DEVELOPMENT OF CASTOR OIL DERIVATIVES AND WAY FORWARD



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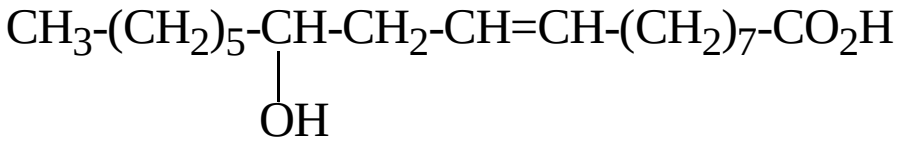
CONCEPT OF PRESENTATION

- Why Castor Oil is Unique?
- Direct Application of Castor Oil
- Simple & Advanced Derivatives of Castor Oil
- Potential Derivatives and Areas of Research
- Castor Oil Biorefinery Concept
- Growth Opportunities for Castor Oil
- Value Added Products – Way Forward…

CASTOR OIL – NATURE'S UNIQUE OIL

Distinguished from Other Vegetable Oils by its High Specific Gravity, Viscosity and Hydroxyl Value

UNIQUE FATTY ACID COMPOSITION

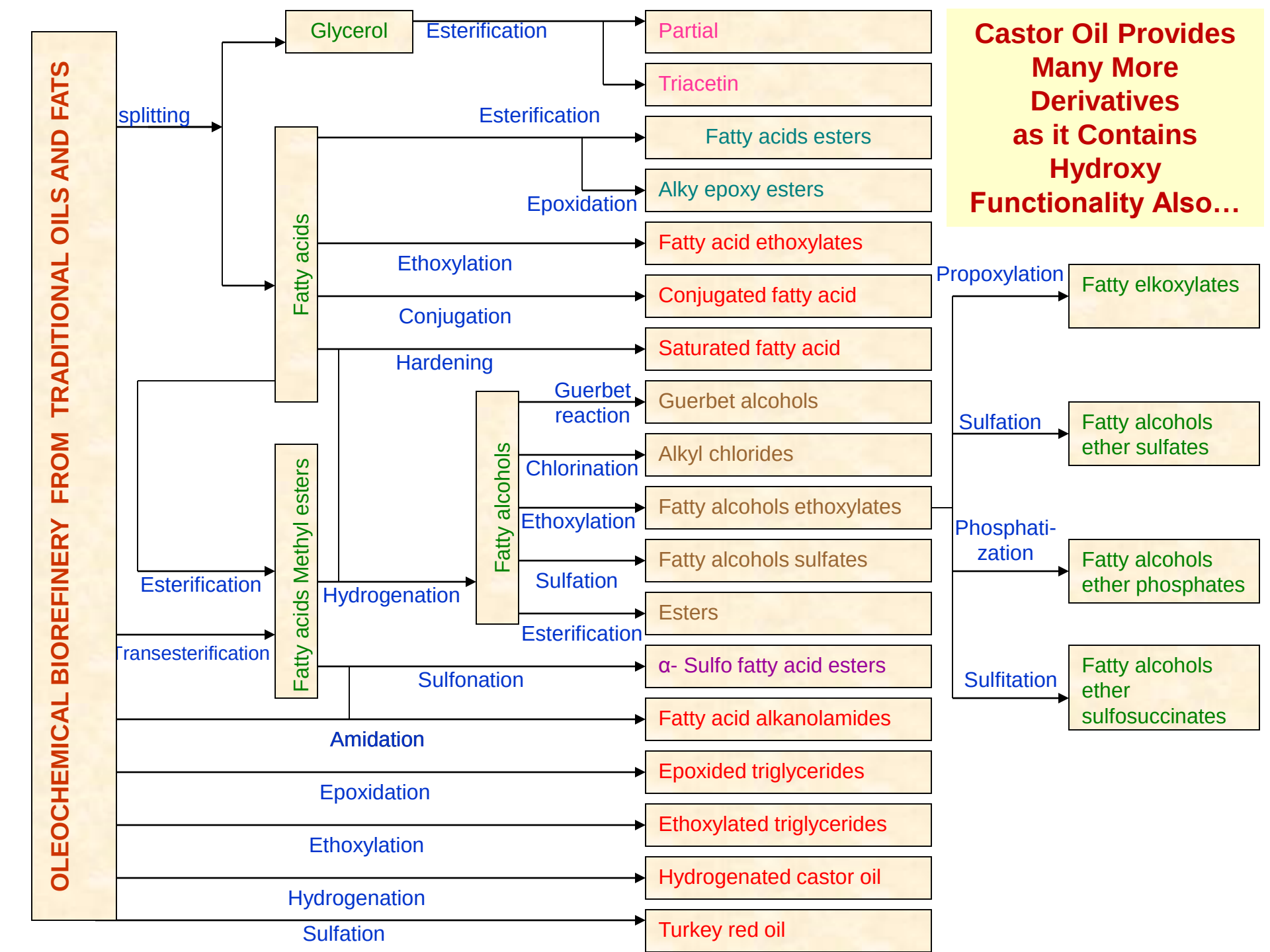


Ricinoleic acid ~90.0
Dihydroxystearic acid ~1.0

Palmitic acid, ~1.0; **Stearic acid, ~1.0**

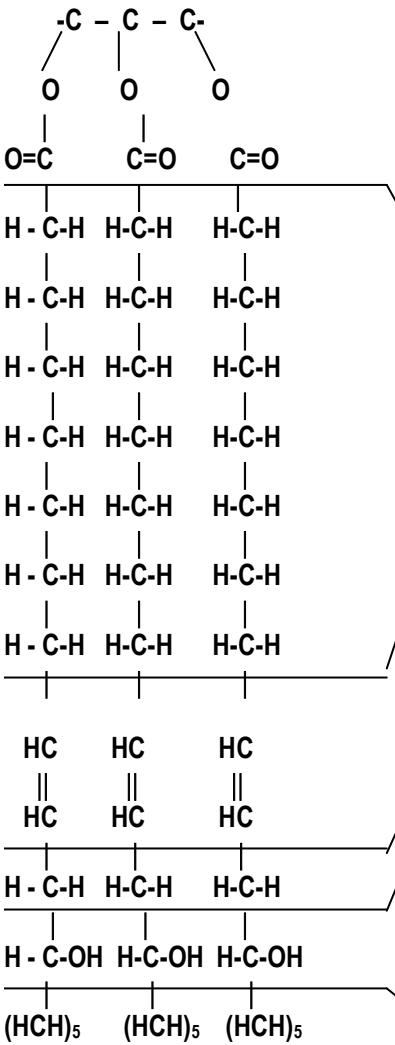
Oleic acid, ~3.0; **Linoleic acid, ~4.0**

Linolenic acid, ~0.5; **Arachidic acid, ~0.5**


OLEOCHEMICAL BIOREFINERY FROM TRADITIONAL OILS AND FATS
splitting
Glycerol
Esterification
Partial
Triacetin
Fatty acids
Esterification
Fatty acids esters
Epoxidation
Alky epoxy esters
Ethoxylation
Fatty acid ethoxylates
Conjugation
Conjugated fatty acid
Hardening
Saturated fatty acid
Fatty acids Methyl esters
Esterification
Transesterification
Hydrogenation
Fatty alcohols
Guerbet reaction
Guerbet alcohols
Chlorination
Alkyl chlorides
Ethoxylation
Fatty alcohols ethoxylates
Sulfation
Fatty alcohols sulfates
Esterification
Esters
Sulfonation
α- Sulfo fatty acid esters
Amidation
Fatty acid alkanolamides
Epoxidation
Epoxided triglycerides
Ethoxylation
Ethoxylated triglycerides
Hydrogenation
Hydrogenated castor oil
Sulfation
Turkey red oil
Propoxylation
Fatty elkoxylates
Sulfation
Fatty alcohols ether sulfates
Phosphati-zation
Fatty alcohols ether phosphates
Sulfitation
Fatty alcohols ether sulfosuccinates
Castor Oil Provides Many More Derivatives as it Contains Hydroxy Functionality Also…

BIOREFINERY OF CASTOR OIL

CASTOR OIL
(Triricinolein)



NATURE OF REACTION	REACTANTS	TYPE OF PRODUCTS
HYDROLYSIS	ACID, ENZYME, CAT.	FATTY ACID, GLYCEROL
ESTERIFICATION	ALCOHOLS	ESTERS
ALCOHOLYSIS	GLYCEROL, GLYCOL POLYOLS, etc	PARTIAL ESTERS
SAPONIFICATION	ALKALI	SOLUBLE/INSOLUBLE SOAPS
HYDROGENOLYSIS	HYDROGEN, CAT.	ALCOHOLS
AMIDATION	ALKYL AMINES	AMINE SALTS, AMIDES
HALOGENATION	$SOCl_2$	ACID CHLORIDES
OXIDATION	HEAT, O_2, CROSS-LINKING AGENT	POLYMERIZED OILS
HYDROGENATION	HYDROGEN, CAT	HYDROXYSTEARATES
EPOXIDATION	HYDR. PEROXIDE	EPOXIDIZED OIL
HALOGENATION	HALOGEN	HALOGENATED OILS
SULFONATION	SULFURIC ACID	SULFONATED OILS
ADDITION REACTIONS	S, MALEIC ACID	POLYMERIZED OILS
DEHYDRATION	HEAT, CATALYST	DCO, DCO-FA
CAUSTIC FUSION	HEAT, ALKALI	SEBACIC ACID/2-OCTANOL
PYROLYSIS	HIGH HEAT	UNDECENOIC ACID/HEPTALDEHYDE
HALOGENATION	PCl_5, $POCl_3$	HALOGENATED CASTOR OIL
ALKOXYLATION	EO, PO	ALKOXYLATED OILS
ESTERIFICATION	ACETIC, PHOSPHORIC, ANHYDRIDES	ALKYL, ALKYLARYL PHOSPHATE ESTERS
SULFATION	SULFURIC ACID	TURKEY RED OIL
URETHANE REACTION	ISOCYANATES	URETHANE POLYMERS

DIRECT APPLICATIONS OF CASTOR OIL

- Illuminant
- Cathartic agent
- Lubricants
- Cosmetic formulations as emollient, carbon black (kajal)
- Creams and jellies
- Vehicle for parenteral administration of steroidal harmones etc.,
- Hair tonic
- Preservative in food grains and pulses
- Many more…

SIMPLE DERIVATIVES OF CASTOR OIL

- Castor oil fatty acids
- Methyl ricinoleate
- Hydrogenated castor oil (HCO)
- Ethoxylated castor oil
- Turkey red oil
- 12-Hdyroxy stearic acid (HSA)
- Methyl 12-HSA
- Dehydrated castor oil (DCO)
- DCO fatty acids.

ADVANCED DERIVATIVES OF CASTOR OIL

- Alkyd resins
- Fatty amides
- Undecenoic acid, heptaldehyde,
- Heptanoic acid, heptanol,
- Sebacic acid, 2-octanol,
- Sebacic acid esters,
- Castor oil-based polyols

- Historically, many of the products and technologies from castor oil were developed outside the country
- Very little open information about the Niche Products of castor oil being produced outside the country…

AREAS OF APPLICATIONS OF SELECTED DERIVATIVES OF CASTOR OIL

DERIVATIVE	AREAS OF APPLICATIONS
Alkyl esters	Cosmetics, plasticizers, lubricants
Hydrogenated castor oil	Lubricants, greases and additive in variety of formulations
Dehydrated castor oil and its acids	Coatings, inks, sealants and related products
Ethoxylated castor oil	Surfactants, emulsifiers, lubricants in textile, coatings and cosmetics
Sulfonated (sulfated) castor oil (Turkey Red Oil)	Surfactants, lubricants
Polyurethane encapsulants	Encapsulants for Electronics and telecommunications, coatings
Oxidized/polymerized castor oil	Coatings, inks, sealants
Sebacic acid	Component of Nylon 6,10; esters as aircraft lubricants and plasticizers for vinyl films including food wrap
Nylon 11 from undecenoic acid	Engineering plastic (the largest single use of the castor oil

Applications Range from the Glamorous Uses to Areas of National Security Involving Engineering Plastics, Aviation Lubricants, Polymers for Electronics & Telecommunications

CASTOR OIL DERIVATIVES

POTENTIAL DERIVATIVES AND AREAS OF RESEARCH

February 24, 2018

Castor Oil – Extra-ordinary Feedstock for Variety of Products

- **C_7 Compounds – Aldehyde / acid / alcohol**
- **Estolide & Undecenoic acid-based derivatives**
- **Variety of Hydroxy fatty alcohols, Polyols, Dicarboxylic acids and Triacylglycerols with terminal carboxylic acid in the alkyl chain, Cyclic Acetals, Hydroxy Aziridines, Fatty Aminodiols and their derivatives as organic intermediates**
- **Castor oil biodiesel – Attractive as an additive to diesel (less than 1%) to increase the lubricity**
- **Quaternary ammonium salts (fabric softener)**
- **Different alkanolamides of RA**
- **Furanoids, γ-Decalactone**
- **Betaines, Imadazolines (amphoteric surfactants)**
- **Cetyl Myristoleate with *cis*-9 myristoleic acid (natural source) exhibits anti-arthritis and anti-inflammatory properties – IICT synthesized *cis*-10 myristoleic acid from undecenoic acid and prepared cetyl *cis*-10-myristoleate with the same activity**
- **Selected Potential Areas Presented in the following Slides…**

ENRICHMENT OF RICINOLEIC ACID FROM CASTOR OIL FATTY ACIDS

- **Castor oil contains 87-90% Ricinoleic Acid**

- **Enrichment of 'RA' to higher concentrations helps in achieving clean reactions with minimum % of other fatty acids**

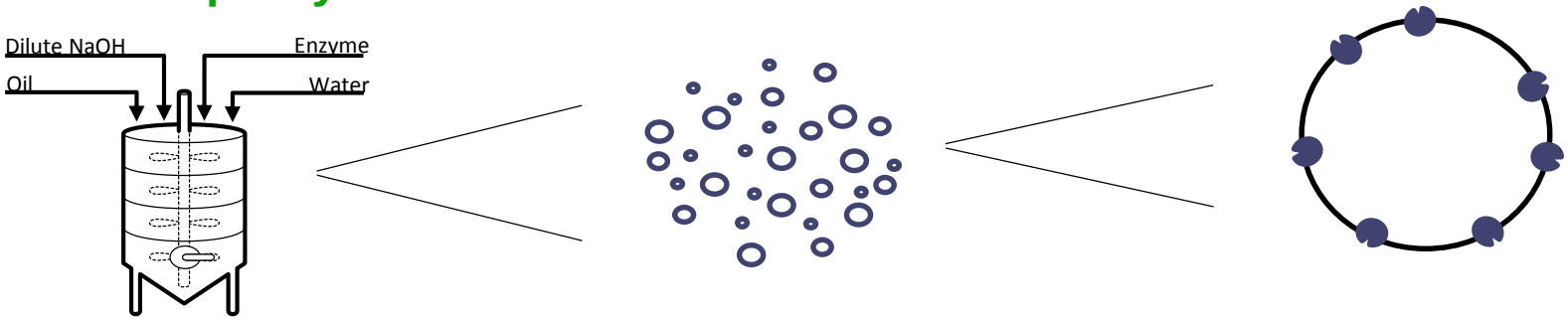
- **Processes for the Products like Alkylricinoleates, Undecenoic acid, Sebacic acid etc., will have several advantages with high purity of RA**

- **CSIR-IICT developed a lab scale process in this direction and achieved upto 97-98% purity of ricinoleic acid (without distillation) – Industry may exploit this by networking with IICT for commercial exploitation**

- **High purity RA may change the scenario of the present approaches for value addition**

ENZYMATIC APPROACH FOR RICINOLEIC ACID PRODUCTION

Disadvantages of Traditional Fat Splitting of Castor Oil: High energy consumption, High effluent costs, High CAPEX, Corrosion of equipment, Product quality issues from side-reactions like Estolide formation



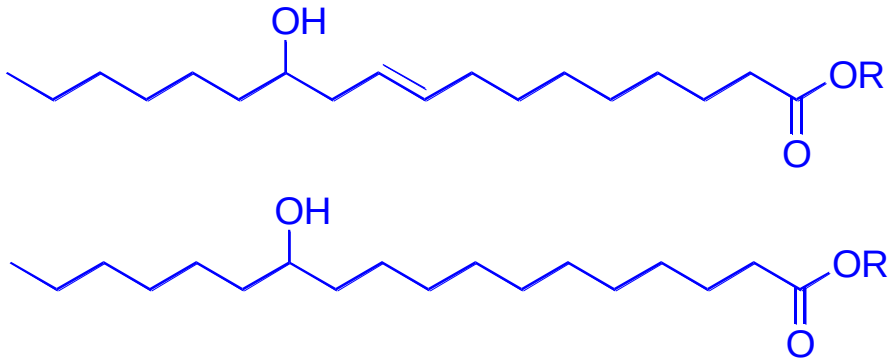
ADVANTAGES OF ENZYMATIC APPROACH

- **NOVOZYMES developed an attractive Lipase for the fat splitting**
- **Novozymes Lipase operates at ambient temperature and pressure, Low energy consumption, Low CAPEX**
- **pH range 4-10, Initial conditioning by $NaOH$ addition, 5-100 ppm**
- **Mixing is important to create and sustain an emulsion,**
- **Lipase is highly amphiphilic and will be positioned at the oil/water interface**
- **Significant reduction of side-reactions, Higher yields, Acceptable cost of liquid formulated enzymes, Low environmental impact**

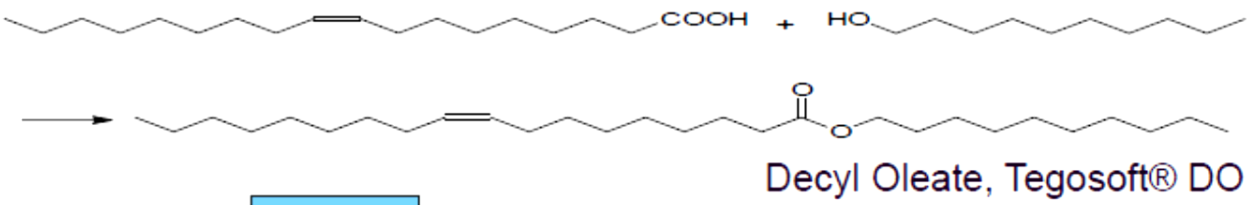
CHALLENGES: Thermostability, pH dependency, Conversion and reaction time, Separation performance

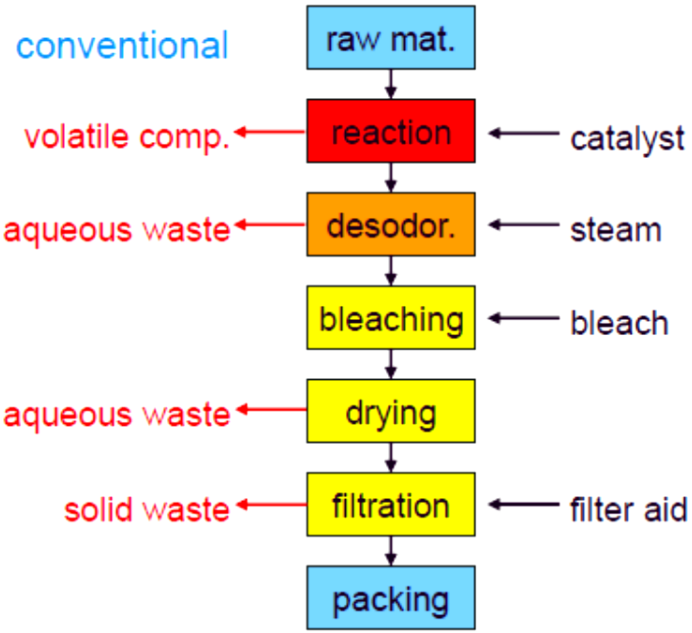
ALKYL RICINOLEATES & ALKYL 12-HYDROXY STEARATES

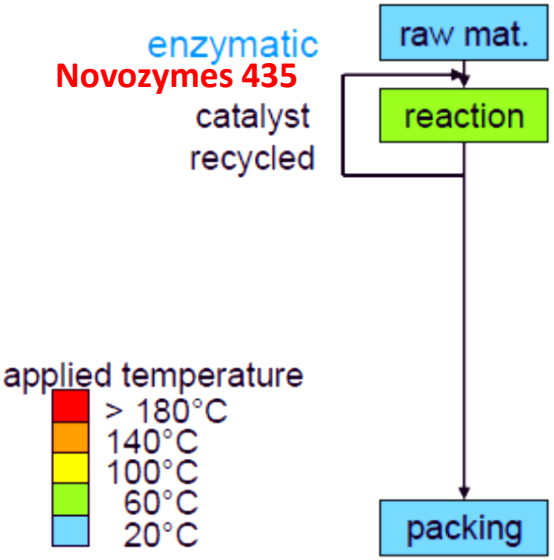
- **Hydroxy fatty acids and their derivatives are used in cosmetics, paints and coatings, lubricants and the food industry**
- **Useful chemical intermediates in the synthesis of fine chemicals and pharmaceuticals, particularly when they are optically pure**
- **Non-comedogenic esters – Imparts mildness, Soft Emolliency, Oxidation Stability, Dye carrying capacity**
- **Preparation without formation of estolides using enzymatic method**



Conventional *vs* Enzymatic Production of Alkyl Esters



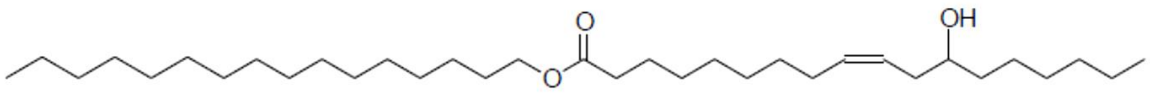




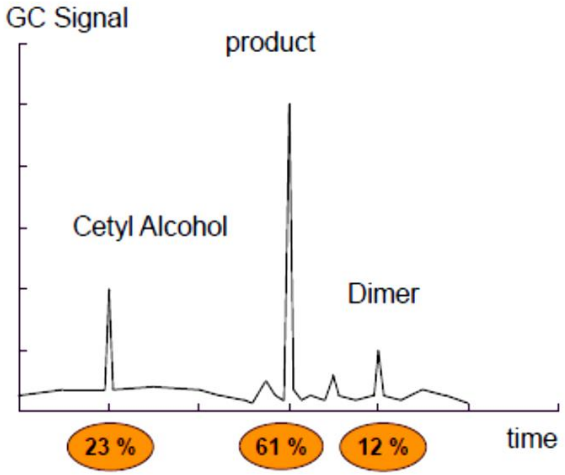
Any type of Alkyl Ricinoleates can be prepared using Novozymes 435

Improved Quality with Enzymatic Process

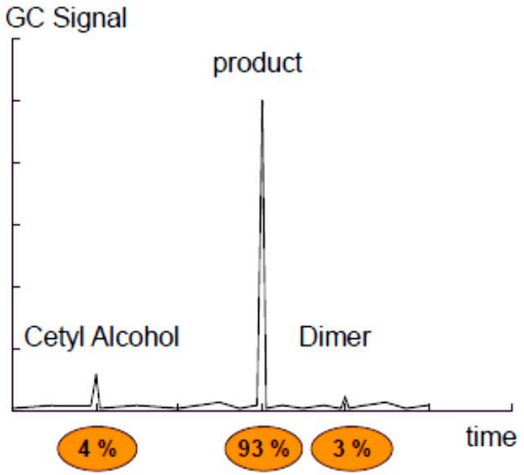
Cetyl Ricinoleate, a cosmetic wax (TEGOSOFT® CR)



Conventional Product



Enzymatically produced TEGOSOFT® CR

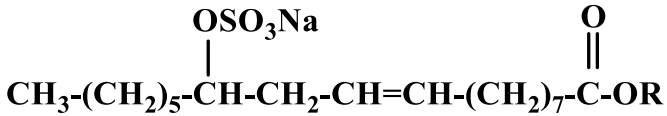


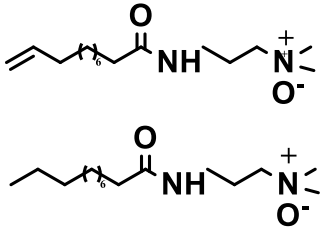
Enzymatic Process using Novozymes 435

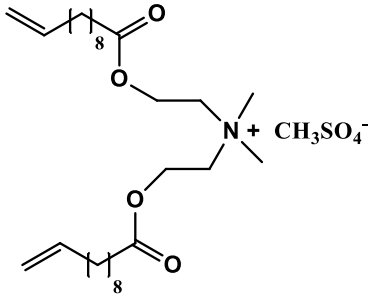
CASTOR OIL AS A FEEDSTOCK FOR LUBRICANTS AND GREASES

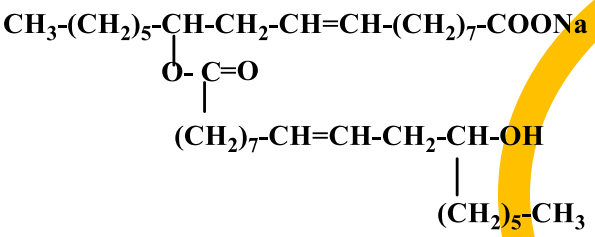
- Non-toxic renewable source, High biodegradability
- High viscosity index, slight change of viscosity with temp
- High lubricity, reduces friction as compared to petroleum lubes
- FDA approved lubricant for machinery for hard candy and tablets (drugs)
- Potential castor oil-based derivatives for lubricant industry: Recinoleic acid, Castor oil esters, Blown castor oil, Dimer acid, Heptanoic acid, Metallic salts, Sebacic acid, Polyol esters, Estolides as starting material for emulsifiers, pigment dispersants, 12-Hydroxy stearic acid and its methyl ester
- HCO Ethoxylates – antistatic modification of synthetic fibres
- HCO & 12-HSA Lithium soaps as outstanding thickeners in greases for automotive, industrial and marine applications with Good water resistance, Excellent structural and shear stability having Largest market share among soap-based greases
- Li salts of 12-HSA and dicarboxylic acids (e.g., sebacic acid) as thickeners for aviation and speed travel

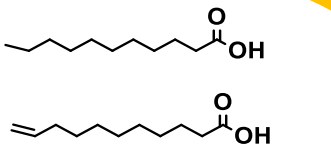
CASTOR OIL-BASED SURFACTANTS

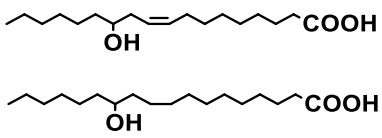


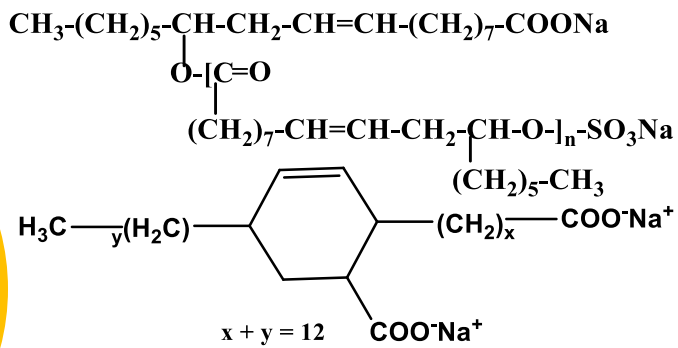


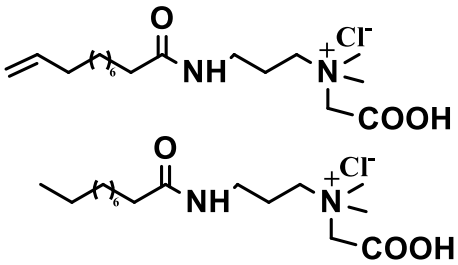


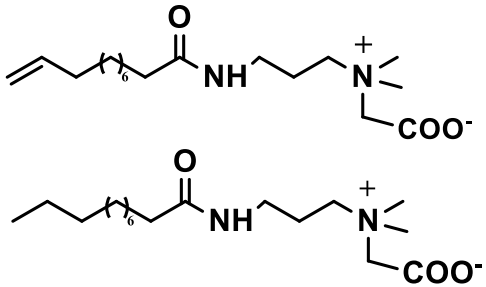


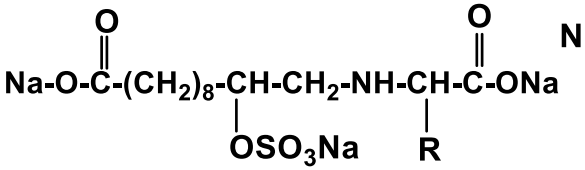


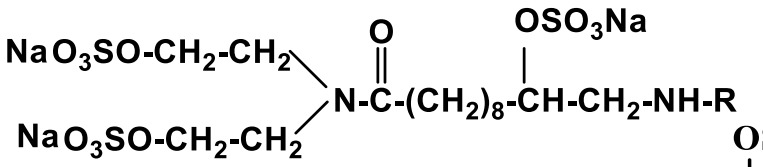


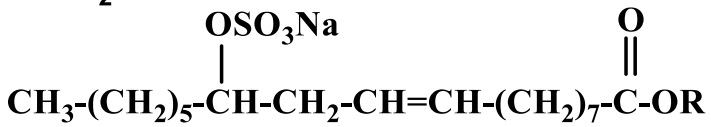








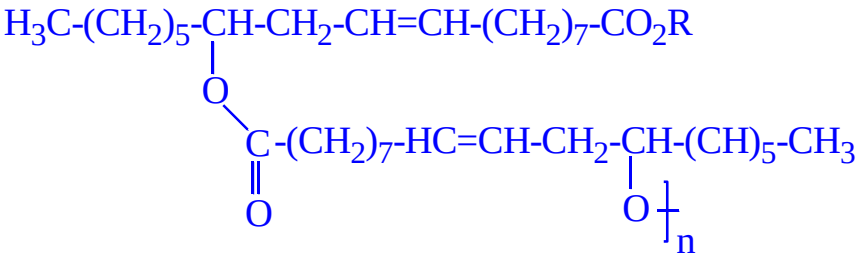




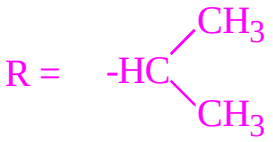
- More than 50 Cationic and Anionic Surfactants based on castor oil derivatives were Prepared by CSIR-IICT With good foam and extraordinary calcium tolerance properties

ESTOLIDE … POTENTIAL MOLECULE

- **Unique oligomeric fatty acids that contain a secondary ester linkage on the backbone of one of the fatty acid chains**
- **Exhibits high viscosity indices, good oxidative stability and biodegradability.**
- **Variety of potential applications as lubricants, greases, plastics, inks, cosmetics and surfactants.**
- **Prepared from homopolymerization of hydroxy fatty acids or unsaturated fatty acids**



R = H (Polyricinoleic acid)
R = Me (Methyl polyricinoleate)

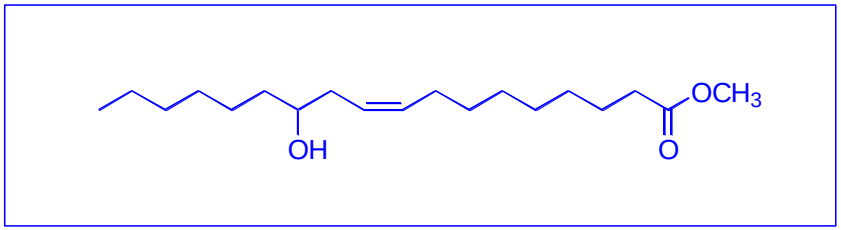


(Isopropyl polyricinoleate)

R = $-H_2C-CH_2-CH_2-CH_3$ (n - Butyl polyricinoleate)

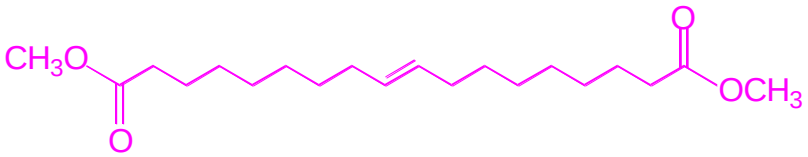
(2-Ethyl 1-hexyl polyricinoleate)

METATHESIS FOR SPECIALTY PRODUCTS FROM CASTOR OIL



Methyl-12-hydroxy-9-octadecenoate

Self metathesis

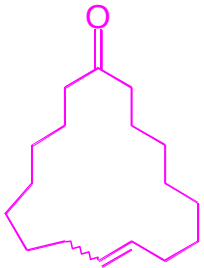


Dimethyl 9-octadecene-1,8-dioate

+

9-Octadecene-7,12-diol
(Useful Intermediate in preparation of synthetic rubbers, surfactants, fragrances and polyurethanes)

i) Dieckmann condensation
ii) Hydrolysis / decarboxylation



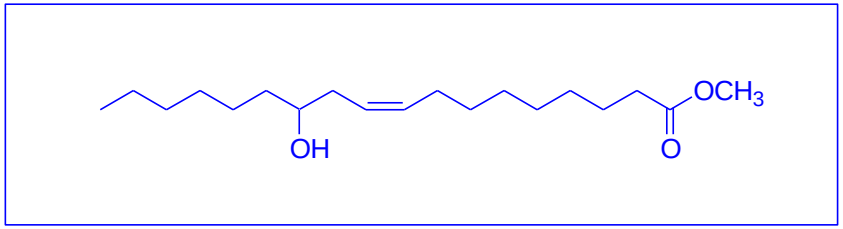
Civetone
(Attractive Intermediate in Musk perfumes)

As of Now, Metathesis requires Expensive Catalysts, but it is an Extra-ordinary Area for Preparing Niche Products

…METATHESIS

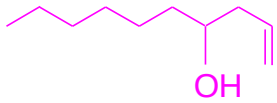
Higher unsaturated diesters; different -OH substituted higher alkenes

Cross Metathesis with higher olefins (undecenoic acid, oleic, erucic, etc.)



Methyl-12-hydroxy-9-octadecenoate

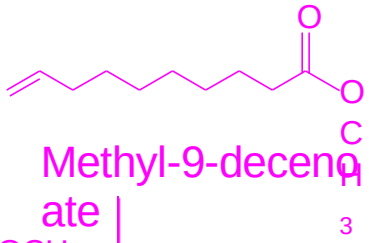
Cross Metathesis with ethylene



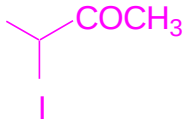
1-decene-4-ol

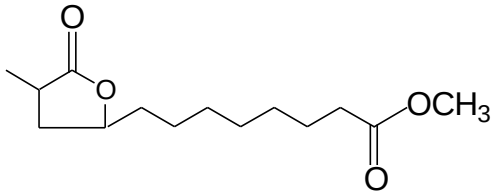
(Allylic alcohol, useful intermediates in preparation of synthetic surfactants, polyurethanes)

+



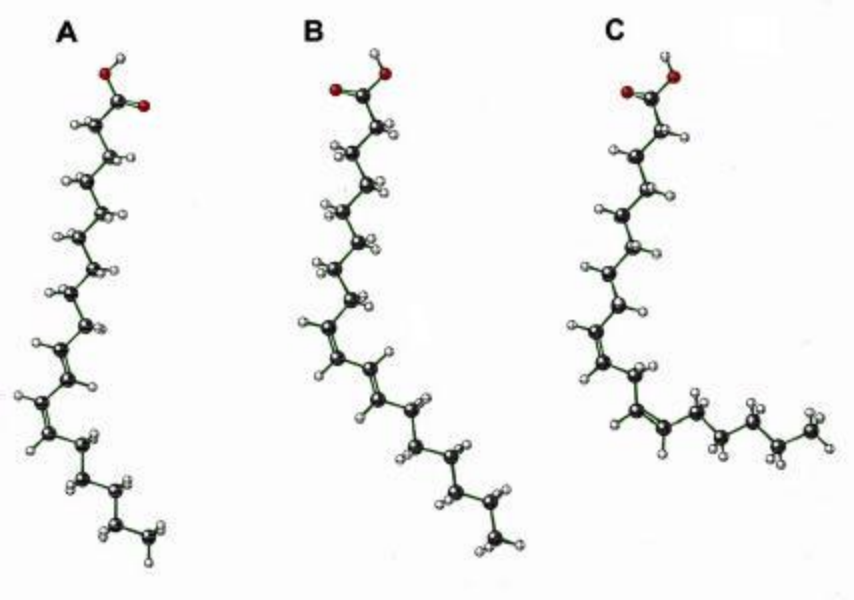
Methyl-9-decenoate





CONJUGATED LINOLEIC ACID (CLA)

Anti carcinogen,
Reduces body fats and
Several health benefits



A. ***trans*-10, *cis*-12 CLA (A), *cis*-9**
B. ***Cis-9, trans*-11 CLA (B) and**
C. ***cis*-9, *cis*-12 octadecadienoic acid (linoleic acid)**

Castor Oil is a good raw material for the preparation of CLA by alkaline isomerization using heterogeneous catalyst

CASTOR BIOREFINERY

CASTOR PLANT

Eri Silk
Eri Pupal Protein
Eri Pupal Oil
(Omega 3- fatty acid rich)

Cake

Protein, Starch, Oil

Surfactants, Lubricants Fertilizer etc.,

Fatty Acid Alkyl Esters

Crude Glycerol

Variety of Value-added Products

Biodiesel, Lubricants, Additives etc.,

Different Grades of Glycerol

Variety of Value-added Products

February 24, 2018

Eri Pupal Oil

PROPERTY	CASTOR FED PUPAL OIL
Oil content (%)	18-20
Free fatty acid (%)	0.75
Peroxide value (ppm)	2.1-2.6
Unsap matter (%)	2.0

FATTY ACID	CASTOR FED PUPAL OIL	MULBERRY FED PUPAL OIL
14:0	0.5	0.2
16:0	29.6	25.2
16:1	1.6	0.6
18:0	3.3	9.7
18:1	15.0	26.2
18:2	5.7	4.9
18:3 (n-6)	0.3	-
18:3 (n-3)	43.3	33.1
20:1	0.1	-

CASTOR OIL BIOREFINERY

- **Castor oil is a nature's gift to Indian soil – It is the only oil containing about 90% of hydroxy fatty acid**

- **Several global research Institutes looking at castor oil as an alternative source to replace petroleum based organic chemicals**

- **More than 77,000 Research Papers Published in the Global Literature based on Castor Seed and Oils**

- **Extra-ordinary timing for India to coin the concept of castor oil biorefinery for the preparation of traditional and novel derivatives in several areas of applications like soaps, detergents, cosmetics, paints, textiles, lubricants, dyes, coatings, plastics, pharmaceuticals, perfumes etc.,**

DSIR'S INITIATIVE IN 2008

- **Department of Scientific Industrial Research, Govt. of India sponsored a project to GITCO for preparing a "Comprehensive Status Study on Castor oil and its Derivatives in India"**

- **GITCO report stated the following reasons for the slow growth of castor derivatives in the country**

- ✓ **Fluctuation in price of castor oil**
- ✓ **Advanced derivatives of castor oil requires more investment**
- ✓ **Lack of organized & updated data on domestic & international market**
- ✓ **No Proven & Cost Effective Technologies**
- ✓ **No authentic data on export & import data of castor oil derivatives**
- ✓ **A dedicated research institute is required for castor oil research**

CASTOR OIL… GOLD MINE FOR WHOM?

- India is the world leader in castor seed & oil production and also major exporter of castor oil
- Global castor derivatives markets – Highly dependent on India
- Why India could not exploit the situation?
- Indian Industry needs an innovative action plan in collaboration with R & D Institutes
- Let us learn from the Business Models of US for soybean oil and Malaysia for Palm oil…
- Castor oil is a small volume TECHNICAL COMMODITY Compared to other oils and India must exploit this scenario…
- Indian R&D and Industry must take up innovative research projects to Convert Castor Oil into an Indian Gold Mine…

GROWTH OPPORTUNITIES FOR CASTOR OIL IN INDIA…

- Castor Biorefinery Concept for Exploiting Castor Oil…
- How the Imported Countries are exploiting castor oil for value addition?
- Development of New products with Niche applications
- Industry must look for Proprietary Products & Proprietary Technologies
- Strong R&D is Required to compete Globally… Must strengthen In-house R & D of Industry or R & D Institution – Industry tie-ups
- To Establish market leadership as a Consortium of Industry within the country

CASTOR OIL DERIVATIVES…. WAY FORWARD…

- Grass Root Survey of the Demand & Forecast of the Derivative Market & Prioritization (Industry)
- To Develop New Derivatives for Traditional Products of Castor Oil: Collaborative Research (Industry & R&D Institutes)
- Cutting Edge Research for Development of Castor Oil Derivatives in the Area of Bioplastics, Biolubricants, Biogreases etc., (Industry & R&D Institutes)
- Special Status to be Given for Castor Oil Derivatives and its Research (Govt)
- To Initiate a Mission-mode Programme like Technology Mission on Oilseeds & Pulses (Govt)
- To Provide High Incentives for the Export of Castor Oil Derivatives compared to Castor Oil (Govt.)

- **Indian Industry needs an innovative action plan in collaboration with R & D Institutes like CSIR-IICT having Intellectual Strengths and Modern Processing and Analytical Equipment Facilities**

- **In the present scenario R&D Institutes can not take up research without industry support – Industry must exploit the Intellectual capability of Indian Scientists & Make use of available Infrastructure at the Research Institutes**

- **SEA must take lead role to form a meaningful consortium and project castor oil as an Indian oil with an innovative action plan**

- **SEA in collaboration with industry must conduct a "Technical Survey" on Castor oil value addition in the similar lines what it is being done for "Castor Crop Survey"**

- **We must gear up with all our resources and expertise together for technology developments for improved realization and value addition to castor oil**

THANK YOU…