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Valorization of Castor Oil for Polymer Applications

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Bordeaux, February 18th 2011

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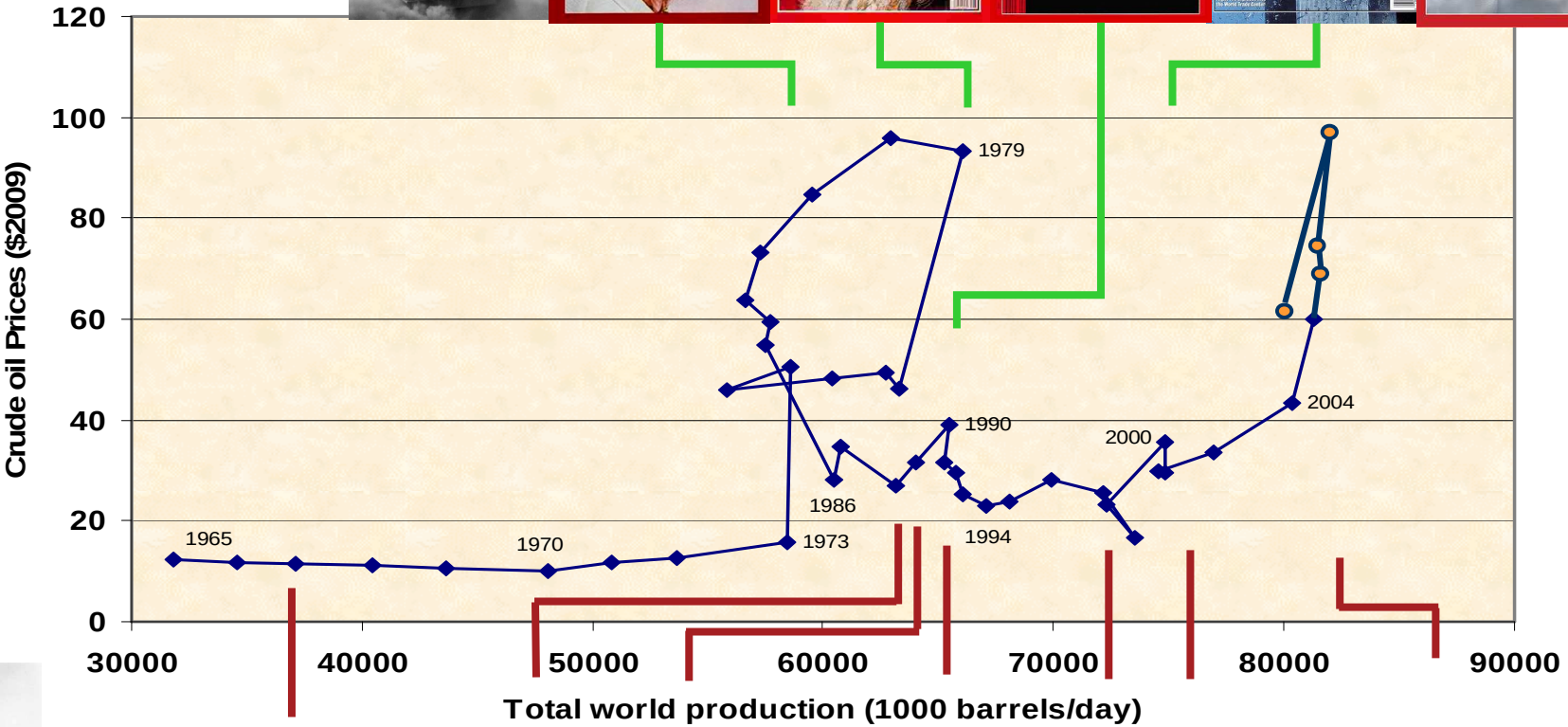
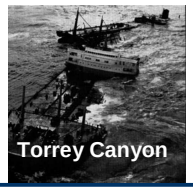
ARKEMA RENEWABLES

Crude Oil Price/Supply





Large demand for Bio-fuels, and very high governmental support

TABLE 7

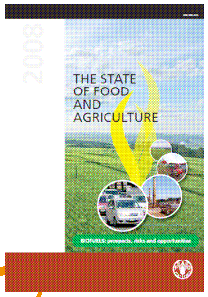
Approximate average and variable rates of support per litre of biofuel in selected OECD economies

OECD economy	ETHANOL		BIODIESEL	
	Average	Variable	Average	Variable
	(US$/litre)[1]	(US$/litre)[1]	(US$/litre)[1]	(US$/litre)[1]
United States of America[2]	0.28	Federal: 0.15 States: 0.00–0.26	0.55	Federal: 0.26 States: 0.00–26
European Union[3]	1.00	0.00–0.90	0.70	0.00–0.50
Canada[4]	0.40	Federal: up to 0.10 Provinces: 0.00–0.20	0.20	Federal: up to 0.20 Provinces: 0.00–0.14
Australia[5]	0.36	0.32	0.35	0.32
Switzerland[6]	0.60	0.60	1.00	0.60–2.00

Notes:

[1] Values (except in the case of the United States of America and Australia) are rounded to the nearest US$0.10.
[2] Lower bound of reported range. Some payments are budget-limited.
[3] Refers to support provided by Member States.
[4] Provisional estimates; includes incentives introduced on 1 April 2008. Federal and most provincial supports are budget-limited.
[5] Data refer to the fiscal year beginning 1 July 2006. Payments are not budget-limited.
[6] Range for biodiesel depends on source and type of feedstock. Some payments are limited to a fixed number of litres.

Source: Steenblik, 2007, p. 39.



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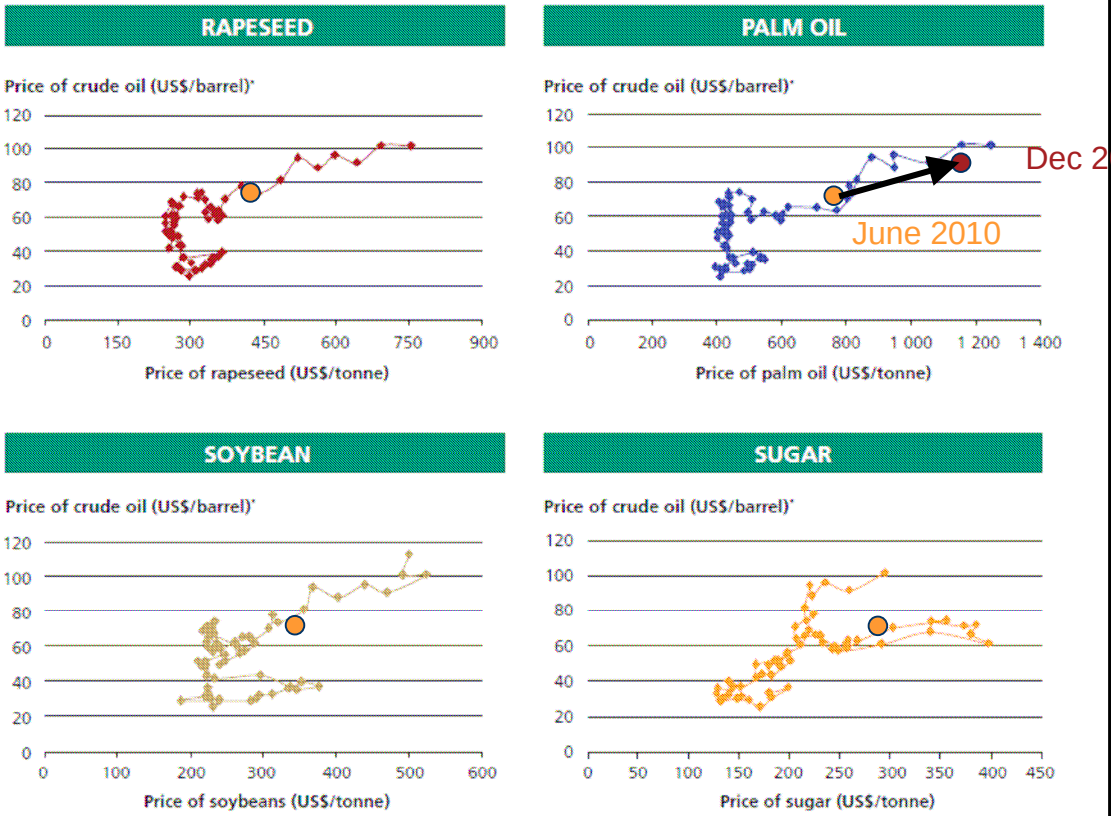
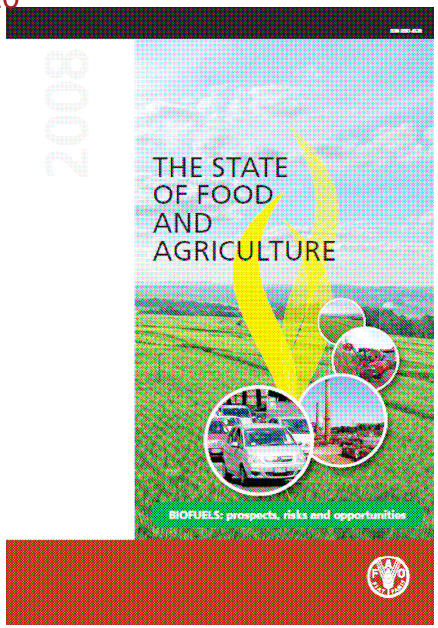
Food vs fuel

FIGURE 14
Price relationships between crude oil and other biofuel feedstocks, 2003–08



* Monthly prices since 2003.

Sources: Crude oil prices: Brent crude, Chicago Board of Trade (US$ per barrel), downloaded from the Commodity Research Bureau Web site (http://www.crbtrader.com/crbindex/) on 10 June 2008.
Commodity prices from FAO international commodity price database.



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Edible vs Non-edible Oils / Fatty acid types

Seeds	C16:0	C18:0	C18:1	C18:2	C18:3	Other	Iodine Nr
Rape seed (v. low erucic)	*3-6*	*1-3*	*55-67*	*16-26*	*6-14*		96-117
Safflower (high linoleic)	*3-6*	*1-4*	*11-21*	*73-79*	*tr*	*0.2*	*140-150*
Safflower (high oleic)	*3-6*	*1-4*	*73-79*	*10-16*	*tr*		*90-110*
Jatropha Curcas	*12-17*	*5-10*	*37-63*	*19-41*		*1-2 C20*	*93-107*
Castor	***1-2***	***1-2***	***3-4***	***5-6***	***0.5-1***	***87-88*** ***(C18:1, OH)***	***82-90***
Pongamia pinnata	*3-8*	*2-9*	*44-71*	*10-18*		*15-20* *(C20~C24)*	*80-96*
Rubber seed	*7-11*	*9-12*	*18-30*	*33-39*	*20-26*		*121-148*
Sal	*5-9*	*34-48*	*34-45*	*2-3*		*6-12 C20*	*33-45*
Neem Oil	*13-16*	*14-24*	*49-62*	*2-16*	*-*	*1-3 C20*	*65-80*

Castor

- Castor is indigenous to the Mediterranean Basin, Easter Africa and India.Today it is widespread throughout tropical regions.In areas with a suitable climate (tropical regions), castor establishes easily and can often be found on unused land.

Castor production

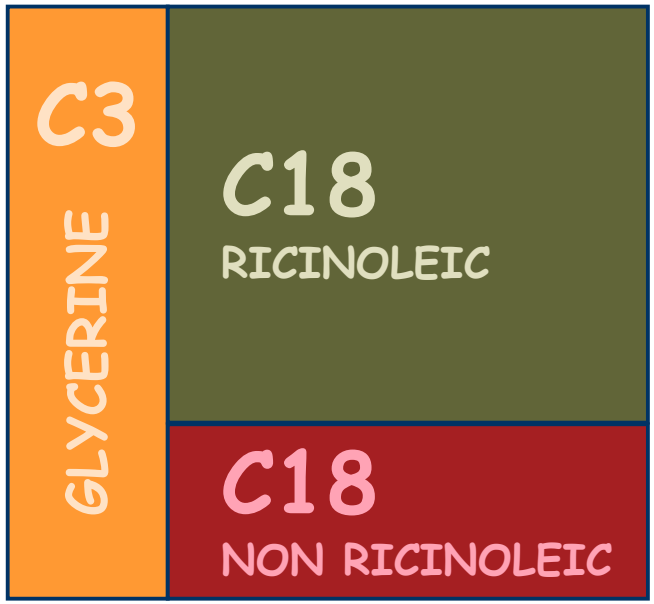
Country	Production (Tons)	Note
India	830 000	
China	210 000	
Brazil	91 510	
Ethiopia	15 000	FAO Estimate
Paraguay	12 000	FAO Estimate
Thailand	11 052	
Vietnam	5 000	
South Africa	4 900	
Philippines	4 500	FAO Estimate
Angola	3 500	FAO Estimate
World	1 209 756	FAO Estimate

Source: Food and Agricultural Organization of United Nations. Economic and Social department: the Statistical Division

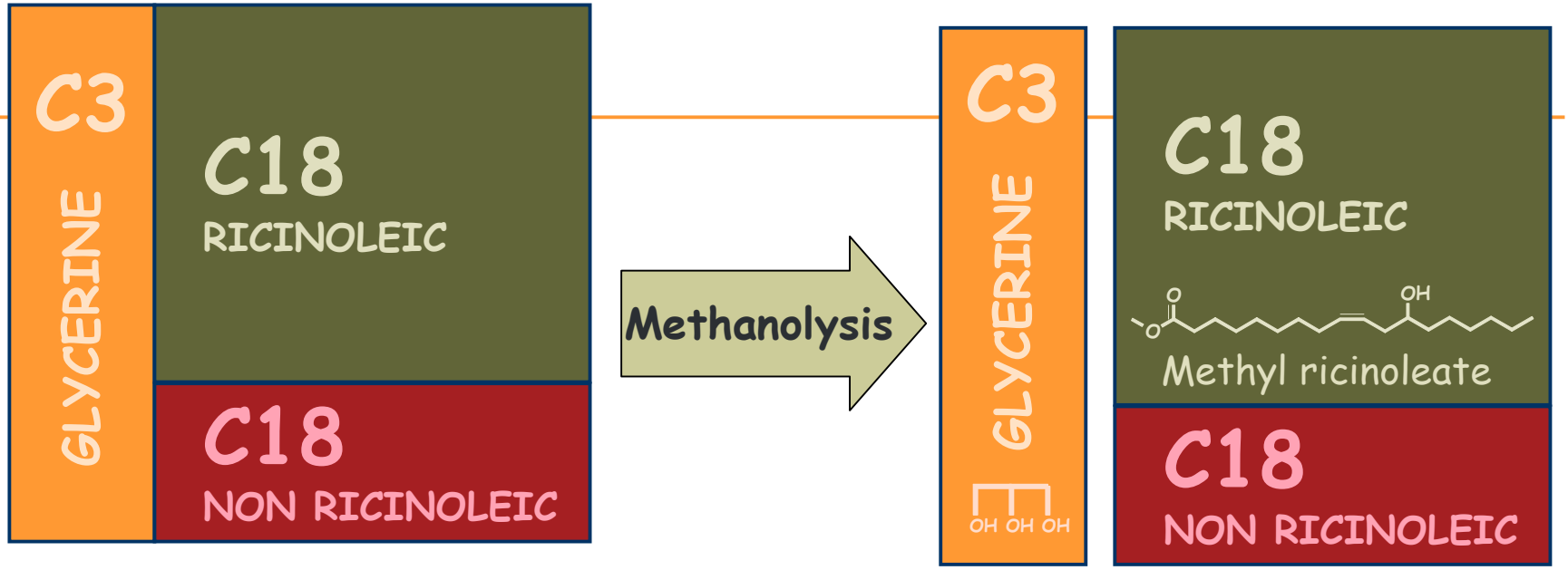
When 18 equals to 11 + 7 …

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 Marseille 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



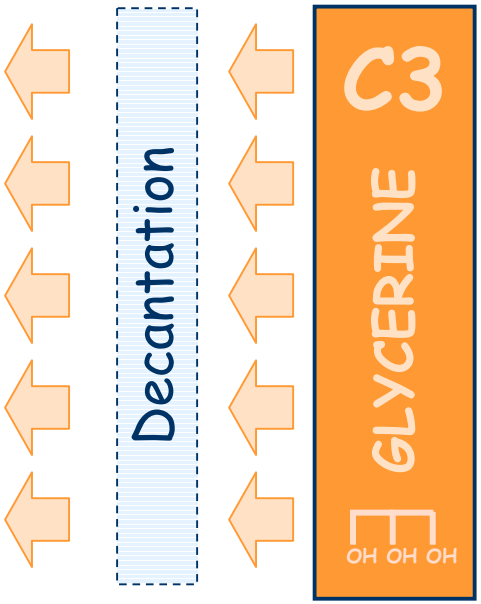
Mixture of Fatty acids triglycerides



Valorisation of glycerine :

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

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

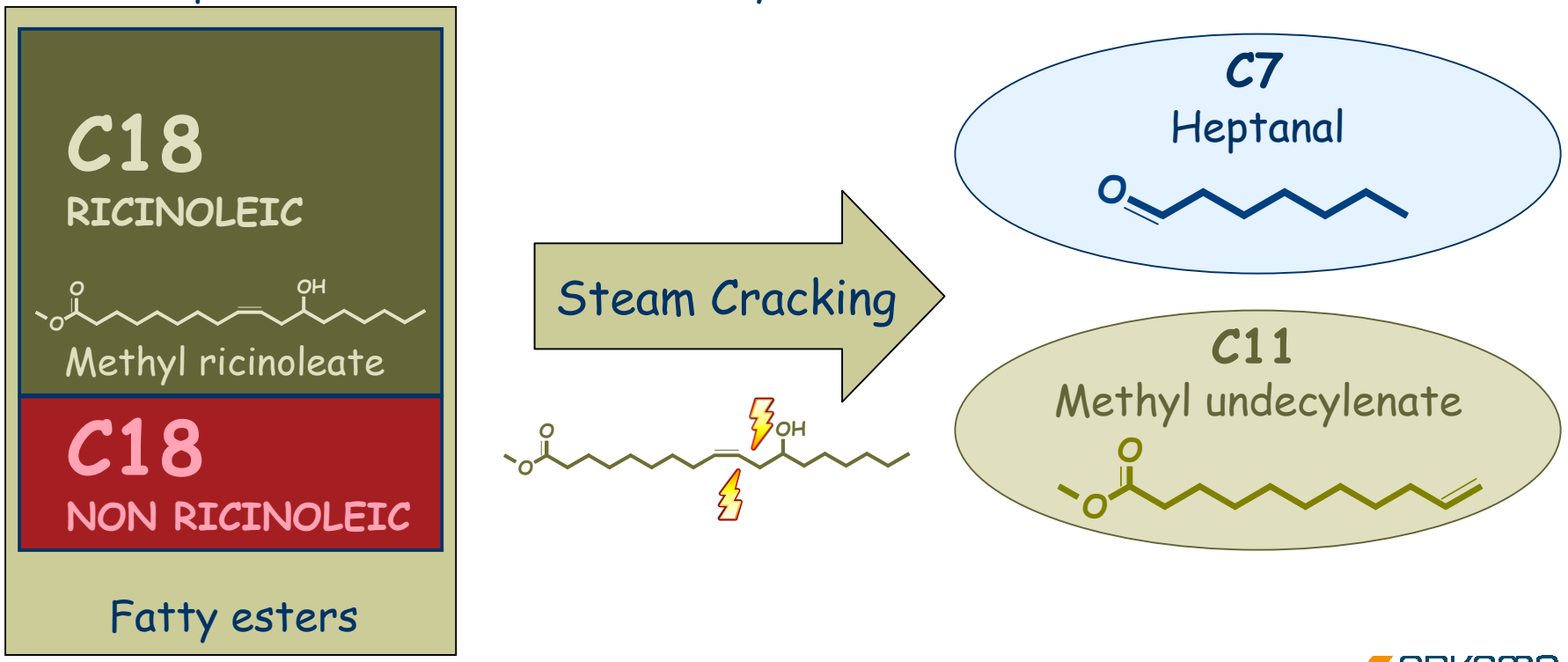


Steam Cracking

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 Marseille 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.



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.

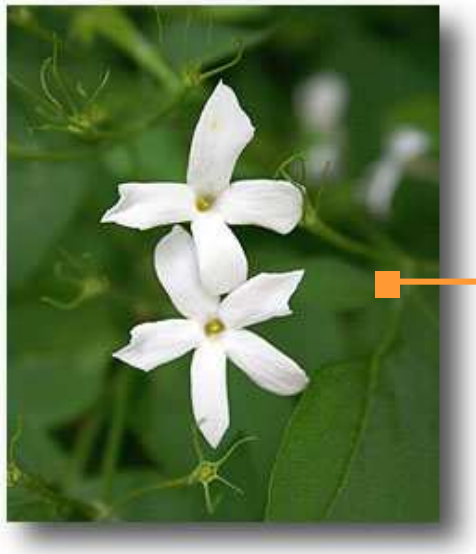
Aldehyde, alcohol and acid are the three main chemical derivatives of C7.

Main characteristics :

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

Applications of heptanal

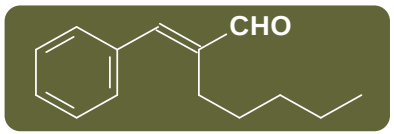
Synthesis intermediate for the fragrance and aroma industry.



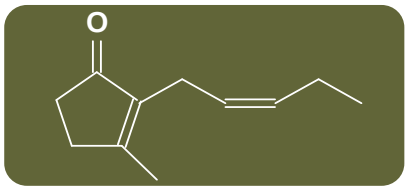
An perfume aromas related to C7 aldehyde is **JASMINE**. This aroma is detectable in many washing powders, soaps, candies and other jasmine perfumed products.

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

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



- Jasmonoids



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).

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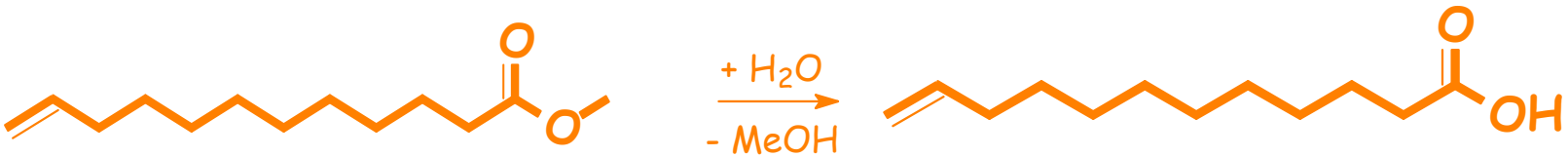
C11 derivatives

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

They are versatile molecules for chemical synthesis.



methyl undecylenate

undecylenic acid

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.

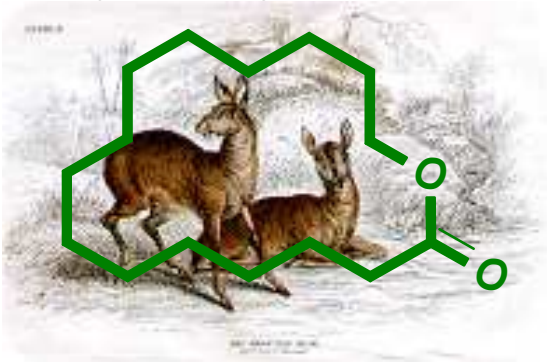
One of the safest, ecological, most economical and highly effective natural bacteriostatic and antifungal agents

C11 derivatives

… 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)



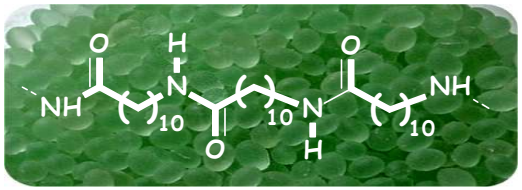
Polymers from Amino-undecanoic acid

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®.

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 !

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A "Building Block" strategy

plants

HARVESTING

seeds

GRINDING

natural oil

MONOMER SYNTHESIS

amino 11
- monomer -

Others Bio-based Building blocks

Fossil blocks

Rilsan® PA11
- hard block -

20 to 94%

POLYMERIZATION

POLYMERIZATION

COPOLYMERIZATION

COPOLYMERIZATION

Rilsan® Fine Powders

Rilsan® PA11

Copolyamides

biobased Pebax®

Rilsan FINE POWDERS

Rilsan

platamid Rnew

Rilsan Clear

Rilsan High Temperature

pebax Rnew

1948

2007

2008

2009

2008

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Rilsan® Polyamide 11

Rilsan®

The only High Performance polymer 100% based on renewable resources

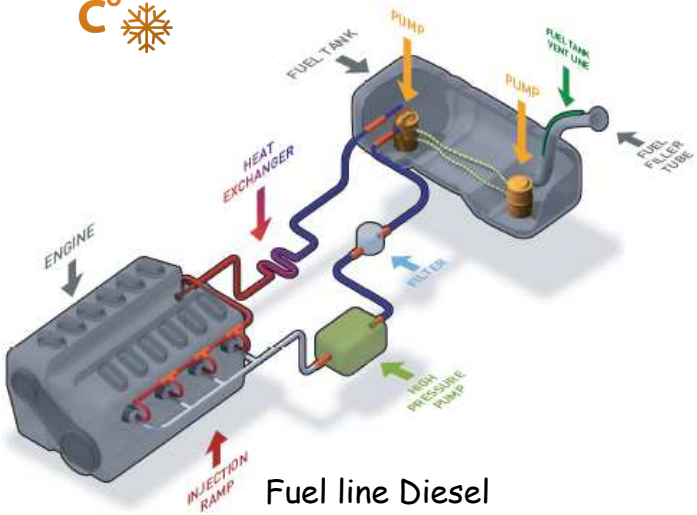
Impact Resistance Toughness

Lightness

Processability

ARKEMA RENEWABLES

Heat resistance



Fuel line Diesel

Chemical resistance

Biomass Based

(issued by JORA)

2006 Bioplastics Awards Winner

crops offer a sustainable alternative for industrial bio-based

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Pebax® Rnew Polyether Block Amide

pebax® Rnew

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

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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 :

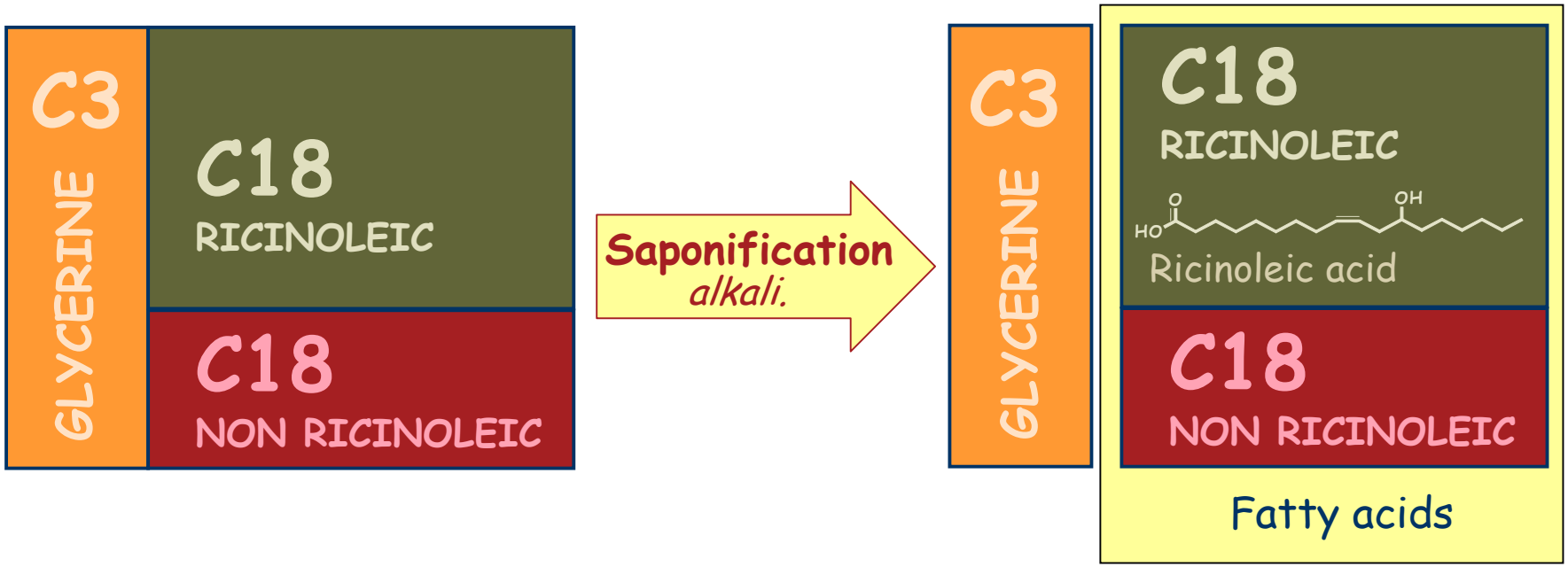
- Metal working fluids / Cutting oils (lubricity for anti-wear additive when sulfurized),
- Fat liquors for leather treatment,
- Concrete mold release agents (biodegradable, fluid oil, easy to emulsify),
- Grease and lubrication formulations,
- Anti-foaming agents.

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.

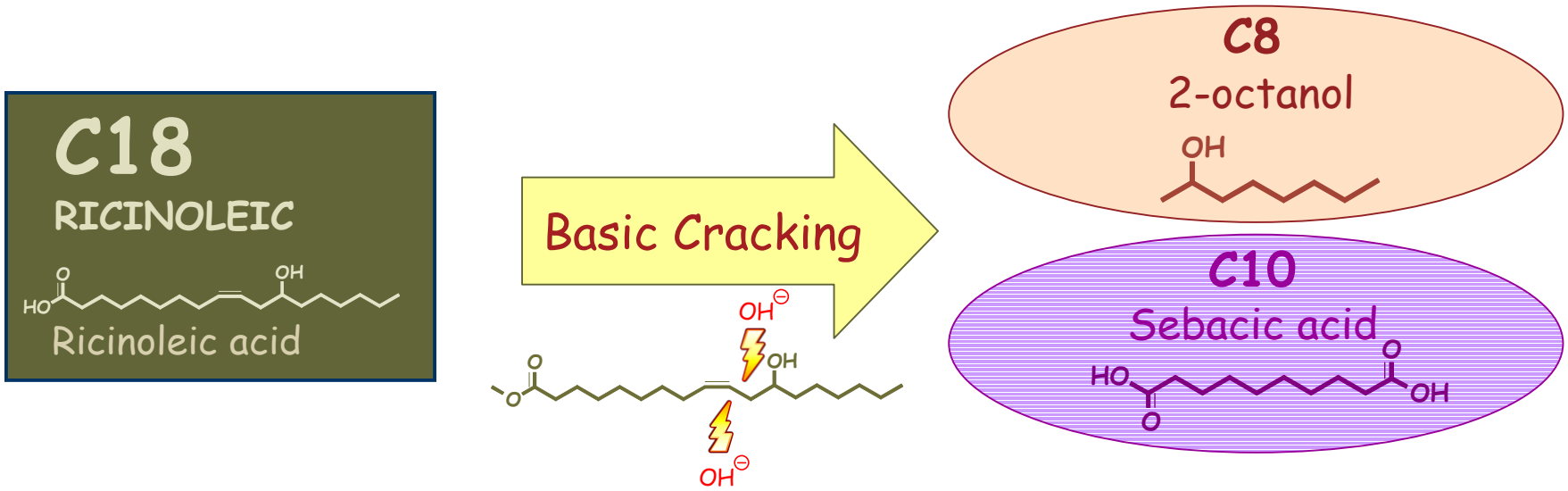
When 18 equals to 10 + 8 …

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 …

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 diamine

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-fatting 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 Bio-refinery !

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Thank you for your attention