



The world is our inspiration



Journées CHEVREUL 2009

TROPICAL LIPIDS

Production, Applications and Socio-Economy

Example of Industrial Valorisation
of derivative products of Castor Oil

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Paris, Tuesday 7th april 2009





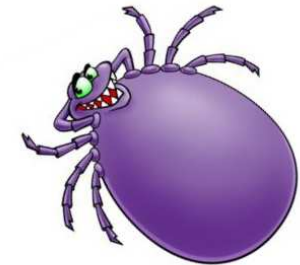
Castor Oil ... an environmental friendly resource



Nature owes a lot to Castor Oil ... starting with beavers. Indeed, very long-time hunted for their fur and *Castoreum* exploitation, they owe their survival to the replacement of *Castoreum* by Castor Oil for its medicinal "virtues" and many applications in perfumery.

From the latin word *castor*, Castor Oil keeps only the name in memory of its applications, but it has absolutely nothing in common chemically.

Regarding the name *ricinus*, it is in reference to the resemblance between Castor Beans and ticks that the Swedish naturalist Carolus Linnaeus was giving scientific name to *ricinus communis* plants over 200 years ago.



Despite all these links with the animal world, Castor Oil is a product of plant origin.



Castor Beans Plant grows everywhere in all conditions

Castor Beans Plants are mainly cultivated in sub-tropical regions (India, Brazil, China). But it grows also under temperate climate ... even under our latitudes as shown on these pictures taken in Metz and Concarneau ...

Castor Beans Plant fructifies all along the year and is drought resistant.



It can be grown on poor land, does not damage local food crops or contribute to deforestation.

To ensure only ripe seeds collection harvesting is done manually so mechanization is very limited.



Castor Oil ... as versatile as a Swiss Army Knife

Known since antiquity, Castor Oil has been used as medicine (purgative / laxative). Now, it remains present in small quantities as excipient in many **pharmaceutical** specialties.

In **cosmetics**, it is used as base of beauty oils, shampoo or hair masks and also as a plasticizer in nail polish, lipsticks, creams and lotions, or as colour fixative.

Industrial applications : Castor Oil has excellent performances as lubricant for engines operating at very high speed.

It is used in the **chemical industry** in the polyurethane sector for the manufacture of lacquers, varnishes, polishes and wax substitutes.

Castor Oil also finds applications under a **dehydrated** (DCO), **hydrogenated** (HCO) or **sulphated** (Turkey Red Oil) form.

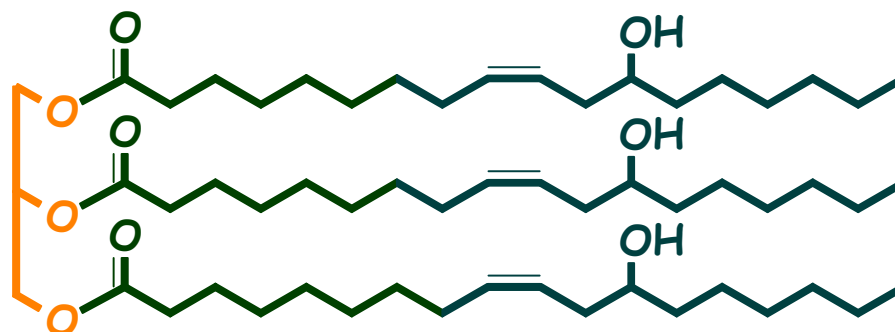




Castor oil ... chemically unique

Castor Oil is the only vegetal oil containing an **hydroxyl group** in the triglyceride structure.

TRIGLYCERIDE



Castor Beans seeds contains 40 to 60 % of oil wich is made of 80 to 85 % of ricinoleic acid.

This such particular structure is the key to explain the result of this equation :

$$18 = 11 + 7 \text{ or } 10 + 8 \dots$$

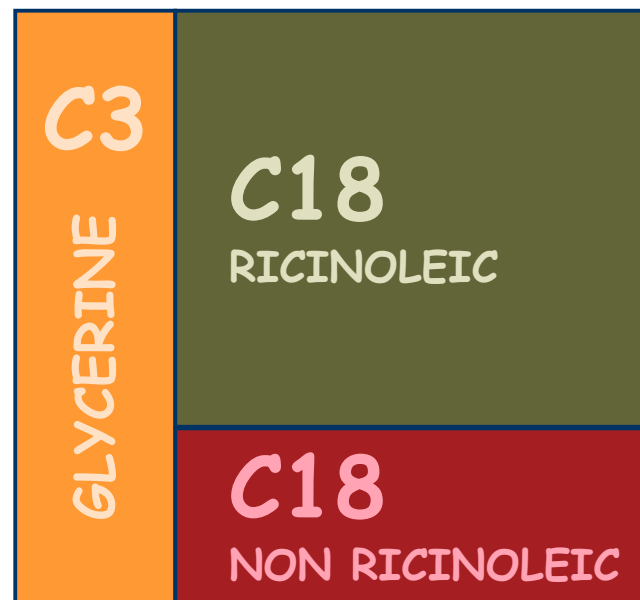


When 18 equals to 11 + 7 ...

The behaviour of Castor Oil when heated to high temperature has intrigued chemists since 1845. Since that time Castor Oil chemistry has evolved significantly. The process in use at the Arkema Marseilles plant is in fact unique in the world. Castor Oil is a biodegradable and renewable resource for a large range of raw materials.



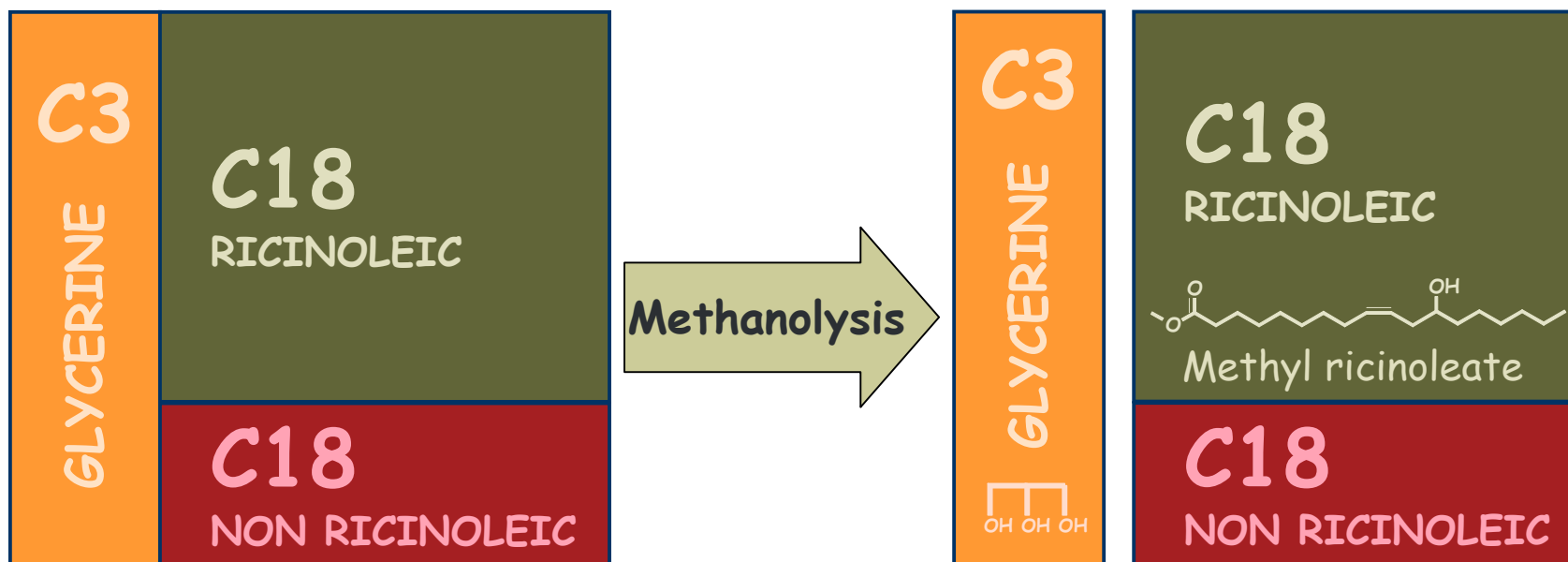
Castor Oil



Mixture of Fatty acids
triglycerides



When 18 equals to 11 + 7 ...





When 18 equals to 11 + 7 ...

Valorisation of glycerine :

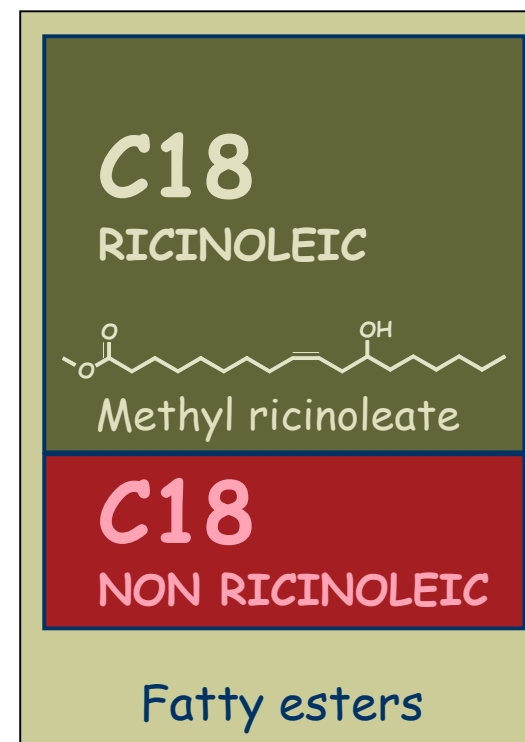
- wetting and lubricating agent in handcreams, suntan lotions and soaps hair care.



- anti-freezing,
- bio-resourced compounds such as acrolein, propylene glycol ...

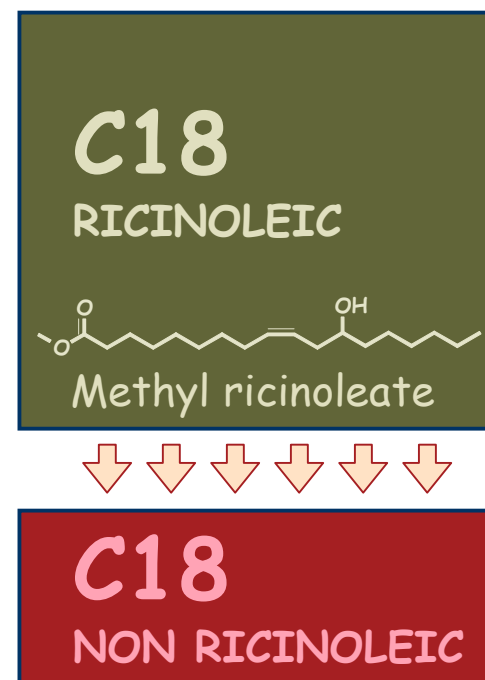
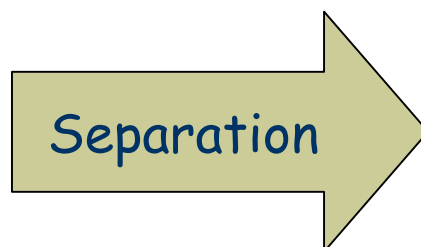
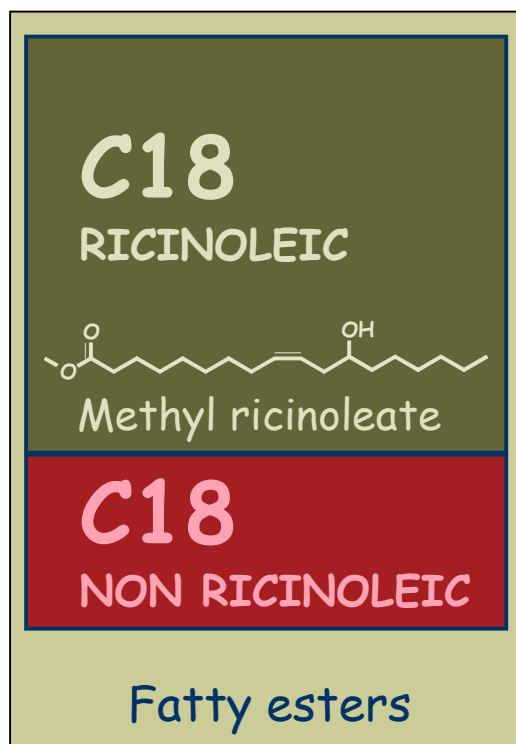


Decantation





When 18 equals to 11 + 7 ...





When 18 equals to 11 + 7 ...

Steam Cracking (pyrolysis at elevated temperature) cleaves ricinoleic acid ester into two parts: one part consisting of **7 carbon atoms** and the other of **11 carbon atoms**. The Marseilles process equation is $C18 = C11 + C7$.

A whole range of innovative chemistries and end use products are generated from these base reaction products. These products are used in every-day life, to improve our comfort and safety.



Steam Cracking





C7 derivatives

... from perfumes to technical products

The C7 molecule has seven aligned carbon atoms and is known for the **olfactory qualities** of certain of its derivatives. In its natural state, it is present in wine as oenanthol.



The low freezing point of this chain makes it well suited for **lubricant applications**.



Aldehyde, alcohol and acid are the three main chemical derivatives of C7.



Main characteristics :

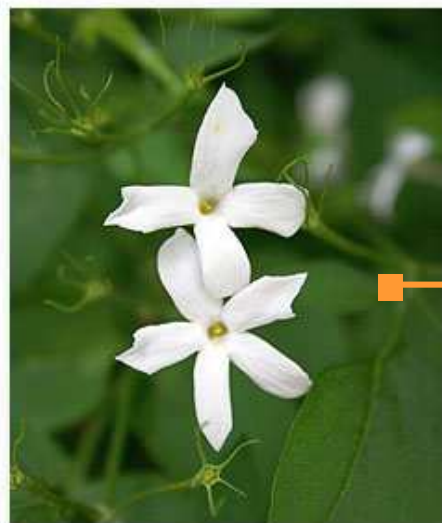
- 100% linearity (compared to synthetic route)
- high purity
- 100% bio-based raw material



Applications of heptanal

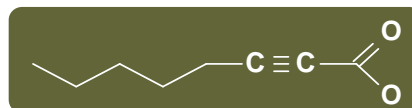


Synthesis intermediate for the fragrance and aroma industry.

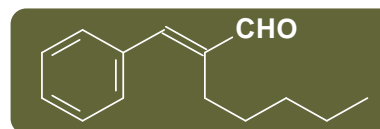


An perfume aromas related to C7 aldehyde is **JASMINE**. This aroma is detectable in many washing powders, soaps, candies and other jasmine perfumed products.

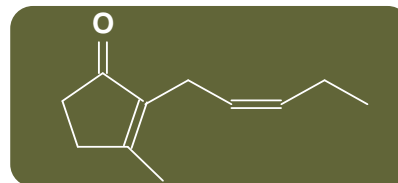
- natural odor : fresh, green, like vegetable
- methyl-heptyne carboxylate : green and floral note



- ACA : α n-aryl cinnamic aldehyde : synthetic jasmine



- Jasmonoids





Applications of heptanol



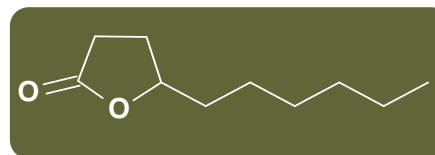
Synthesis intermediate in the fragrance and aroma industry (with fruit taste)

Trace quantities are used in perfumes to provide a peach-apricot aroma.



- γ -decalactone :

coconut, vanilla flavour (dairy products, beverage)



- Esters with fruit notes (heptyl butyrate, octanoate ...)



Synthesis intermediate for plasticizers for polymers.





Applications of heptanoic acid



The diversity of applications of this acid is surprising :

- Valorised in the form of esters as civil **lubricant** for military aircraft jet engines, car engines and refrigerant.



→ compared to C6/C8/C10 analogues

- better compromise in terms of low viscosity at low temperature and low volatility at high temperature,
- very low color 100% linear saturated acid,
- lower pour point,
- higher viscosity index.

- High efficiency of C7 salts as **corrosion inhibitor** (water based hydraulic fluids for automotive, additives in paints, cutting oils, metalworking fluids).





Applications of heptanoic acid



- Chemical intermediates for **Pharmaceuticals and cosmetics**
 - emollient agent / surfactant in personal care (propylene glycol diheptanoate, stearyl heptanoate ...) and in pharmaceutical gel (neopentylglycol diheptanoate)



- Chemical intermediates for **aromas and perfumes**.



- natural, green grassy and fruity ester like odour in banana flavours and in coffee, dairy products, passion fruit ...



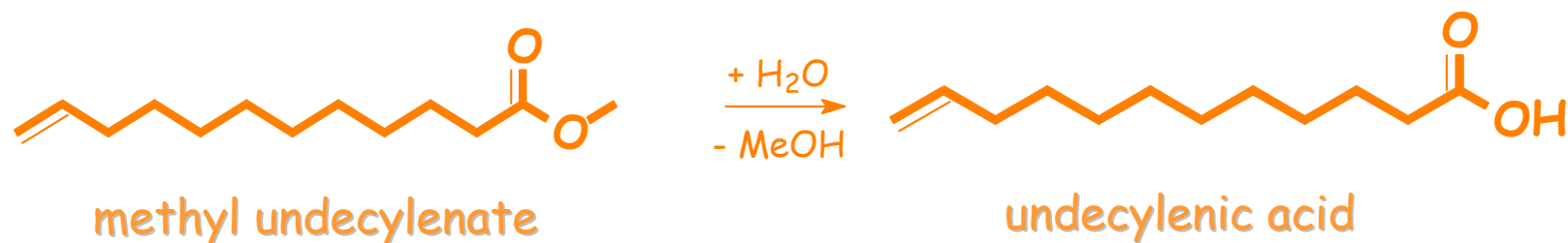
- Synthesis intermediate for **plasticizers** for polymers.
- Improves the properties of **herbicides**.



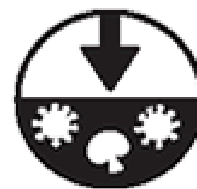
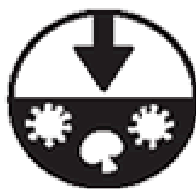
C11 derivatives

Derivatives of methyl undecylenate have the rare property of being both **long** and **bi functional**.

They are versatile molecules for chemical synthesis.



Both are used for their natural **bioactivity** and **fungi resistance**.





C11 derivatives from pharmaceuticals ...



Bioactivity and fungi resistance.

- In nature, trace quantities of C11 acid are found in sweat, tears and hair fats. Under salt form (Zn/Ca), it is used in **pharmaceuticals** for human skincare preparations.

- ie :
- treatment of *athletes' foot*
 - effective against denture stomatitis
 - herpes ...

→ combining surfactant as well as natural bioresistance properties



- Bacteriostatic action in **baby diapers**.

One of the safest, ecological, most economical and highly effective natural bacteriostatic and antifungal agents



C11 derivatives

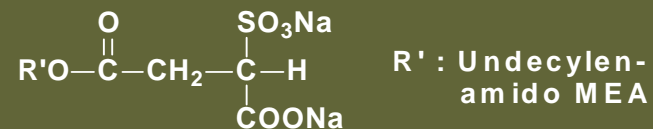
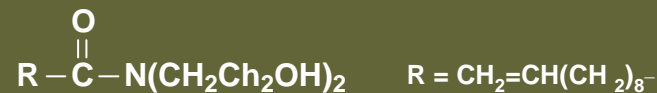
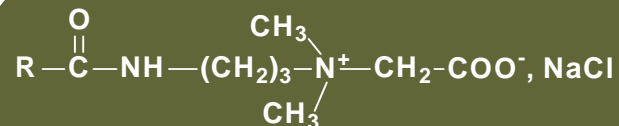
... Cosmetics - Personal Care ...



- Hair care / anti-dandruff shampoos
- Deodorant
- Beauty creams
- (antiseptic) Soaps
- Bacteriostatic emulsifier for cosmetics

→ as surfactants, like

- **Betain C11 = Amphoram U (CECA)**
undecylenamido propyl betaine
- **undecylenic acid diethanolamid**
- **disodium undecylenamido MEA-sulfosuccinate**



... safe and natural bacteriostatic agent compared to chemical biocides (imidazoles, tolnaftates) used in cosmetics.



C11 derivatives

... to Perfumes

- Undecylenic Acid (fruity-rosy note)
- Methyl Undecylenate (heavy citrus note) for lilac based perfumes and anti-odors.
- Chemical intermediates for perfumes.
 - Undecenal for rose or jasmine based formulations, key component for quality perfumes (fixing agent) and quality enhancer for large volume products.
 - Undecenol (citrus, floral note), volume / natural freshness to floral compositions, effect increasing, especially in soap formulations.
 - Macrocyclic musks
 - ie : Cyclopentadecanolid (Exaltolide, Pentalide, Thibetolide)





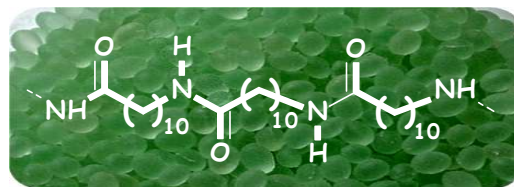
Polymers from Amino-undecanoic acid

In the middle of the 30's, the French chemists succeeded to synthesize a monomer from undecylenic acid :

11-amino-undecanoic acid



As early as 1947, they created a new polymer from renewable sources : "PA11" polyamide, as it is known to chemists, sold under the name of Rilsan®.

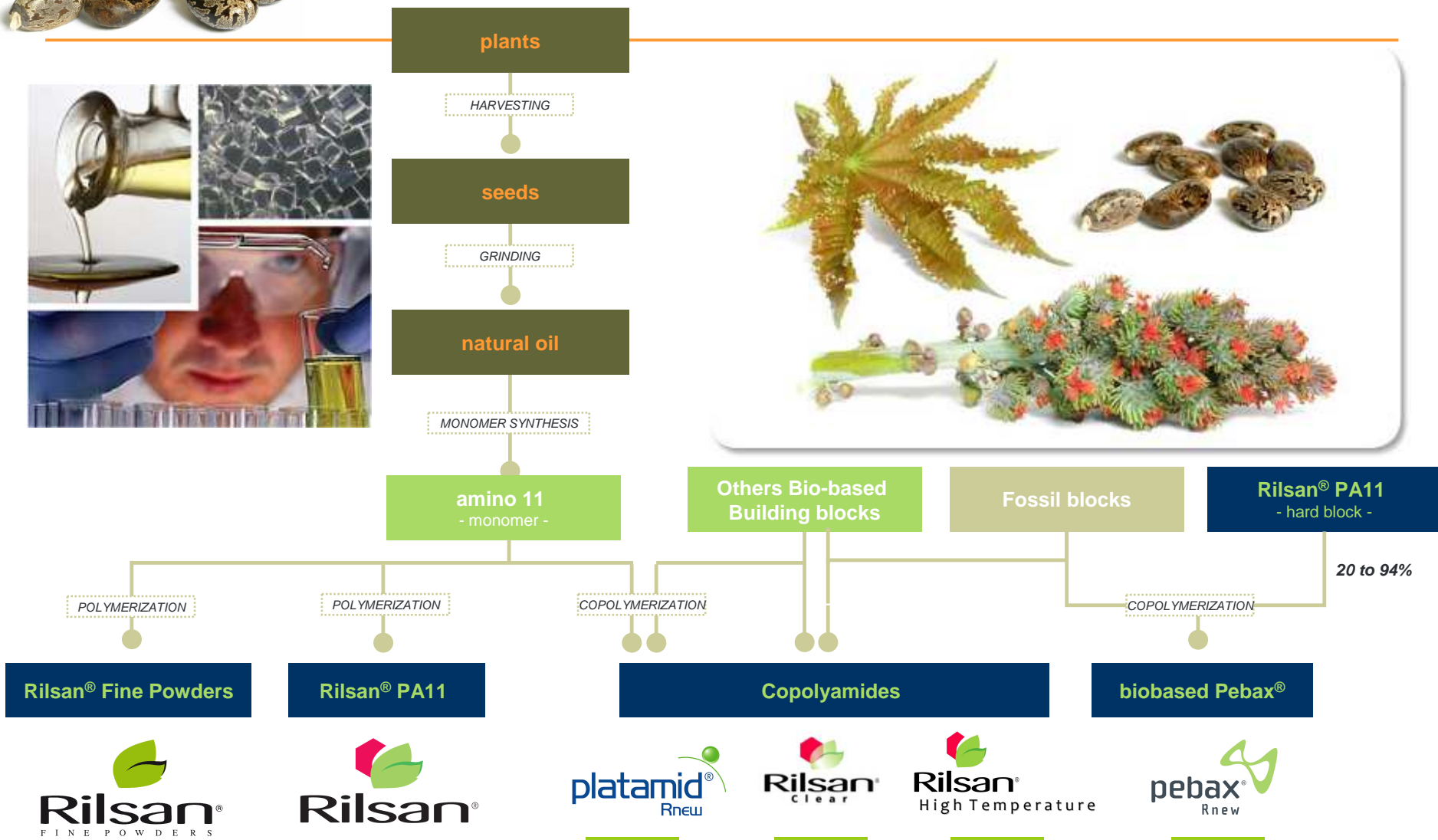


By coupling 11-amino-undecanoic acid with other monomers, ARKEMA is developing a whole range of biobased polymers : **Rnew®**.

Different polymers, but one aim :

high performance and sustainability !

A "Building Block" strategy



1948



2007

2008

2009

2008





Rilsan® Polyamide 11



The only **High Performance** polymer **100%** based on renewable resources

 **Impact Resistance**
Toughness



 **Lightness**

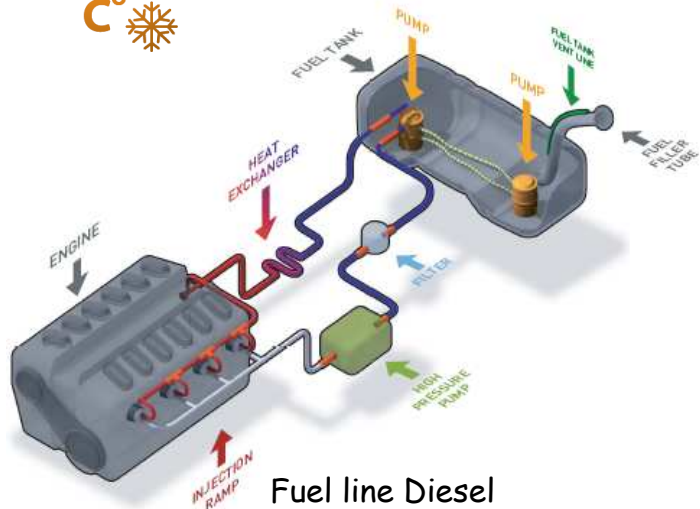


 **Processability**



Biomass Based
(issued by JORA)

 **Heat resistance**



 **Chemical resistance**



2006
Bioplastics
Awards
Winner


ARKEMA
The world is our inspiration



Pebax® Rnew Polyether Block Amide



First engineering thermoplastic Elastomer range made from Renewable resources

20 to 94% of renewable carbon resources

 Mechanical



 Flexibility



 Weather Resistance



 Selective Molecule Diffusion

 Touch Feeling



 Lightness



 Antistatic





No waste, everything is valorised !!!

C18

NON RICINOLEIC

Esterol A is made up of saturated and unsaturated natural fatty acid methylic esters like stearic, oleic or linoleic acid.

Esterol A is mainly used as machining oils due to good lubricating properties (oiliness, anti-wear properties). It finds a lot of applications in a large range of domains :



- Metal working fluids / Cutting oils (lubricity for anti-wear additive when sulfurized),
- Fat liquors for leather treatment,
- Concrete mold release agents (biodegradable, fluid oil, easy to emulsify),
- Grease and lubrication formulations,
- Anti-foaming agents.

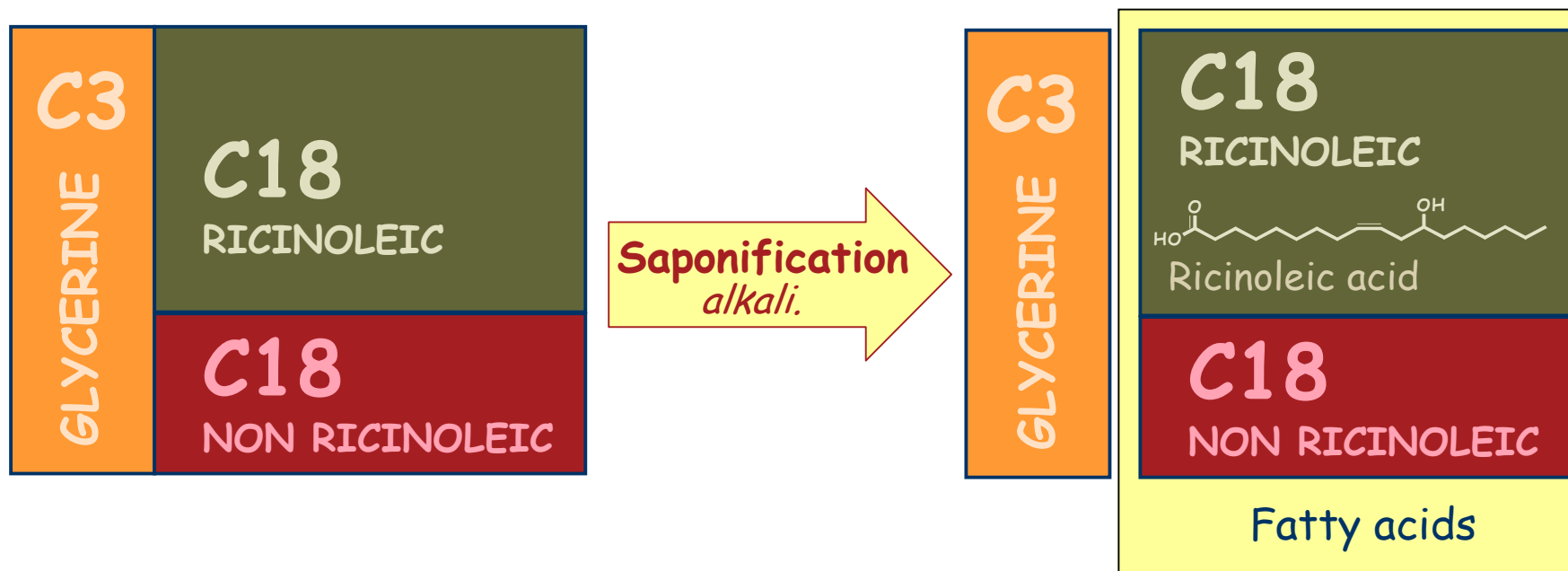


When 18 equals to 10 + 8 ...

Ricinoleic derivatives can either react as described previously (steam cracking) or under alkaline conditions (caustic pyrolysis). With the second reaction conditions, the equation $18=11+7$ becomes $18=10+8$ leading to different final products.



In a first step, ricinoleic acid and glycerine are recovered by heating Castor Oil to high temperatures (about 250 °C) with alkali (**saponification**).





When 18 equals to 10 + 8 ...

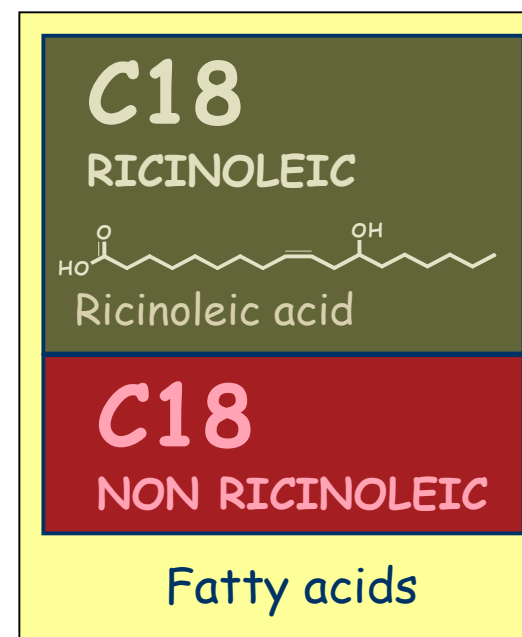
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C₃
GLYCERINE



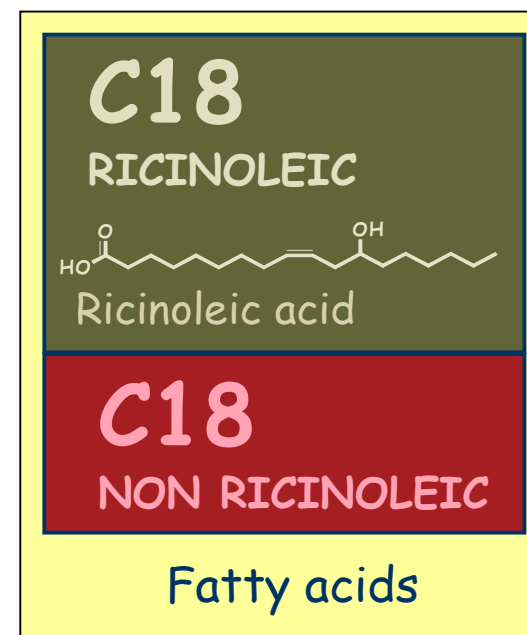
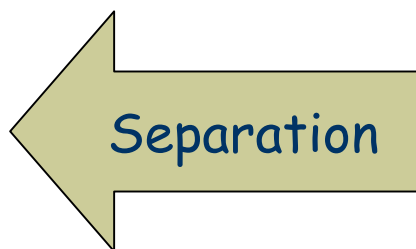
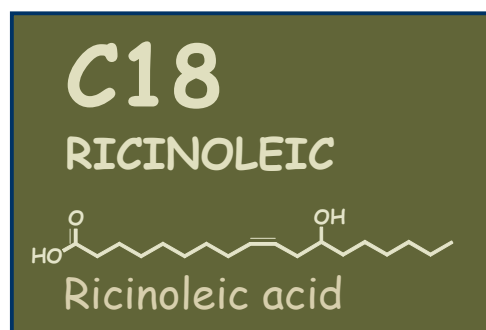
Decantation





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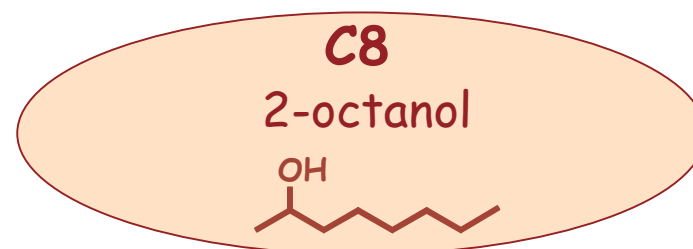
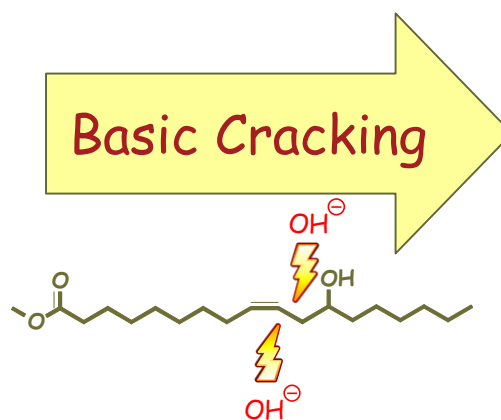
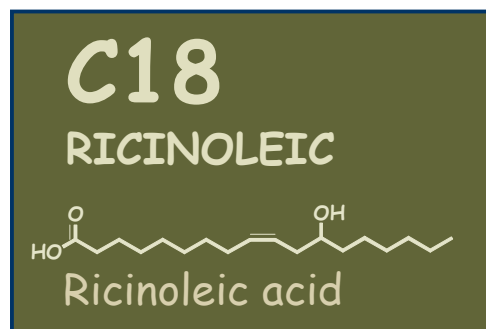


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In a second step, ricinoleic acid is cleaved to give capryl alcohol (2-octanol) and sebacic acid (C10 α,ω -diacid).





Properties and uses of Sebacic Acid

Sebacic acid is a linear saturated C10 acid comprising two carboxylic acid functions on each termination.



Sebacic acid can be used as such or as an intermediate in **lubricants**, **hydraulic fluids**, **cosmetics**, **candles**, **aromatics**, **antiseptics** and **painting materials**.

Sebacic acid can be used for partially bio resourced polymers :

↳ ie : **nylon 6.10** is obtained by coupling sebacic acid with hexamethylene diisocyanate



Furthermore, sebacic acid esters are used as **plasticizers** for different polymers and synthetic rubbers (dibutyl sebacate DBS) and in the manufacture of dioctyl sebacate (**lubricant** for jet and in air-cooled combustion engines).



Properties and uses of 2-Octanol

The 2-octanol (capryl alcohol) is mainly used as a raw material for producing intermediates in **flavors** and **perfumes** industry.



In **cosmetics**, it is an intermediate for the preparation of **caprylic/capric triglyceride (CCT)** use as emollient, excellent as a super-fattening oil in soap-making and improves spreading of skincare formulas.

Capryl alcohol can be used as a possible alternate for 2-ethylhexanol or isooctyl alcohol in the preparation of diesters **plasticizers** : **dicapryl esters** such as **dioctyl phthalate (DOP)**, **dioctyl adipate (DOA)**.

2-octanol is used as a **solvent**. It is also used as a mineral **floatation agent** and for producing **emulsifiers**, **defoaming** and **anti-bubbling agents**.



Castor Oil : a vegetal refinery !

As a conclusion, a little summarize of all the applications of Castor Oil derivatives ...

Undecylenic acid
methyl undecylenate
heptanol
heptanoic acid
heptanal
Castor oil

Esterol A
11-aminoundecanoic acid

Rilsan^{Clear} platamid^{Rnew}
Rilsan[®] pebax^{Rnew}
Rilsan[®] FINE POWDERS

2- octanol
Sebacic acid



Castor Oil : a vegetal refinery !



Thank you all for your attention.