-ethylhexyl esters with coco-oleic estolide 2-ethylhexyl esters. When a commercial antioxidant package supplied by Lubrizol Corp is used the estolide exhibits good oxidative performance. Typical fully formulated commercial crankcase oils have RPVOT values of ~240 minutes. The unformulated estolide, like most all bio-based materials, has a short life span in this test. Even heavily formulated vegetable oils have difficulty reaching 100 minutes in this rigorous method. However, the estolides with reduced iodine values can be easily formulated to exceed petroleum oxidative stability standards and even perform at levels suitable for hydraulic fluids and aviation lubricants (Cermak and Isbell 2003a; Cermak and Isbell 2004a; Cermak and Isbell 2004b; Cermak *et al.*, 2007).

Initial film forming properties have recently been examined (Biresaw *et al.*, 2007) for the oleic based estolides including the saturate-capped estolides. The studies indicated that estolides have improved film forming properties when compared to underivatized vegetable oils but perform at a nearly equal level to poly alpha olefins. The mixed estolides had better film properties than the homo-oligomeric materials. Additional wear studies by Kurth *et al.*, (2007) demonstrated that oleic estolides had good coefficient of friction (COF) properties and the oleic estolide had the lowest COF of the series of simply fatty esters to which it was compared. Kurth's study provided some degree of correlation of the molecular size to the possibility that the molecule would provide multiple sites for adsorption to a metal surface, thus better lubricity. The oleic estolide was the largest molecule in the study and provided the greatest lubricity.

3.3. Estolides from epoxy fatty acids

The last class of estolides to discuss is derived from the ring opening of epoxy esters as shown in Figure 7. The epoxide functionality provides a ready handle to conduct a ring opening reaction which is catalyzed *insitu* by the capping fatty acid and a subsequent condensation with the capping group to form an α -hydroxy estolide. Pages and Alfos (2001) report a facile synthesis of epoxidized sunflower methyl esters in a neat reaction with oleic acid and report complete formation of estolide. Awang *et al.*, (2007a) ring open epoxystearic acid to the dihydroxystearic acid and homopolymerize the dihydroxy acid under a nitrogen atmosphere at 180°C. Awang provides a characterization of the estolides formed and demonstrates that control of the reaction time can control the extent of oligomerization. Awang's study also observes the synthesis of oligomers up to an EN = 5 under these reaction conditions after a reaction time of 8 hours. Moser *et al.*, (2007) ring open epoxystearate esters by reacting propyl or octyl epoxystearate with a series of fatty acids (propanoic, 2-propanoic, octanoic and 2-ethylhexanoic) to form α -hydroxy estolides. The resulting α -hydroxy estolides were evaluated for cold temperature properties and oxidative stability. The estolide reported to have the best cold temperature properties within the above mentioned series was the propyl ester of an α -hydroxy, 2-ethylhexyl estolide with a pour point of -39°C.

4. CONCLUSIONS

Estolides are novel derivatives of fats that have good physical properties and they are starting to demonstrate usefulness within their own right.

Table 9
Oxidative stability of oleic based estolides by RPVOT

Additive ^a	% Additive	Ratio BHT:ADA	RPVOT for Oleic Estolide 2-EH Ester (min)	RPVOT Coco-Oleic Estolide 2-EH Ester (min)
None	0	NA	8	17
Lubrizol-7652	0.5	NA	50	113
Lubrizol-7652	1.0	NA	132	245
Lubrizol-7652	2.0	NA	274	431
BHT:ADA	1.0	100:0	99	115
BHT:ADA	1.0	75:25	150	185
BHT:ADA	1.0	50:50	209	251
BHT:ADA	1.0	25:75	226	281
BHT:ADA	1.0	0:100	248	326

Data from Cermak *et al.*, (2008). ^aBHT is butyl hydroxy toluene and ADA is alkylated diphenylamine.

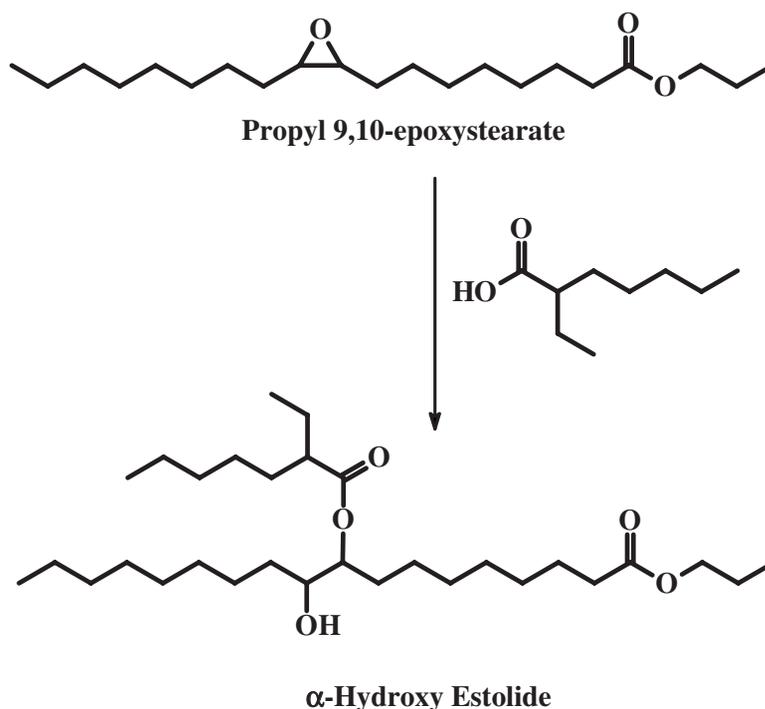


Figure 7
Synthesis of estolides from epoxy esters

Estolides from hydroxy containing fats are the simplest to synthesize. Triglyceride estolides of castor and lesquerella have demonstrated decent performance for their low temperature properties but need additional effort to improve their poor oxidative performance. Free acid estolides from both hydroxy containing fatty acids and unsaturated fatty acids show real promise as base stocks for a wide range of lubricant applications. Their excellent cold temperature properties coupled with their good oxidative stability should see these derivatives in many industrial applications. Synthesis of estolides from unsaturated fatty acids opens the possibility of making estolides with wide ranging physical properties based on their point of linkage and extent of oligomerization. Estolides from unsaturated fatty acid sources are only limited by the availability of novel olefin positions.

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