Biochemistry, nutrition and technology of lipids. Partie I

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Biochemistry, nutrition and technology of lipids

PPGAN UNIRIO



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1. INTRODUCTION

- Generality about lipids /oils
- Few socio-economics data

2. LIPIDS IN ALIMENTATION / NUTRITIONNAL PART

3. BIOCHEMISTRY OF VEGETABLE LIPIDS

- Composition of vegetable lipids
- Analyses of lipids
- Oxidation of lipids

4. TECHNOLOGY OF VEGETABLE LIPIDS

- Processing of oils
- Chemical and enzymatic modifications of lipids
- Processing margarines

5. Few oil monographies

6. Conclusions

Definition of lipids or fats

Not defined by a structure or chemical function but by a common physical property

SOLUBILITY IN ORGANIC APOLAR SOLVANTS (chloroform, hexane, ether…)

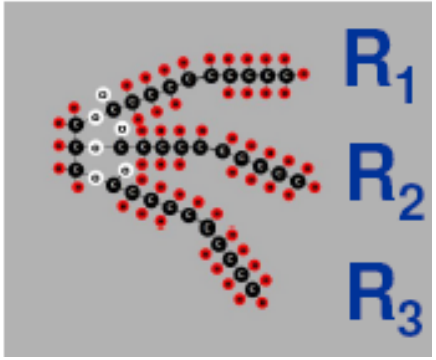
lipides are organic substances insoluble in water …

Generality about oils

Definitions

- ?

Generality about oils



Definitions

Vegetable oils are mainly based on triglycerides which are triesters of fatty acids and glycerol under solid or liquid form.

Oils can contain small amounts of other constituants such as wax esters, free fatty acids, partial glycerides or unsaponifiable substances.

Obtention

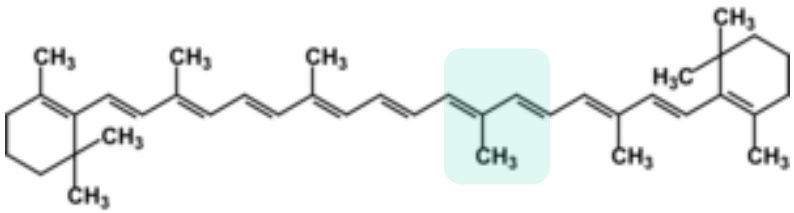
From grains, fruits or kernels by pressure or solvant extraction.

Then possibly refined or hydrogenated.

An appropriate antioxydant can be added if necessary …

?

?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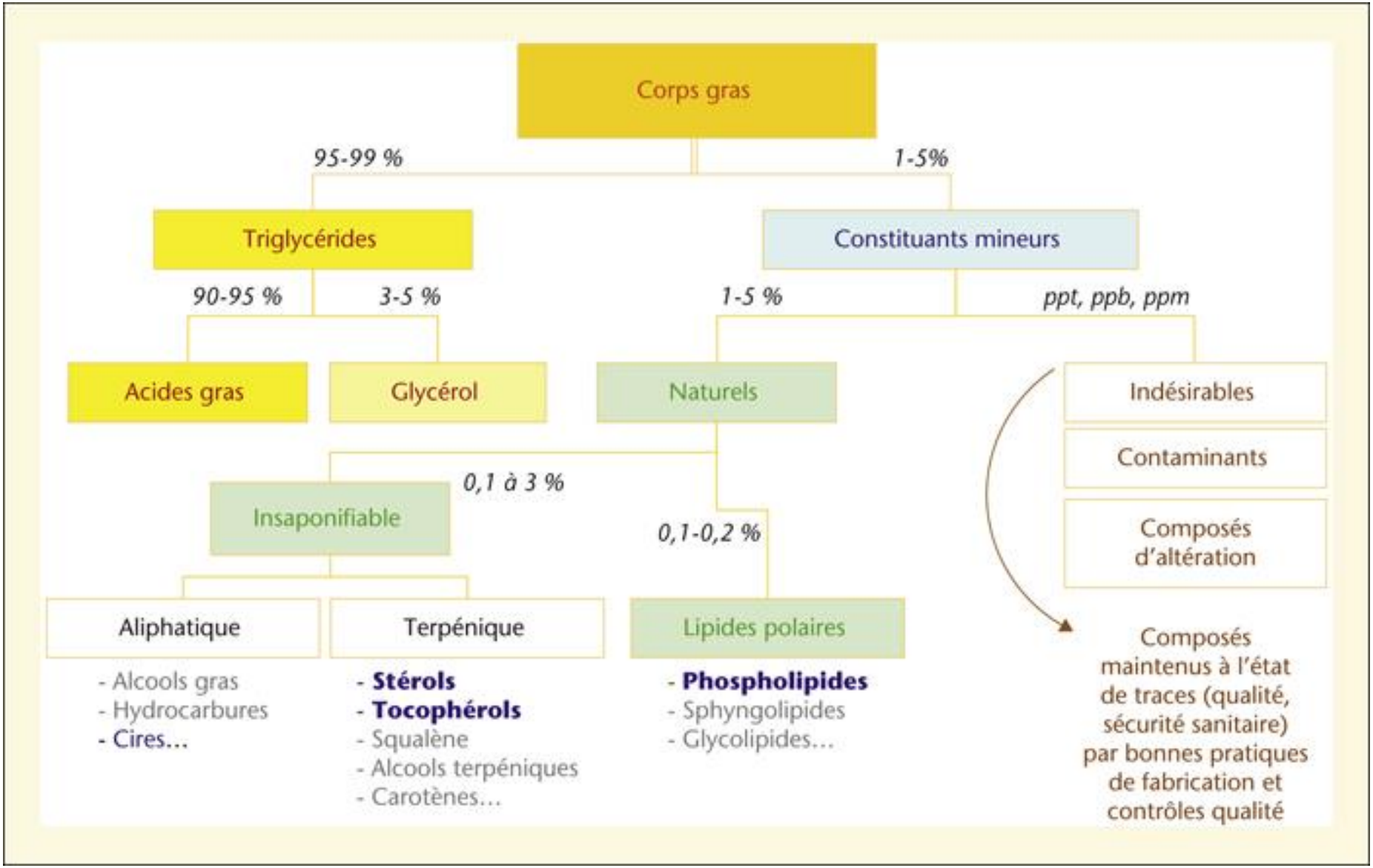

Corps gras
95-99 %
1-5%
Triglycérides
Constituants mineurs
90-95 %
3-5 %
1-5 %
ppt, ppb, ppm
Acides gras
Glycérol
Naturels
Indésirables
Contaminants
Composés d'altération
0,1 à 3 %
Insaponifiable
0,1-0,2 %
Aliphatique
Terpénique
Lipides polaires
- Alcools gras
- Hydrocarbures
- Cires…
- Stérols
- Tocophérols
- Squalène
- Alcools terpéniques
- Carotènes…
- Phospholipides
- Sphyngolipides
- Glycolipides…
Composés maintenus à l'état de traces (qualité, sécurité sanitaire) par bonnes pratiques de fabrication et contrôles qualité

Generality about oils

Raw oil: oil just after extraction whatever the obtention process

Virgin oil: oil obtained from selected premium raw matter with specific extraction process: exclusively mechanical, without solvant, clarification with physical means only, no post-extraction chemical or physical refining process allowed. Extra virgin AI <0.8 (g/100 g), PI <20

Refined oil is obtained by pressure and /or solvant extraction , followed by alcaline reffinery, decoloration, desodorisation from a raw oil

Hydrogenated oil / partially hydrogenated oil is obtained from refined oil further hydrogenated

DGCCRF Direction générale de la concurrence, de la consommation et de la répression des fraudes

Une direction du ministère de l'Économie, de l'Industrie et du Numérique

Huiles d'olive : des améliorations sur l'étiquetage - 26/06/2014

Les normes de commercialisation et d'étiquetage des huiles d'olive viennent d'être modifiées pour garantir au consommateur une meilleure information.

Liens utiles

- Site du Service commun des laboratoires
- Règlement (UE) 1335/2013 modifiant le règlement n° 29/2012
- Règlement (UE) 299/2013 modifiant le règlement n° 2568/91

Les nouvelles dispositions, introduites par la modification des règlements (UE) n° 29/2012 et n° 2568/91, apportent des précisions sur les conditions de conservation des huiles, les mentions obligatoires et facultatives en matière d'étiquetage et les méthodes d'analyses.

Des informations sur la conservation des huiles pour garantir de leur fraîcheur

Pour éviter leur altération, les huiles doivent être conservées à l'abri de la lumière et de la chaleur. L'étiquetage doit désormais indiquer les conditions particulières de conservation des huiles d'olive (vierges extra, vierges, huiles d'olive composées d'huiles d'olive raffinées et d'huile d'olive vierges, huiles de grignons d'olive).

Appellation, provenance, récolte : de nouvelles mentions présentes sur l'emballage

Mentions obligatoires

Seules 4 dénominations de vente sont retenues pour les huiles d'olive destinées aux consommateurs :

- huile d'olive vierge extra (HOVE)
- huile d'olive vierge (HOV)
- huile d'olive composée d'huiles raffinées et d'huiles d'olive vierges
- huile de grignons d'olive

L'indication de la provenance est obligatoire pour les huiles d'olive vierge extra et les huiles d'olive vierges (nom du pays d'origine).

La dénomination de vente et l'indication de la provenance du produit doivent être lisibles (taille des caractères au minimum 1,2 mm) et visibles (une même étiquette ou plusieurs étiquettes ou directement sur le récipient)

CODEX ALIMENTARIUS

INTERNATIONAL FOOD STANDARDS

Food and Agriculture Organization of the United Nations

World Health Organization

E-mail: codex@fao.org - www.codexalimentarius.org

STANDARD FOR OLIVE OILS AND OLIVE POMACE OILS

CODEX STAN 33-1981

Adopted in 1981. Revision: 1989, 2003, 2015. Amendment: 2009, 2013.

3. ESSENTIAL COMPOSITION AND QUALITY FACTORS

Extra virgin olive oil: virgin olive oil with a free acidity, expressed as oleic acid, of not more than 0.8 grams per 100 grams and whose other characteristics correspond to those laid down for this category.

Virgin olive oil: virgin olive oil with a free acidity, expressed as oleic acid, of not more than 2.0 grams per 100 grams and whose other characteristics correspond to those laid down for this category.

Ordinary virgin olive oil: virgin olive oil with a free acidity, expressed as oleic acid, of not more than 3.3 grams per 100 grams and whose other characteristics correspond to those laid down for this category[1].

Refined olive oil: olive oil obtained from virgin olive oils by refining methods which do not lead to alterations in the initial glyceridic structure. It has a free acidity, expressed as oleic acid, of not more than 0.3 grams per 100 grams and its other characteristics correspond to those laid down for this category[1].

Olive oil: oil consisting of a blend of refined olive oil and virgin olive oils suitable for human consumption. It has a free acidity, expressed as oleic acid, of not more than 1 gram per 100 grams and its other characteristics correspond to those laid down for this category[2].

Refined *olive-pomace oil*: oil obtained from crude olive-pomace oil by refining methods which do not lead to alterations in the initial glyceridic structure. It has a free acidity, expressed as oleic acid, of not more than 0.3 grams per 100 grams and its other characteristics correspond to those laid down for this category[1].

Olive*-pomace *oil: oil consisting of a blend of refined olive-pomace oil and virgin olive oils. It has a free acidity, expressed as oleic acid, of not more than 1 gram per 100 grams and its other characteristics correspond to those laid down for this category[2].

Organoleptic characteristics (odour and taste) of virgin olive oils

	Median of the defect	Median of the fruity attribute
Extra virgin olive oil	Me = 0	Me > 0
Virgin olive oil	0 < Me ≤ 2.5	Me > 0
Ordinary virgin olive oil	2.5 < Me ≤ 6.0 *	

* or when the median of the defect is less than or equal to 2.5 and the median of the fruity attribute is equal to 0.

NEW LABELLING RULE IN UE

- ✓ 13 décembre 2014, AAI under reglement (UE) n° 1169/2011 of european parliament and council of 25 october 2011 **about information to consummers** about food products

=> Mandatory to declare precisely the botanic origin of refined vegetable oil and **(for instance, colza oil, palm oil, sunflower oil and not simply vegetable oil);**

NEW LABELLING RULE IN UE

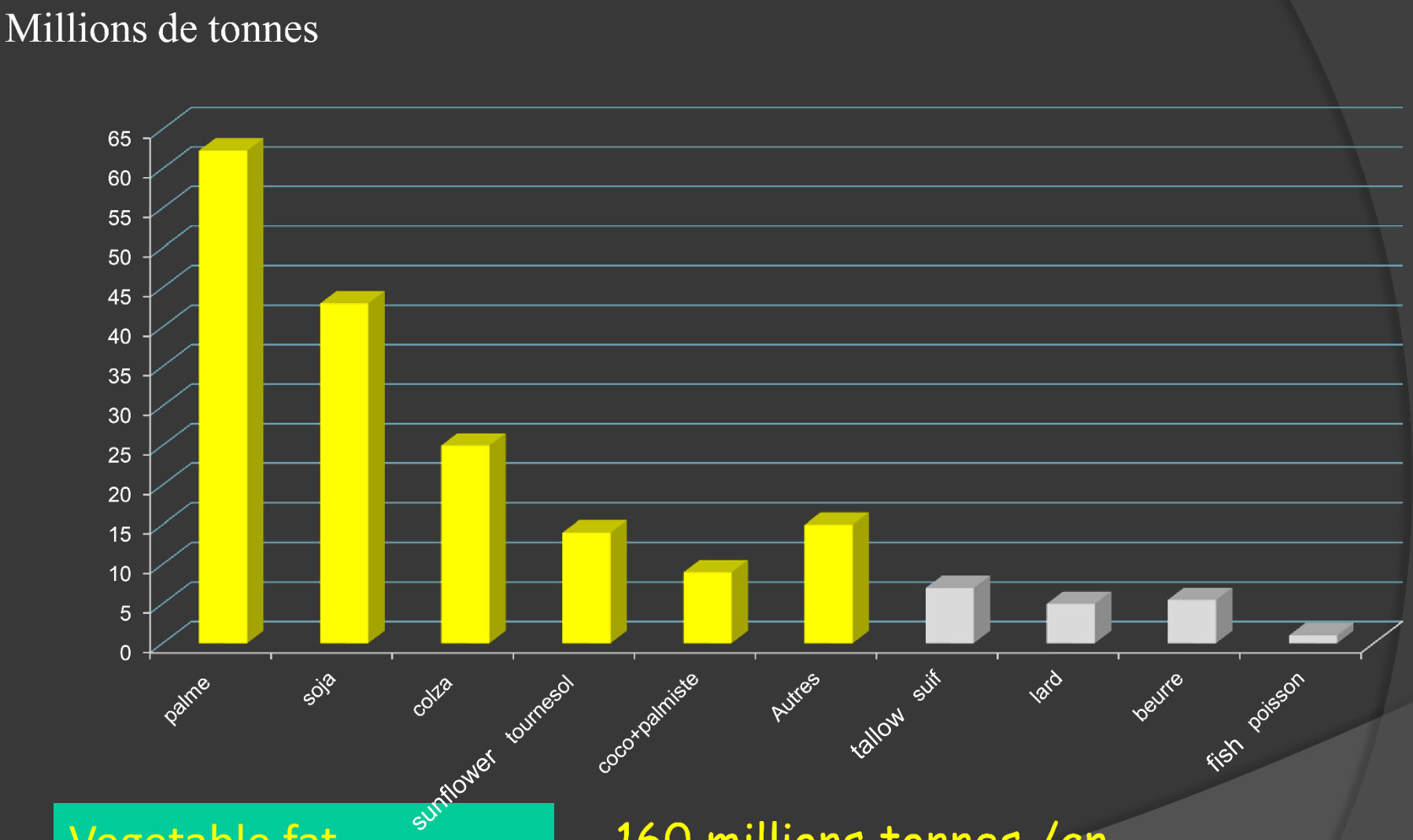
The mention « vegetable oils » has to be replaced by the list of vegetables oils within the considered food product.

In addition, Commission insists on **information visibility** : size of police « x » of minimum 1,2 mm and color easy to detach from background color. Allergens also have to be enlighted by a different color or typography.

Few socio-economic data

Which oil/lipids are the most produced in the world ?

PRODUCTION OF VEGETABLE OILS AND FATS



Vegetable fat
Animal fat

160 millions tonnes /an
24 millions tonnes / an

www.ceopalmoil.com - FAOSTAT

UMR iAte Agropolymer engineering & emerging technologies

Few socio-economic data

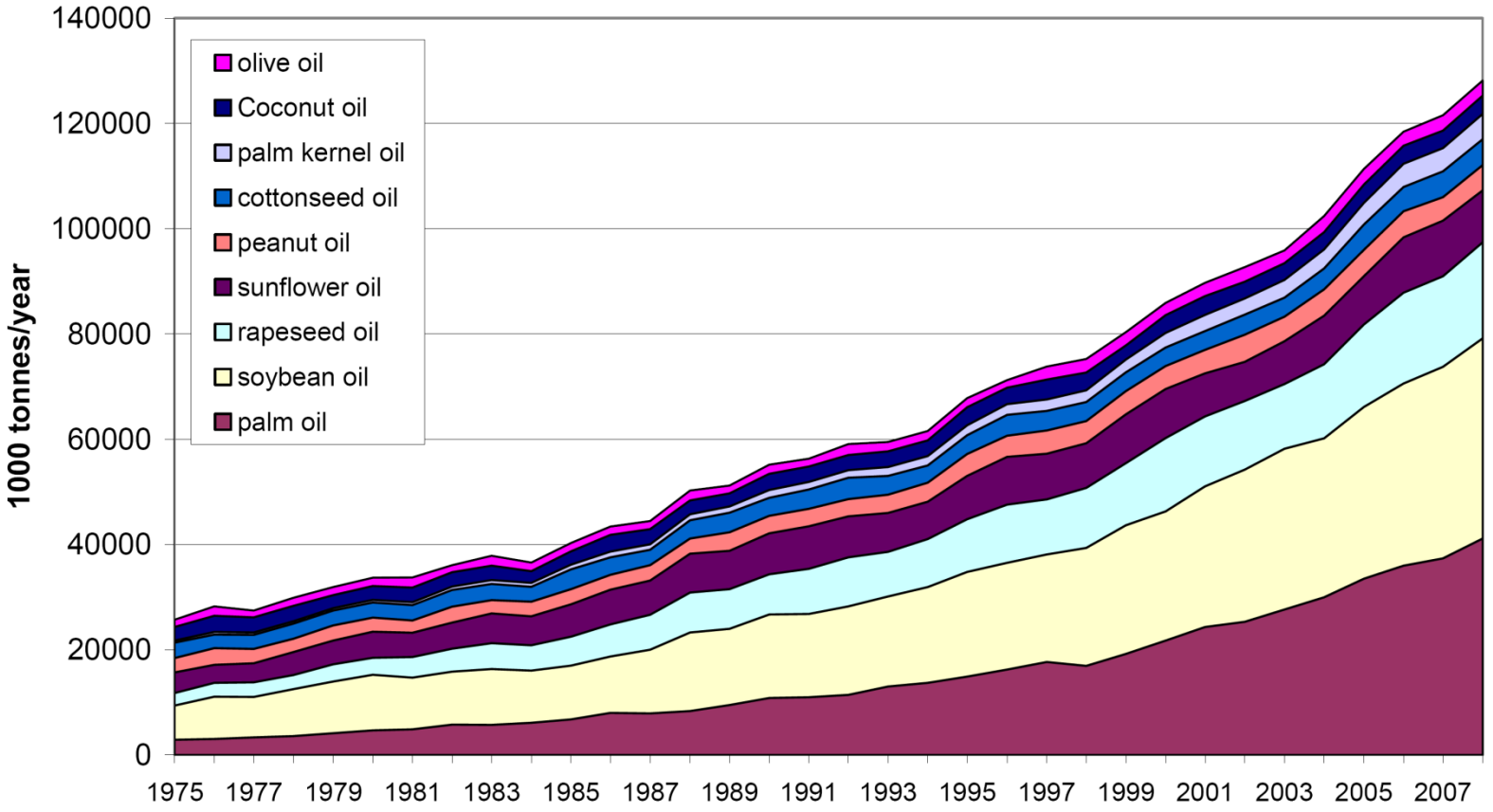


Figure. Global Production of vegetable oils, 1975 – 2007.

Source : www.fas.usda.gov/psdonline

=> Forecast 164 millions t en 2014

Few socio-economic data

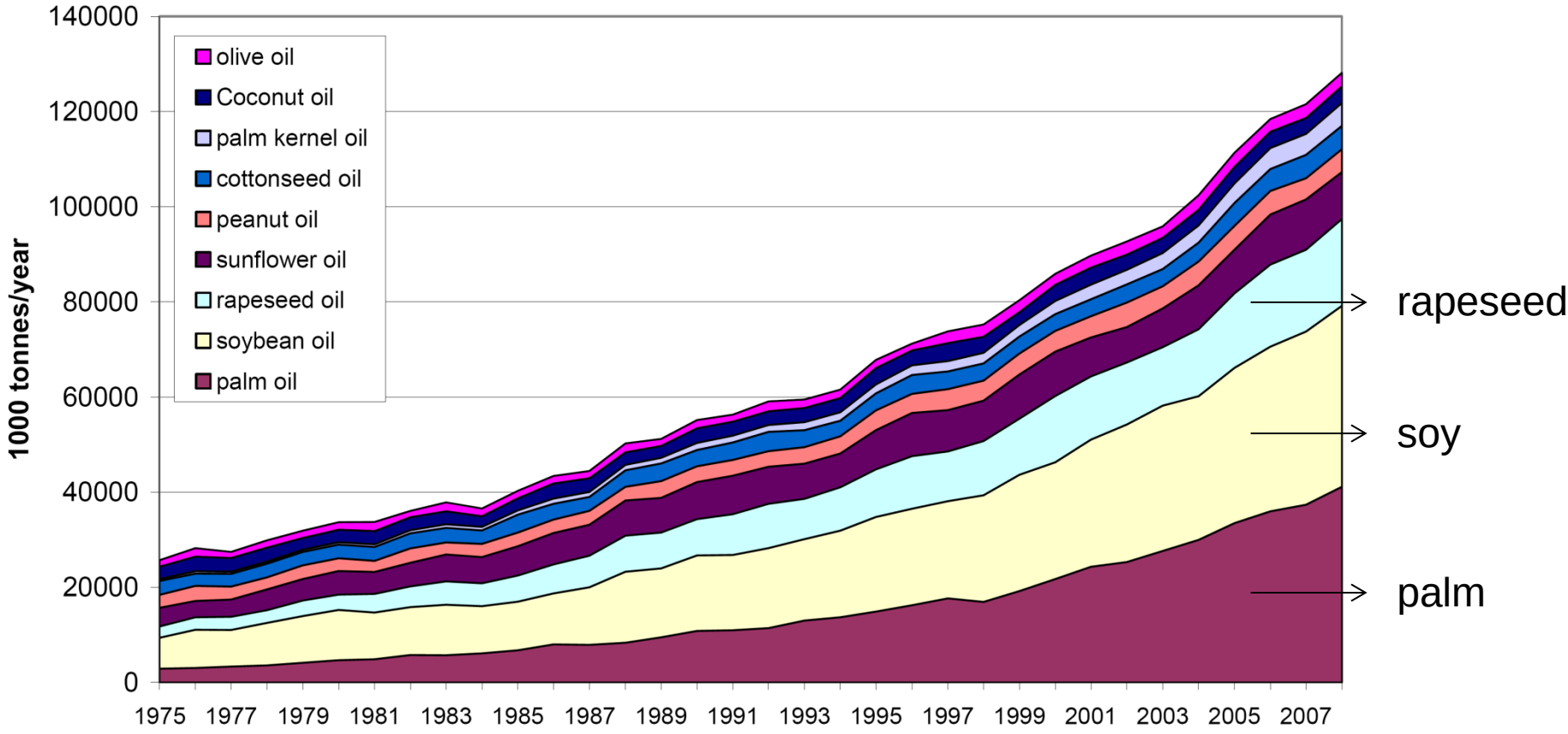
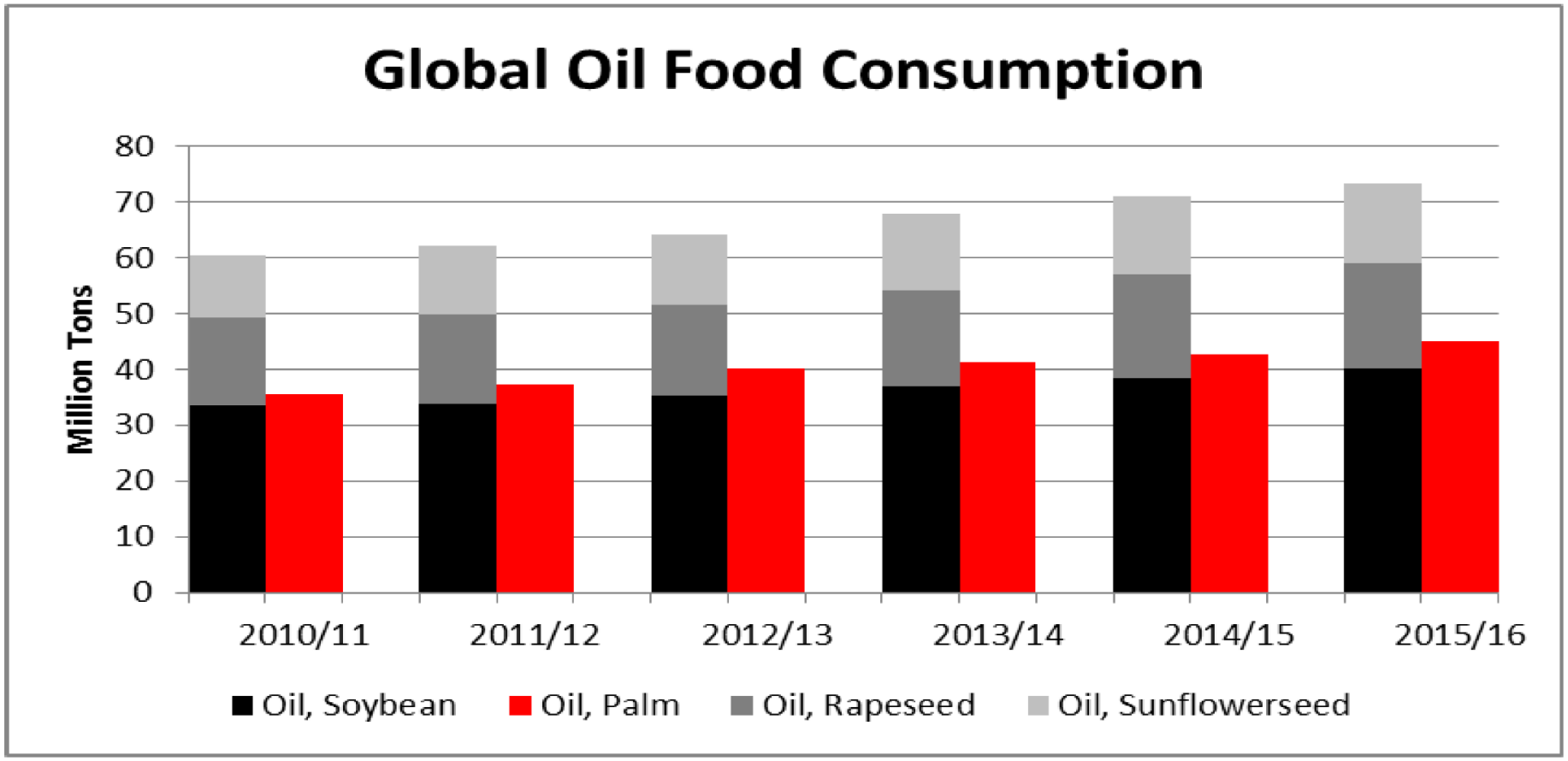


Figure. Global Production of vegetable oils, 1975 – 2007.

Source : www.fas.usda.gov/psdonline

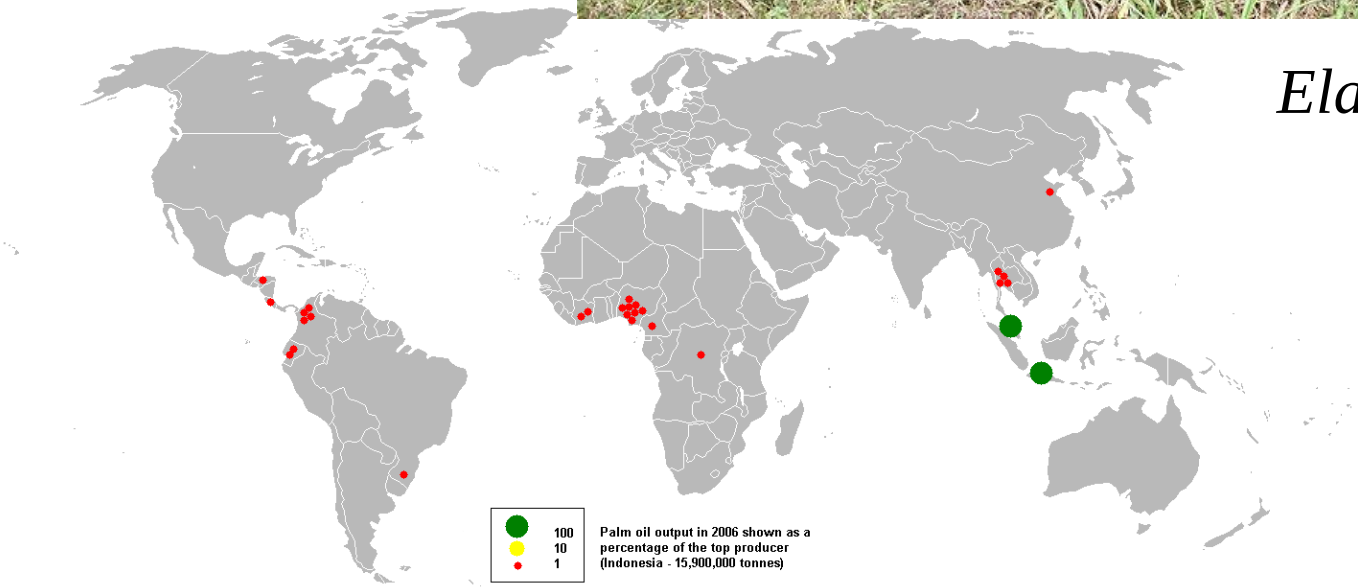
=> Forecast 164 millions t en 2014, real ONIDOL 2012 186 millions t

Few socio-economic data



Growing market but stable contributeurs

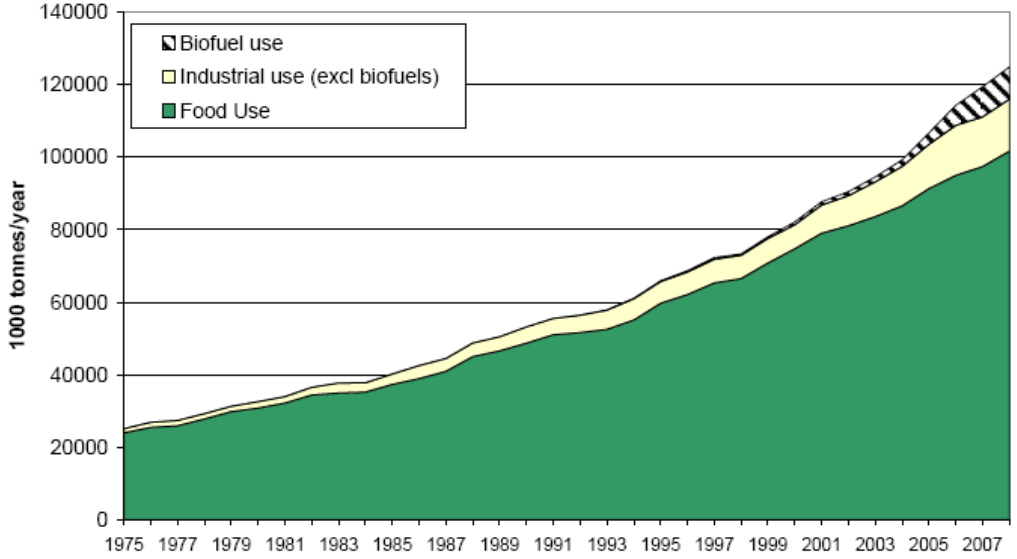
USDA Data May 2015, Oilseeds markets and trade.



Elaeis guineensis

Few socio-economic data

- 80-85 % of annual worldwide oil and fat production is for human food, 5-6 % for animal feeding, ~ 14 %, 15–17 millions t for non food industrial (Gunstone and Hamilton 2001)



- 85 % of global production is vegetal, 15 % animal

- Most important increase for palm = roughly 30 % of vegetable oil production, soya (28%), colza (15%) and sunflower (9%). Other production representent around 20% of market.

Few socio-economic data

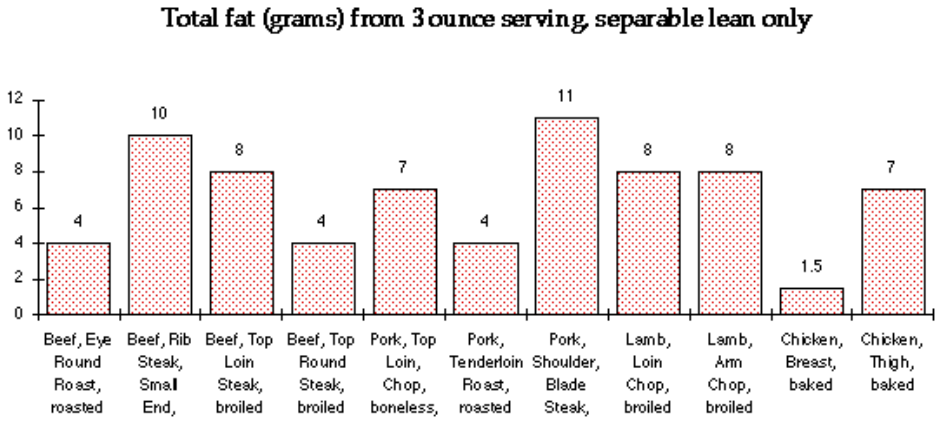
- **Applications of lipids and fats (ITERG, 2015) :**

✓ 75 % in human food application

Lipides in frequently consummed food

~1/3 visible (oil, emulsion),

2/3 are hidden (constitutive lipids of food (for instance in meat tissues 4-19%) + addition in transformed IAA food products for instance panification, biscuits).



+ High VA niche food products: dietetics, supplements

Lipids are central in public health policies : cardiovascular disease, 1 cause of death globally: more people die annually from CVDs than from any other cause (WHO 2015), recommended dietary allowance (RDA) 2010 LA/ALA = 4

Few socio-economic data

- **Applications of lipids and fat (ITERG, 2015) :**

✓ 25 % of oils and fat for non food uses:

⟶ oleochemical market: high demand for oleochemistry in 2030, 30 Millions of tons, rapidly increasing market

Potentially interesting sources that have to be developped: crambs, camelina, calendula, lunaire, euphorbia, lesquerella : all with specific FA of interest but with low yield => improvement necessary to be come good sources.

⟶ cosmetics market: rapidly increasing, lipids and skins have in common lots of componenents, application in oral or dermatologic applications.

ω6- membranar fluidity, barrier properties

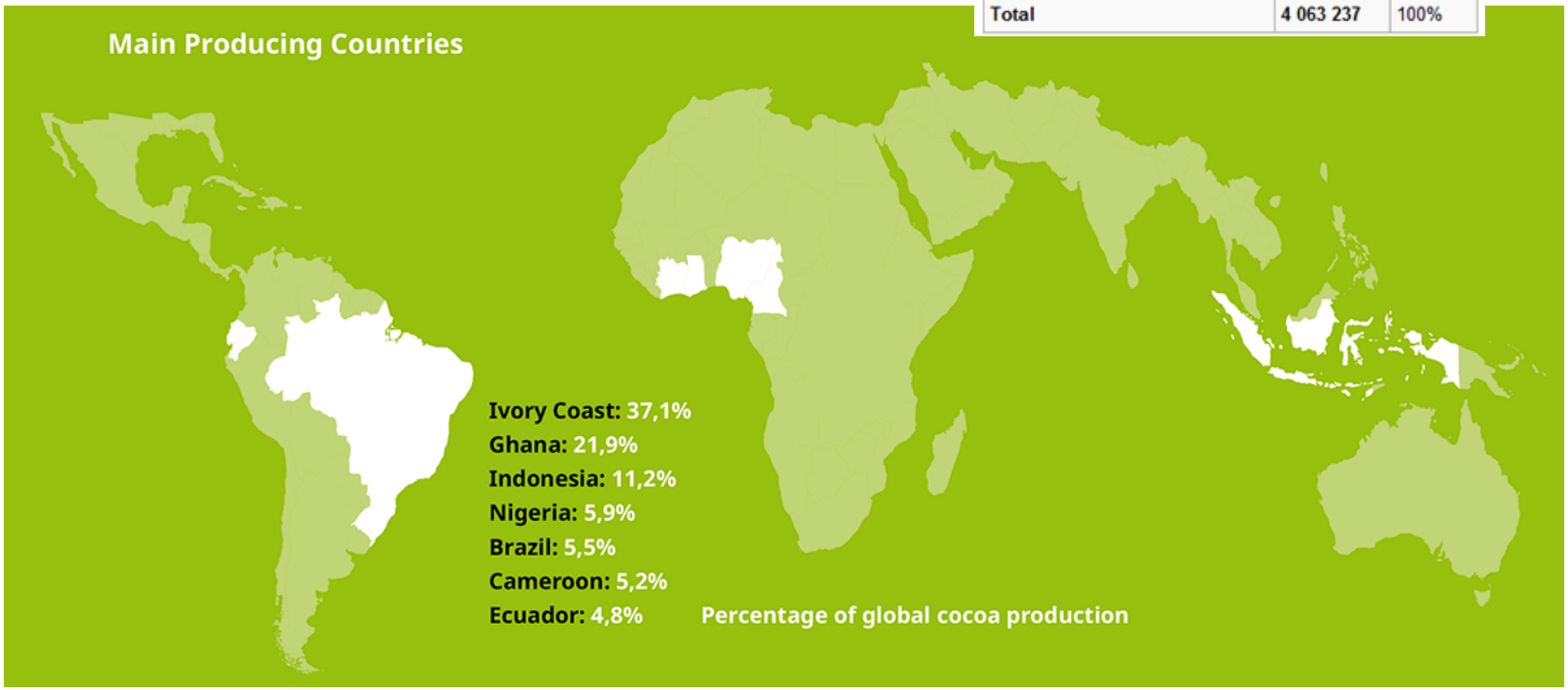
ω3 anti-inflam, main membranar constituants,

ω9 emollient

Use and developments of lots of esters in formulation (adjustement of HLB, waxes…)

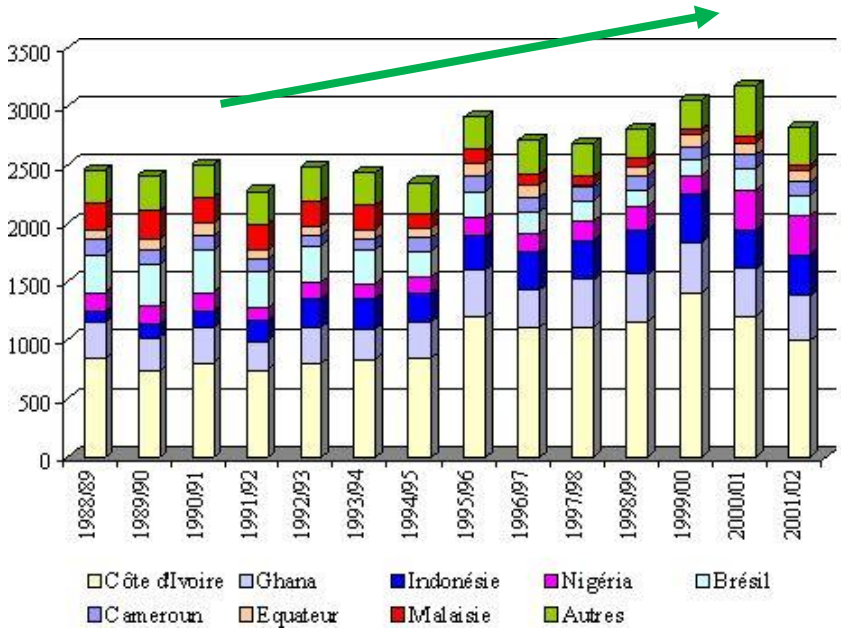
Cocoa butter production in tonnes (FAOSTAT, 2006)

Côte d'Ivoire	1 400 000	34,5 %
Ghana	734 000	18,1 %
Indonésie	580 000	14,3 %
Nigéria	485 000	12,0 %
Brésil	199 412	4,9 %
Cameroun	164 553	4,1 %
Équateur	93 659	2,3 %
Togo	73 000	1,8 %
Papouasie-Nouvelle-Guinée	42 500	1,1 %
Mexique	38 153	0,9 %
Autres pays	252 960	6,2%
Total	**4 063 237**	100%

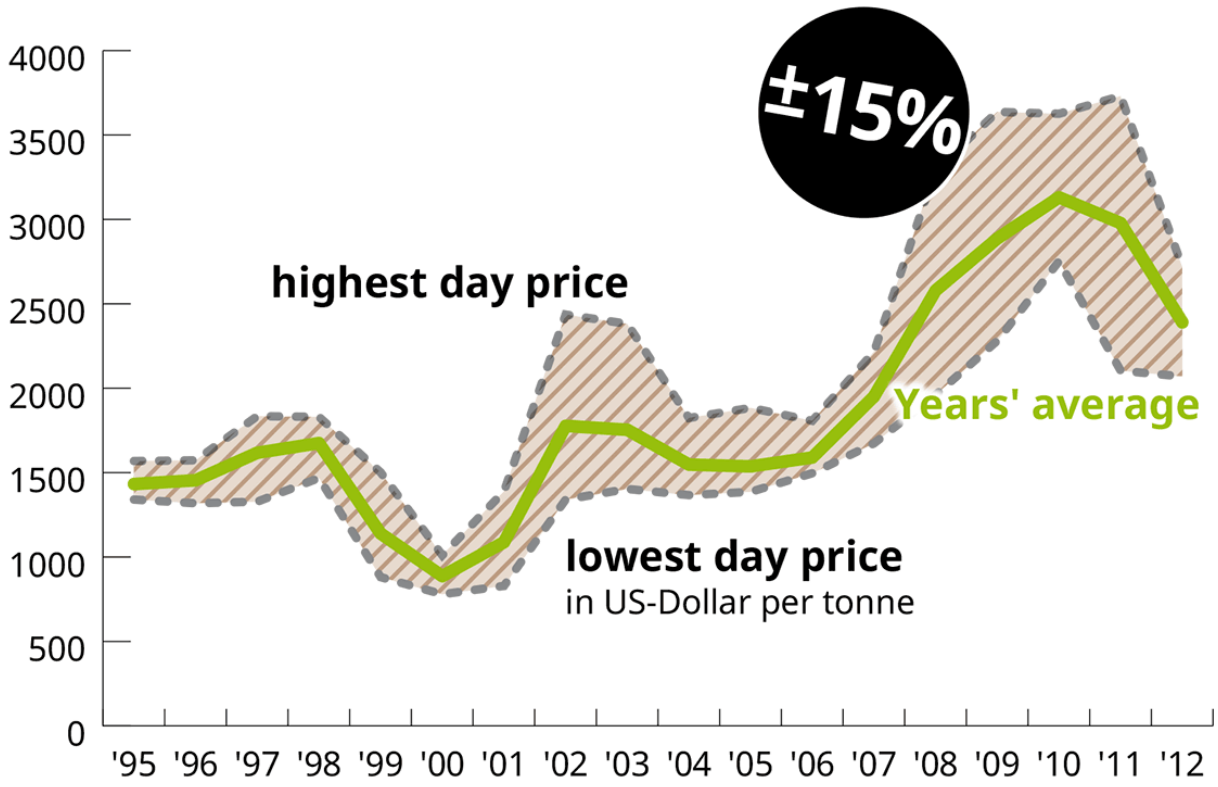


1 2 3 4 5

Harvest/ breaking the pods | **fermentation** | **drying** | **bagging** | **transport/chocolate factory**



Volatility of cocoa prices 1995-2011



SPECIFICITY IN EUROPE – LEGISLATIVE ASPECT

DIRECTIVE 2000/36/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 23 June 2000
relating to cocoa and chocolate products intended for human consumption

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 95 thereof,

Having regard to the proposal from the Commission (1),

Having regard to the opinion of the Economic and Social Committee (2),

(5) The addition to chocolate products of vegetable fats other than cocoa butter, up to a maximum of 5 %, is permitted in certain Member States.

(6) The addition of certain vegetable fats other than cocoa butter to chocolate products, up to a maximum of 5 %, should be permitted in all Member States; those vegetable fats should be cocoa butter equivalents and therefore be defined according to technical and scientific criteria.

ANNEX II

VEGETABLE FATS REFERRED TO IN ARTICLE 2(1)

The vegetable fats referred to in Article 2(1) are, singly or in blends, cocoa butter equivalents and shall comply with the following criteria:

(a) they are non-lauric vegetable fats, which are rich in symmetrical monounsaturated triglycerides of the type POP, POSt and StOSt ([1]);

(b) they are miscible in any proportion with cocoa butter, and are compatible with its physical properties (melting point and crystallisation temperature, melting rate, need for tempering phase);

(c) they are obtained only by the processes of refining and/or fractionation, which excludes enzymatic modification of the triglyceride structure.

In conformity with the above criteria, the following vegetable fats, obtained from the plants listed below, may be used:

Usual name of vegetable fat	Scientific name of the plants from which the fats listed can be obtained
1. Illipe, Borneo tallow or Tengkawang	*Shorea* spp.
2. Palm-oil	*Elaeis guineensis* *Elaeis olifera*
3. Sal	*Shorea robusta*
4. Shea	*Butyrospermum parkii*
5. Kokum gurgi	*Garcinia indica*
6. Mango kernel	*Mangifera indica*

Furthermore, as an exception to the above, Member States may allow the use of coconut oil for the following purpose: in chocolate used for the manufacture of ice cream and similar frozen products.

Lipids and fats sources ?

Usual

Vegetable (grains, fruits …) 85 %
Animals land (mammals, lards…)
or marine 15 %

News

Green technologies

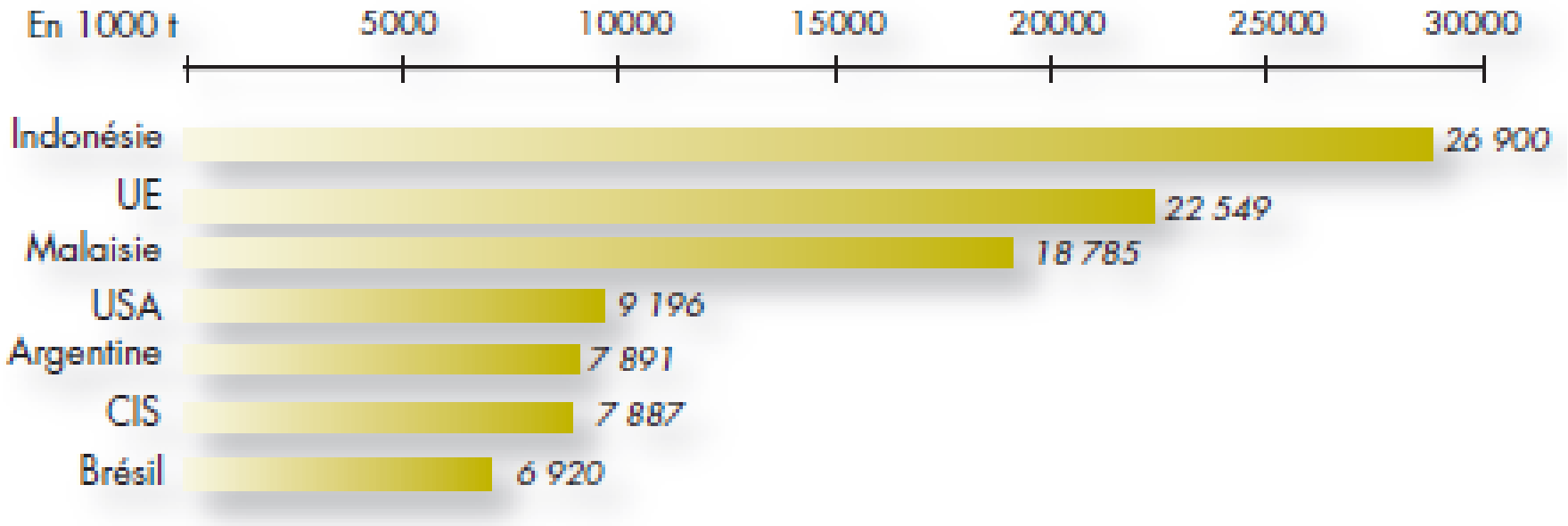
White technologies

Insects

Few socio-economic data

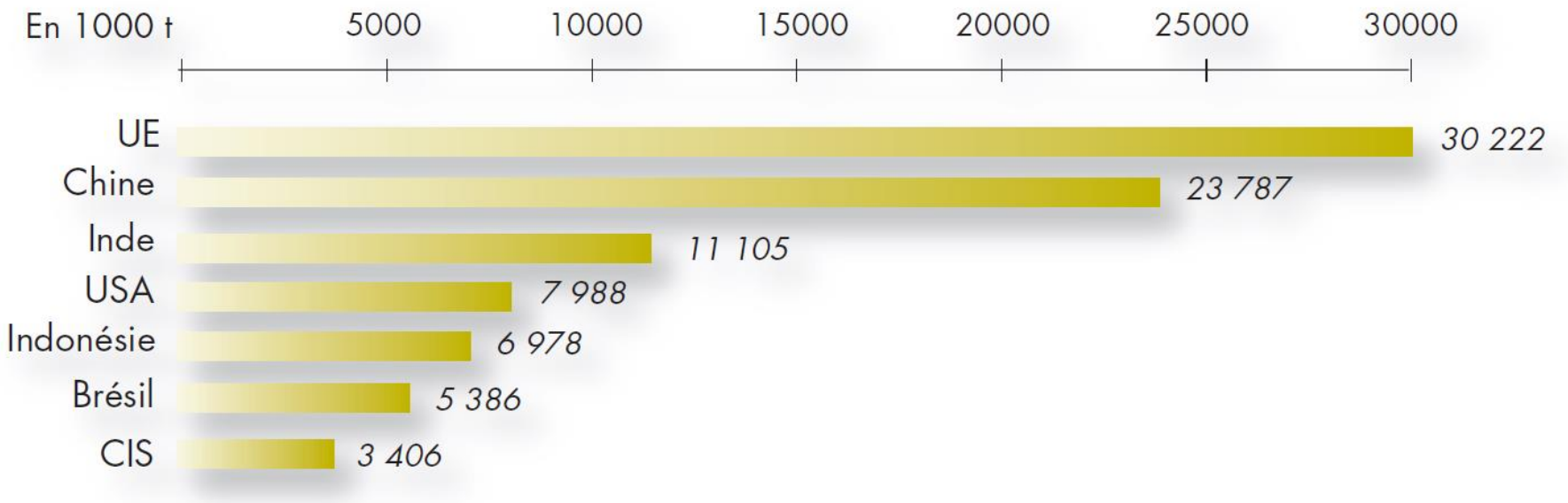
Who consume / product these oils and fats ?

Main producers worldwide 2012



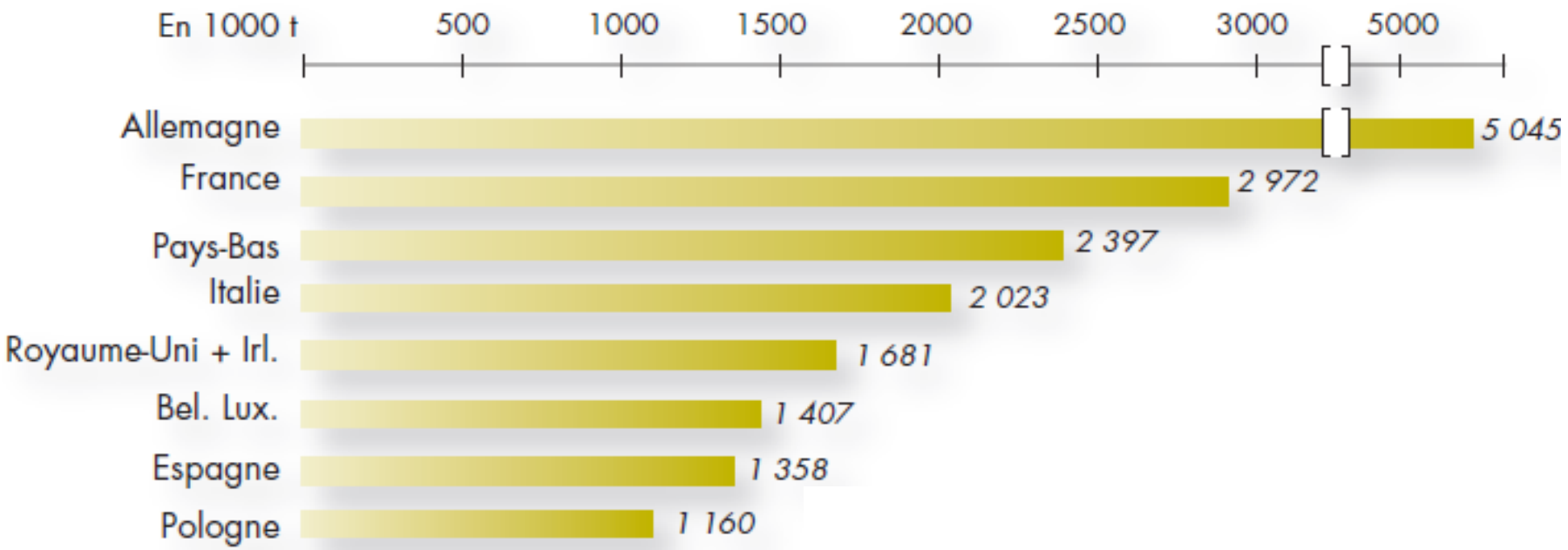
Rapport PROLEA 2012-2013 de la production à la consommation

Main consumers worldwide 2012



Rapport PROLEA 2012-2013 de la production à la consommation

Main consumers worldwidein UE 2012



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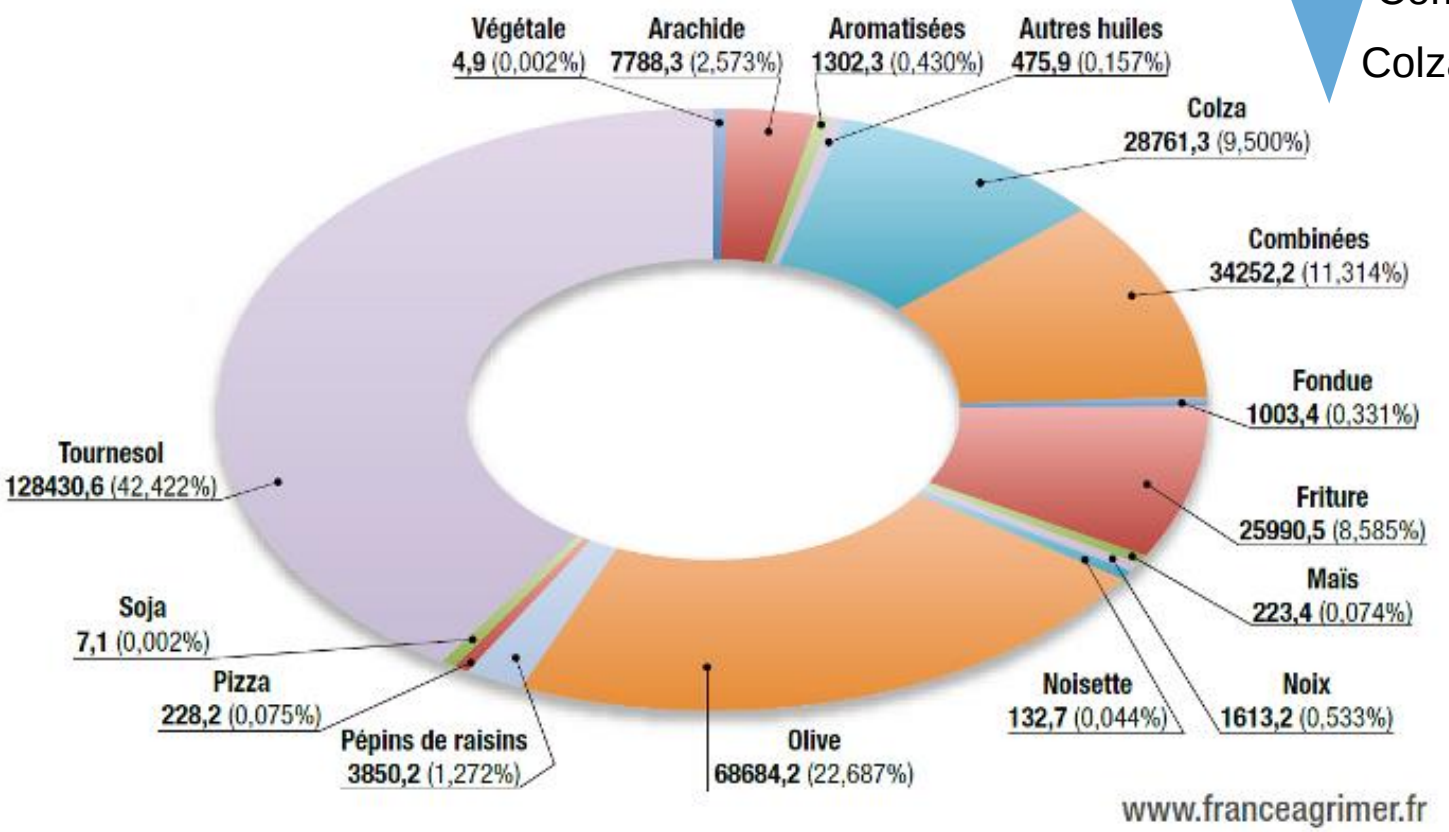
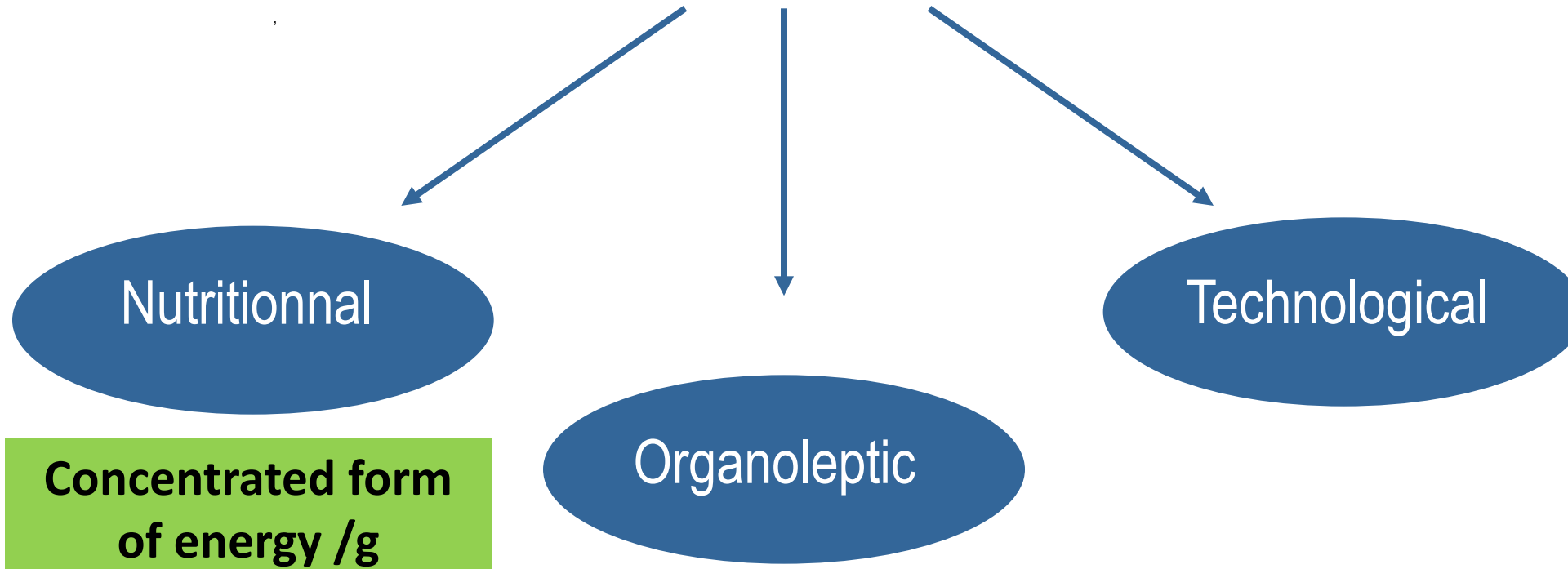
Répartition des ventes en volumes des huiles alimentaires en France (année 2011 - en 1000 tonnes. Données Nielsen)
TOTAL DES VENTES : 302 748 300 litres

Tournesol
Olive
Combined
Colza



French oil supply chain, 2012 = 6,1 Mt of transformed raw matter to produce 3,4 Mt of meals, 2,5 Mt of raw oils and 2 Mt refined oils.

2. Main part played by oil in food ?



Concentrated form of energy /g

Main part played by oil in food ?

Nutritionnal

- Energy
- Essential Fatty acids
- Precursors of prostaglandins, thromboxans, prostacycline, leucotrienes (= eicosanoids)
- Membranar constituants
- Vector of vitamines (A, D, E, K)
- phytosterols, antioxydants

Organoleptic

- Texture
- Arome carrier
- Arome precursor

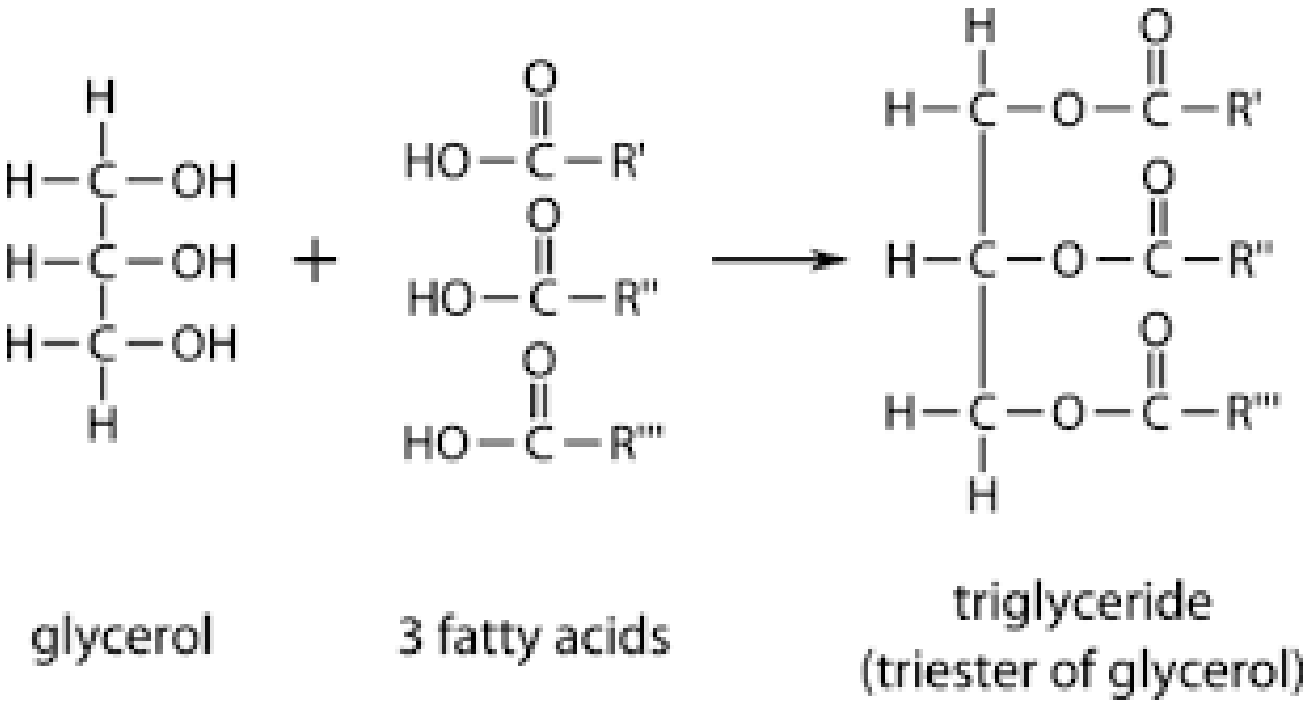
Technological

- heat transfer fluid
- Surface treatment

Main part played by oil in food ?

Nutritionnal

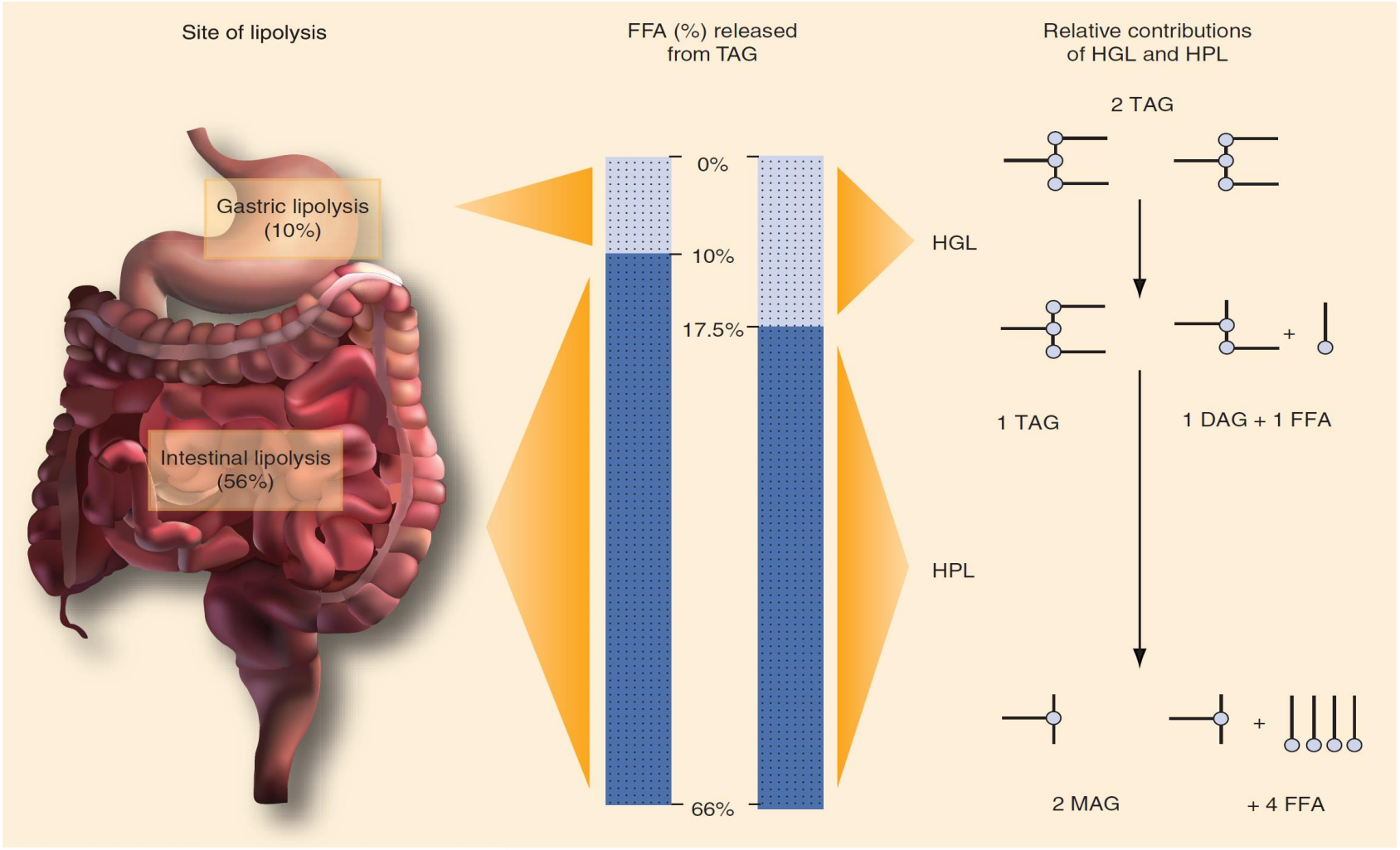
- Energy ? (**9 kcal/g**), digestibility of Triglycerides **98 %**



Main part played by oil in food ?

Nutritionnal

Respective contribution of human gastric and pancreatic lipase to dietary TAG digestion (Bakala et al., Therapeutic deivery, 2012)



DAG: Diacylglycerol; FFA: Free fatty acids; HGL: Human gastric lipase; HPL: Human pancreatic lipase; MAG: Monoacylglycerol; TAG: Triacylglycerol.

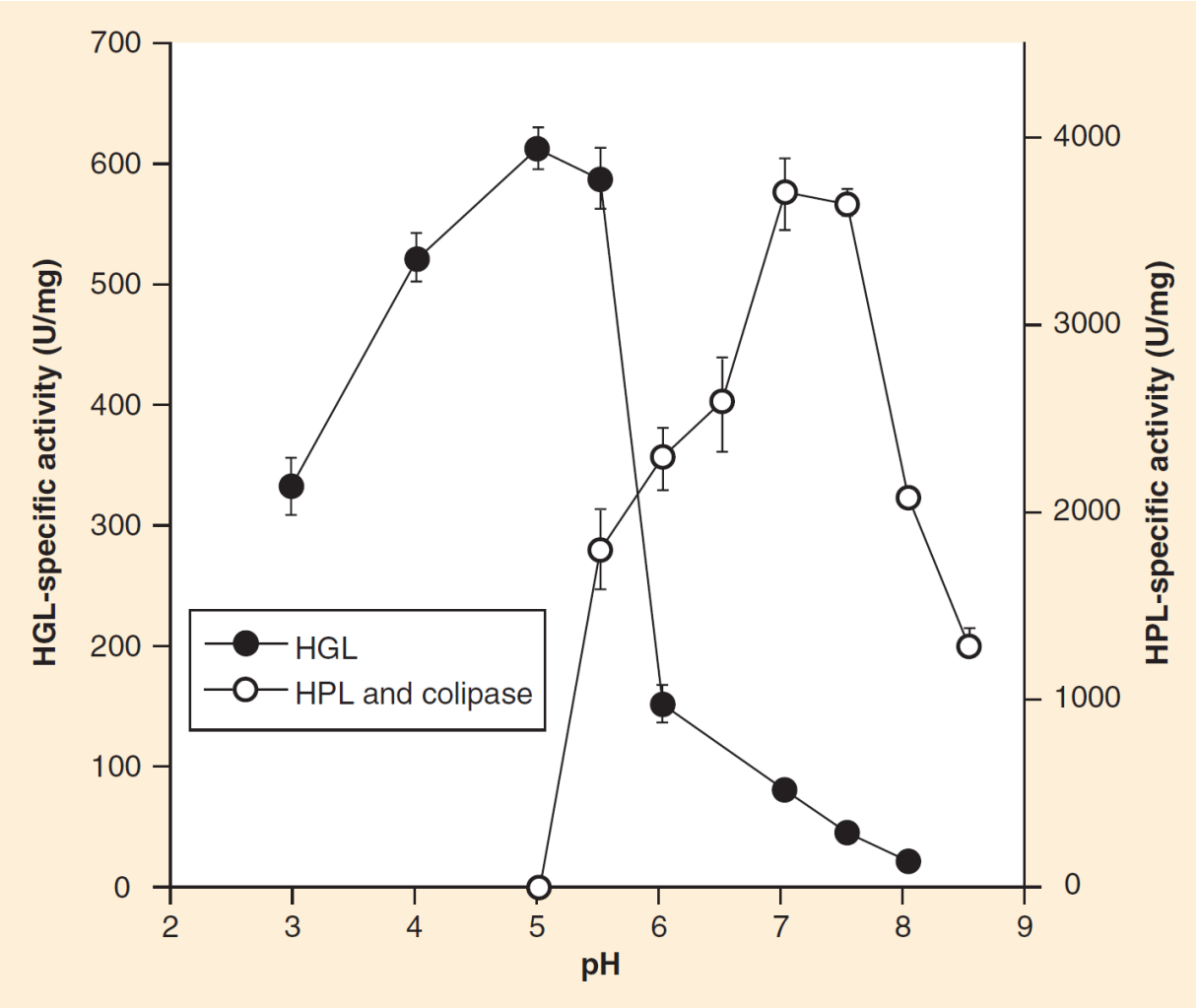
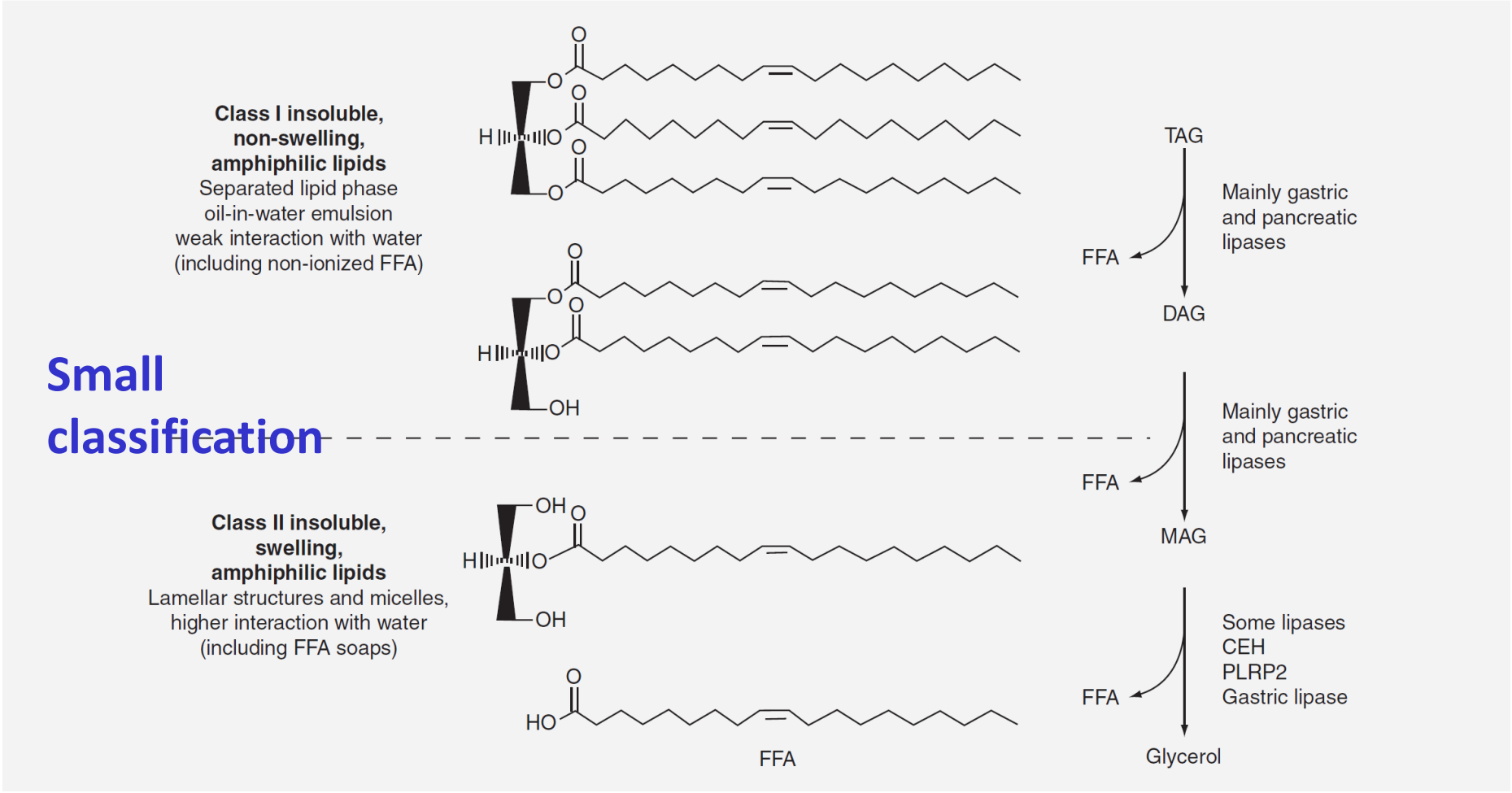
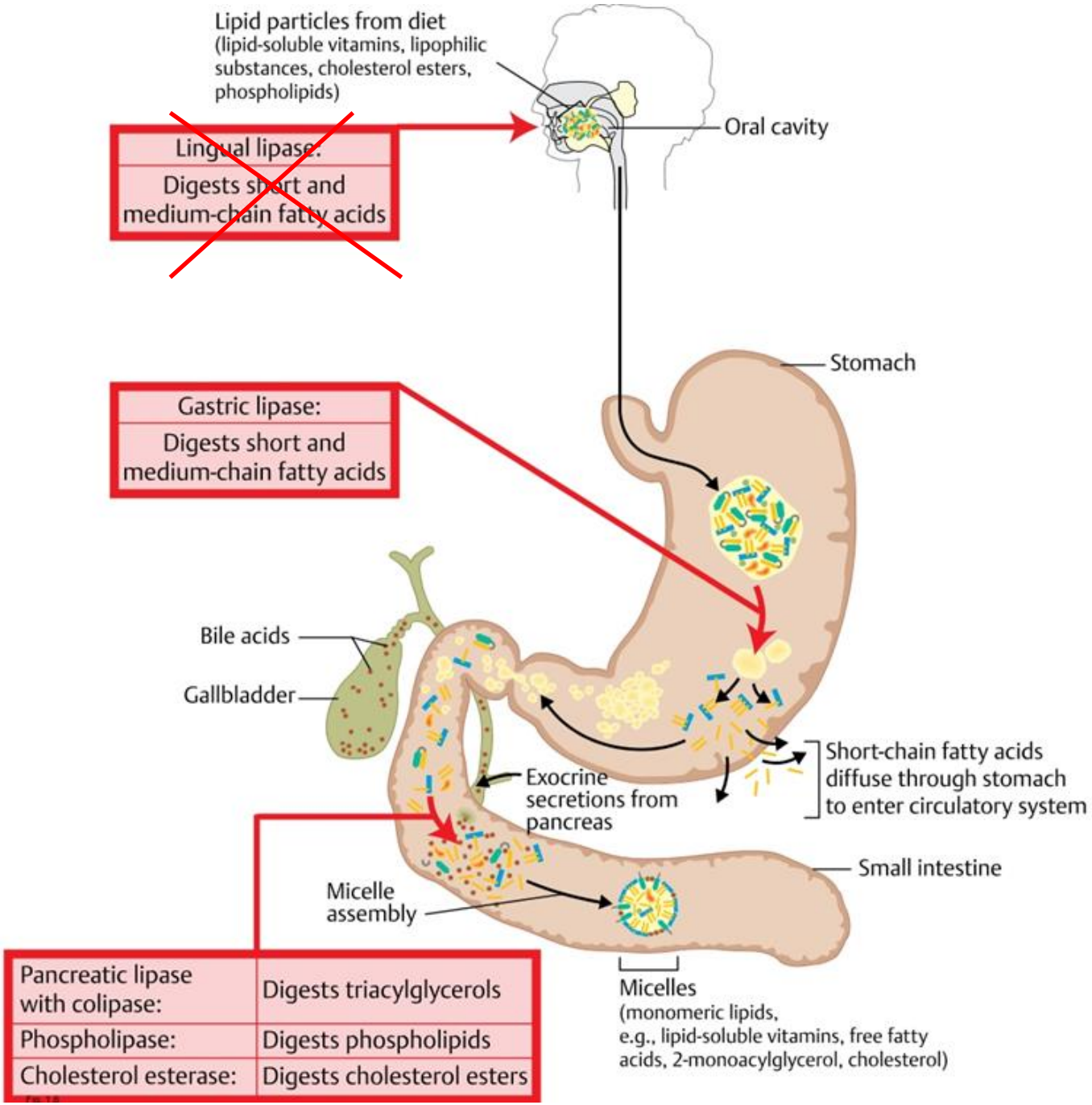


Figure 2. pH-dependent specific activities of human gastric lipases and human pancreatic lipases on long-chain triacylglycerols substrates.
The activity of purified HGL was measured using 30% Intralipid™ (soybean oil emulsified with egg lecithins) as a substrate. The activity of purified HPL and colipase was measured using olive oil emulsified with gum Arabic as a substrate. Both assays were performed in the presence of a micellar concentration of bile salts (4-mM sodium taurodeoxycholate).
HGL: Human gastric lipase; HPL; Human pancreatic lipase.

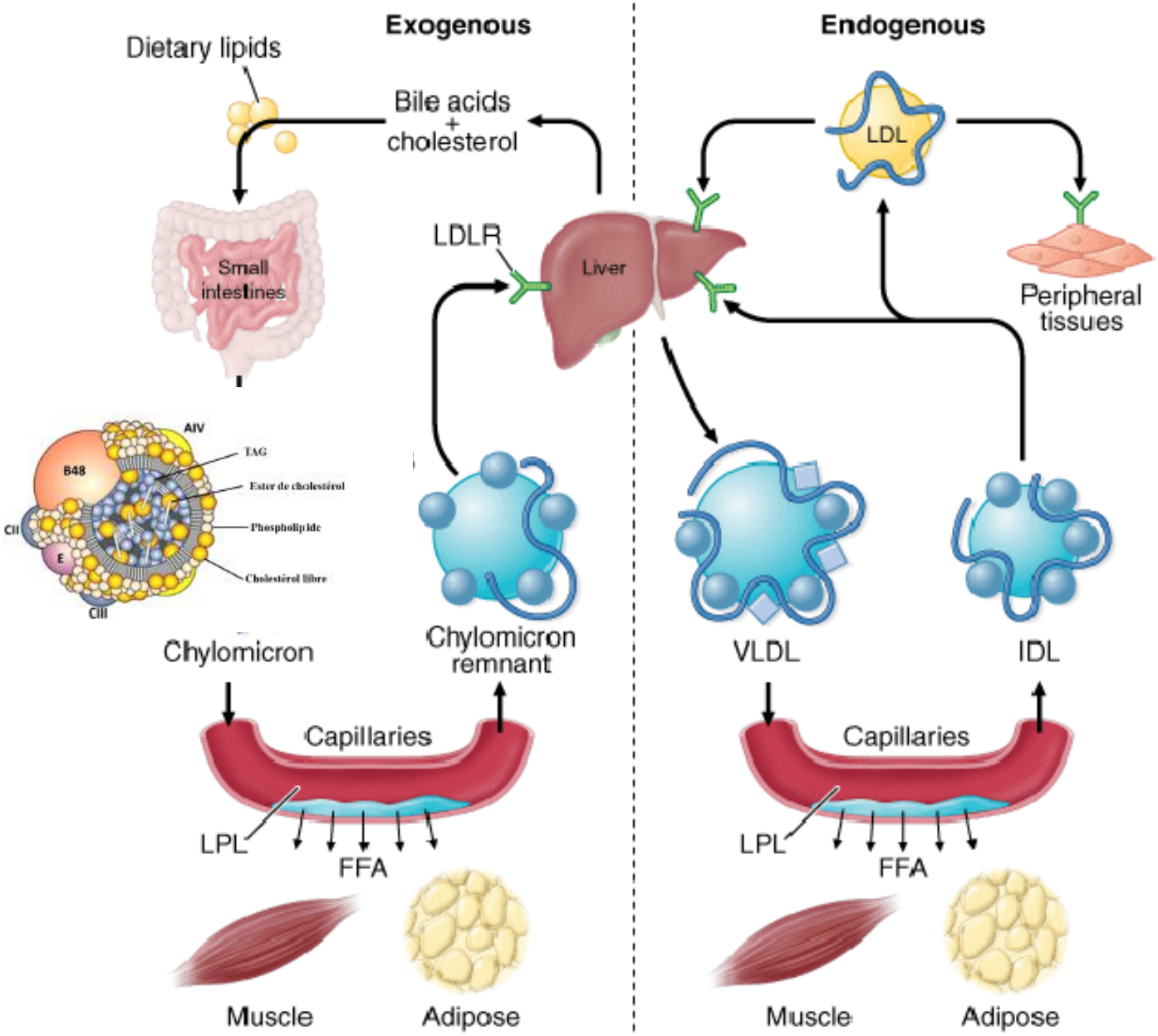
Enzymatic lipolysis of triacylglycerols by digestive lipases

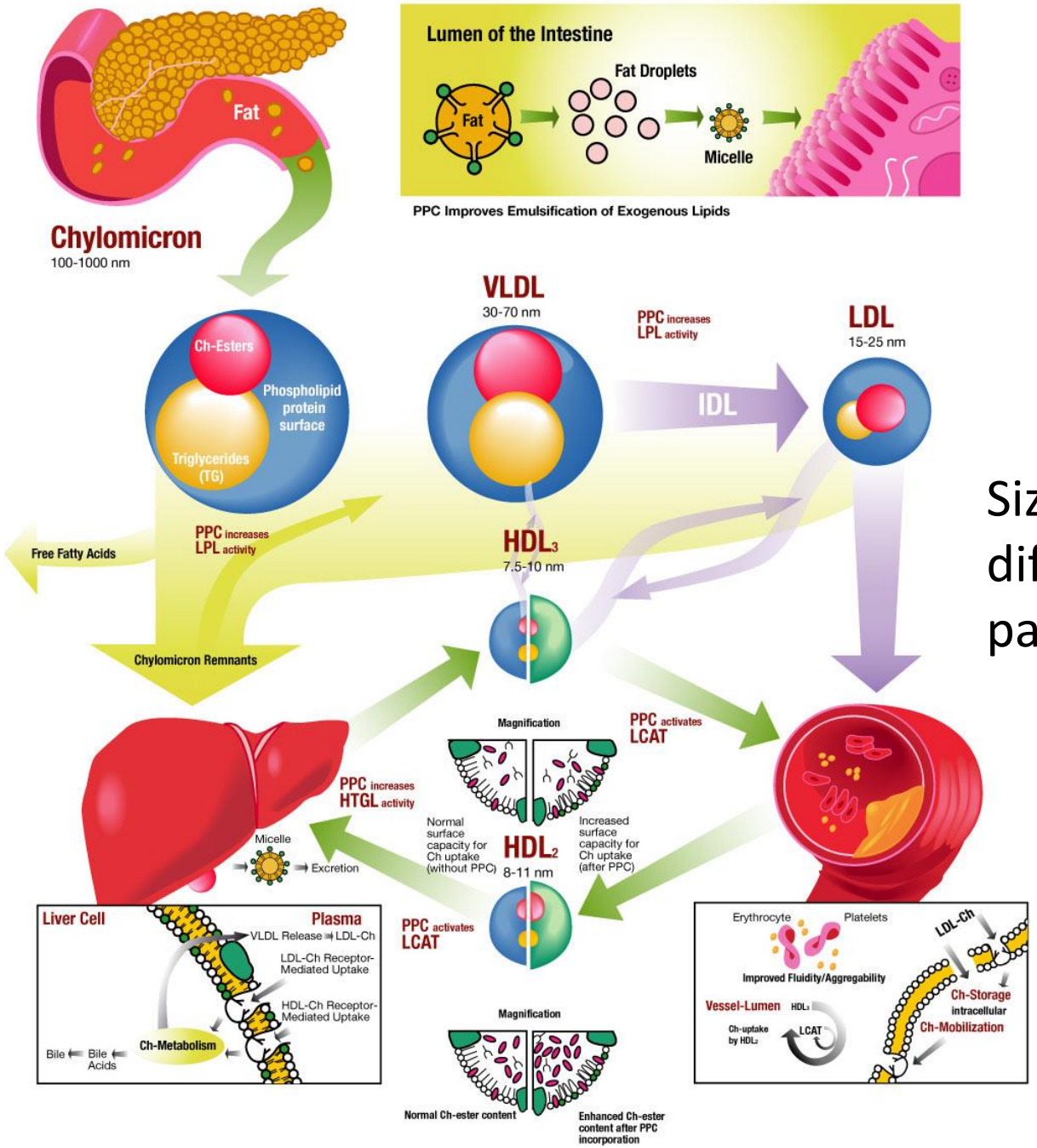


CEH: Carboxyl ester hydrolaze; DAG: Diacylglycerol; FFA: Free fatty acids; MAG: Monoacylglycerol; PLPR2: Pancreatic lipase-related protein 2; TAG: Triacylglycerol.


Lipid particles from diet
(lipid-soluble vitamins, lipophilic substances, cholesterol esters, phospholipids)
Oral cavity
Lingual lipase:
Digests short and medium-chain fatty acids
Stomach
Gastric lipase:
Digests short and medium-chain fatty acids
Bile acids
Gallbladder
Exocrine secretions from pancreas
Short-chain fatty acids diffuse through stomach to enter circulatory system
Small intestine
Micelle assembly
Micelles
(monomeric lipids, e.g., lipid-soluble vitamins, free fatty acids, 2-monoacylglycerol, cholesterol)
Pancreatic lipase with colipase: Digests triacylglycerols
Phospholipase: Digests phospholipids
Cholesterol esterase: Digests cholesterol esters

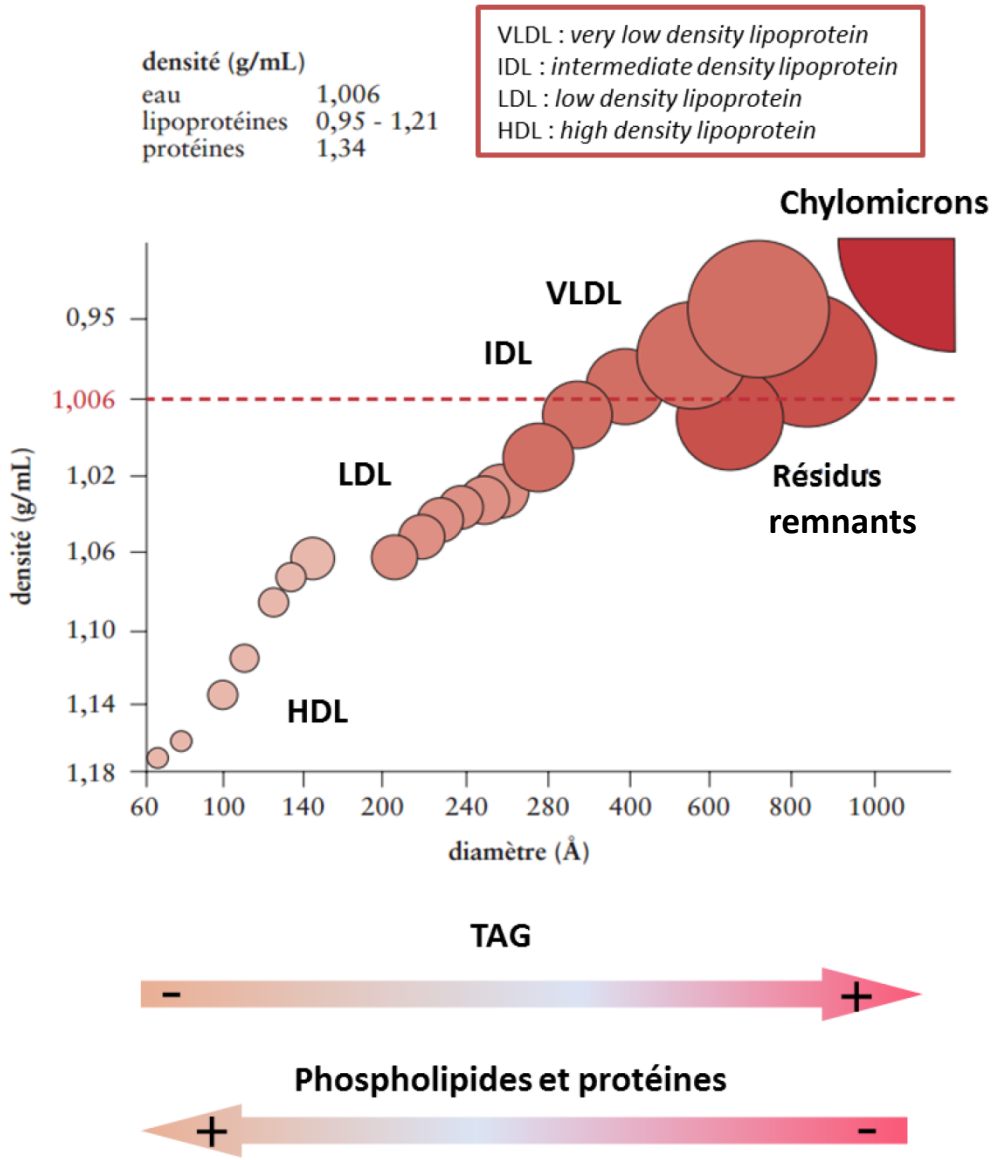
Metabolism of chylomicrons and lipoproteins





Size and traficking of different lipoprotein particles

Relation between size and density of different lipoproteins



Main part played by oil in food ?

Nutritionnal

- Energy (**9 kcal/g**), digestibility of Triglycerides **98 %**
- Essential Fatty acids (linoleic acid LA ω6 et α-linolenic acid ALA ω3)

These two fatty acids (FA) are said essential car human can not synthesize them and they have to be brought by diet

Omega-6
Polyinsaturated oils, flax, corn, safflower

4 %

Omega-3
Balck current (15%), flax (85 %)

1 %

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Omega-3
Balck current (15%), flax (85 %), hemp, colza, soya

1 %

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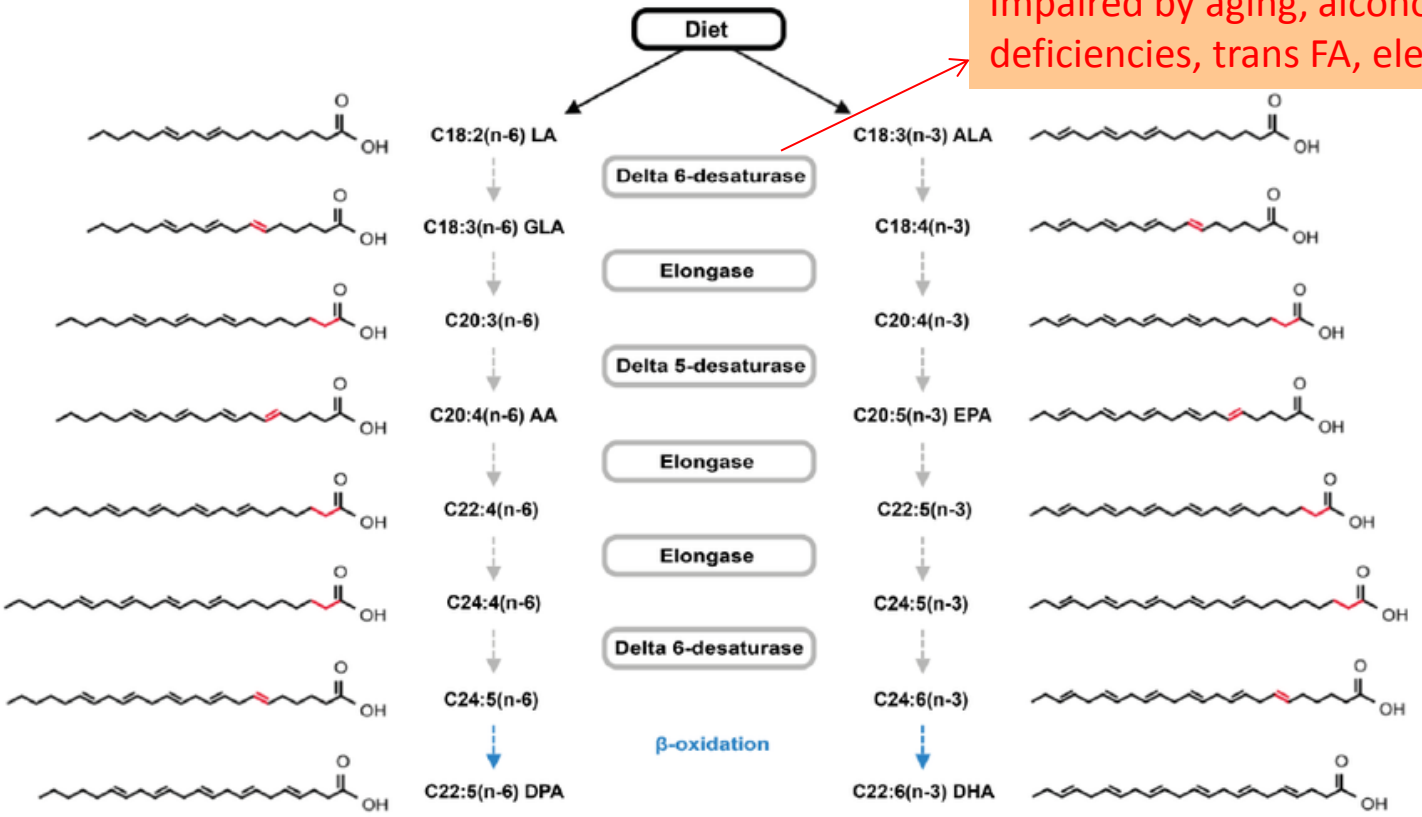

Impaired by aging, alcohol, nutrient deficiencies, trans FA, elevated cholesterol

Omega 6 and omega 3

These FA are involved in several central physiological processus:
Constitution and integrity of cellular membrane, good cardiovascular functions, cerebral functions, inflammatory and hormonal balances…

4 %

1 %

Respect $\omega 6/\omega 3 < 5$ - ANSES - saisine no 2006-SA-0359, WHO 2003

Omega 6 and omega 3

http://www.anses.fr/

Favoris | Suggested Sites | Débuter avec IE8 | Windows Live | MSN France | Aujourd'hui sur MSN | Upgrade Your Browser | News | News | Astro | Météo

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alimentation, environnement, travail

Agence nationale de sécurité sanitaire
de l'alimentation, de l'environnement et du travail

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Alimentation humaine

- Hygiène des aliments & risques biologiques
- Nutrition
- Risques physico-chimiques
- Eaux
- Etudes et enquêtes alimentaires
- Rubrique Consommateurs

Les acides gras oméga 3

Les acides gras oméga 3 appartiennent à la famille des acides gras (lipides) polyinsaturés. Ils sont dits « essentiels » car nécessaires au bon fonctionnement de l'organisme des cellules.
Le précurseur de cette famille, l'acide alpha-linolénique (ALA), est dit indispensable car il est nécessaire au développement et au bon fonctionnement du corps humain, mais que notre corps ne sait pas le fabriquer. Il doit donc obligatoirement être apporté par notre alimentation. A partir de ce composé, l'organisme synthétise d'autres acides gras omega 3, notamment les acides eicosapentaenoïque (EPA).et docosahexaénoique (DHA). Cependant, la conversion de l'ALA en DHA est trop faible pour couvrir les besoins en DHA, ce dernier est donc également considéré comme indispensable et doit être apporté par l'alimentation.

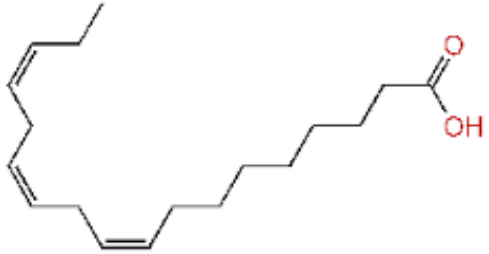
Où trouve-t-on les acides gras (AG) oméga 3 ?

Les aliments les plus riches en oméga 3 proviennent de certains **végétaux terrestres** (la noix, l'huile de colza, de soja, de lin, etc.) **et de certains animaux marins** (les poissons gras comme le saumon, le thon, le maquereau, le hareng, la sardine et l'anchois, etc.)

- Composition nutritionnelle des aliments
- Glucides
- Protéines
- Lipides
- Recommandations nutritionnelles
- Oméga 3
- Acides gras trans
- Vitamines

Omega 6 and omega 3

Omega-3



When elongated give birth to highly unsaturated FA and cellular messangers eicosanoïds

Postive effects

- composition of cell membranes
- Several biochemical process of organism : regulation of blodd pressure, vessels elasticity, immune and anti-inflammatory reactions, blood platelets agregation.

Eicosapentaenoïc (EPA) and docosahexaenoïc acids - (DHA) : present in marine products and more specifically in fatty fish (salmon, herring, tuna, mackerel, sardine…), .

Omega-3

When elongated give birth to highly unsaturated FA and cellular messangers eicosanoïds

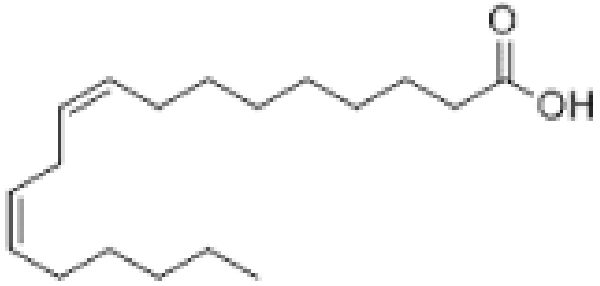
Potential health effects (ANSES, WHO)

- **Compulsory for development and functions of retina, brain and nervous system => specific requirement during gestation, breastfeeding and infancy**
- **- CV effects, can contribute to lower BP in hypertentive, decrease TAG in blood, in people presenting CV pathology can reduce morbidity and mortality WHEN COMBINED with balanced diet/ physical activity**

EPA/DHA:

- **cerebral functions and aging. Positive effect on maintaining mental health (depression, demence, Alzheimer disease)**
- **Prevention of age-related macular degeneration (AMD)**

Omega-6



Play an important part in good funtionning of nervous, cardiovascular and immunitary systems and nerveux, are central in allergic reactions, inflammatory reactions and healing processes.

Consummed in exces, omega-6 FA can :

- impair the beneficial health effects of oméga-3, notably with regards to CV protection.

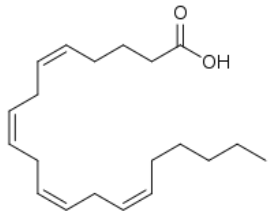
- Induce pains and inflammatory illnessess such as asthma and arthritis.

- ++ present in modern food diet: maize, sunflower, soya, carthame, grapeseed oils, etc.
- Minimal biological need in LA ~ 2 % TEI, which corresponds roughly to 4,4 g/j for a total intake of 2000 Kcal/j. ANSES => ANC à 4 % of TEI.

Gamma-linolenic acid (GLA, C18:3 *cis 6,9,12*) not to be confused with ALA (C18:3 cis 9,12,15), is synthesized by body from LA **(C18:2 *cis 9,12*)** under the action of Delta-6 desaturase.

- But conversion can get LIMITED by: excessive consumptin of cholesterol and of « bad fat » (trans, saturated, etc.), alcohol, aging, diabetes…
- Food product, direct source of GLA: borage oil (24 %), evening primrose oil (8 %), blackcurrent oil (18 % d'AGL) and spiruline.

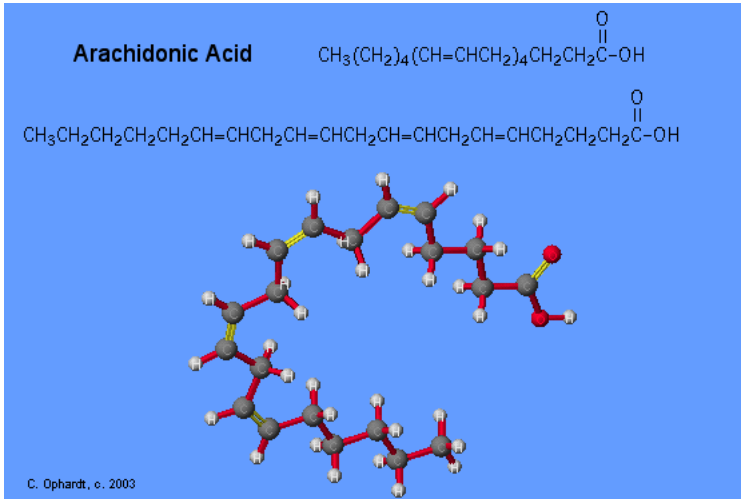
Arachidonic acid (AA, C20:4, w6). Present in PL (PE, PC, PI) in liver, muscle, brains. Key inflamatory intermediate, vaso-dilator. Egg yolk is a direct source

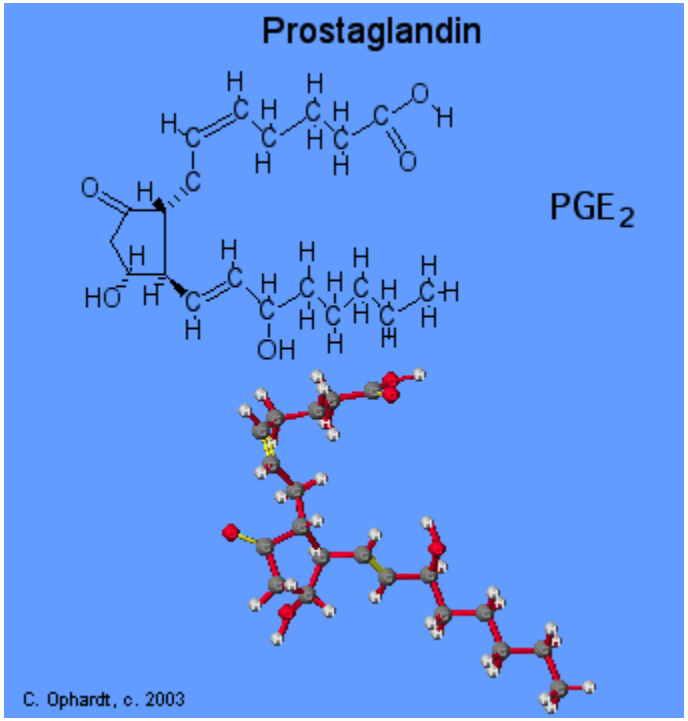


Main part played by oil in food ?

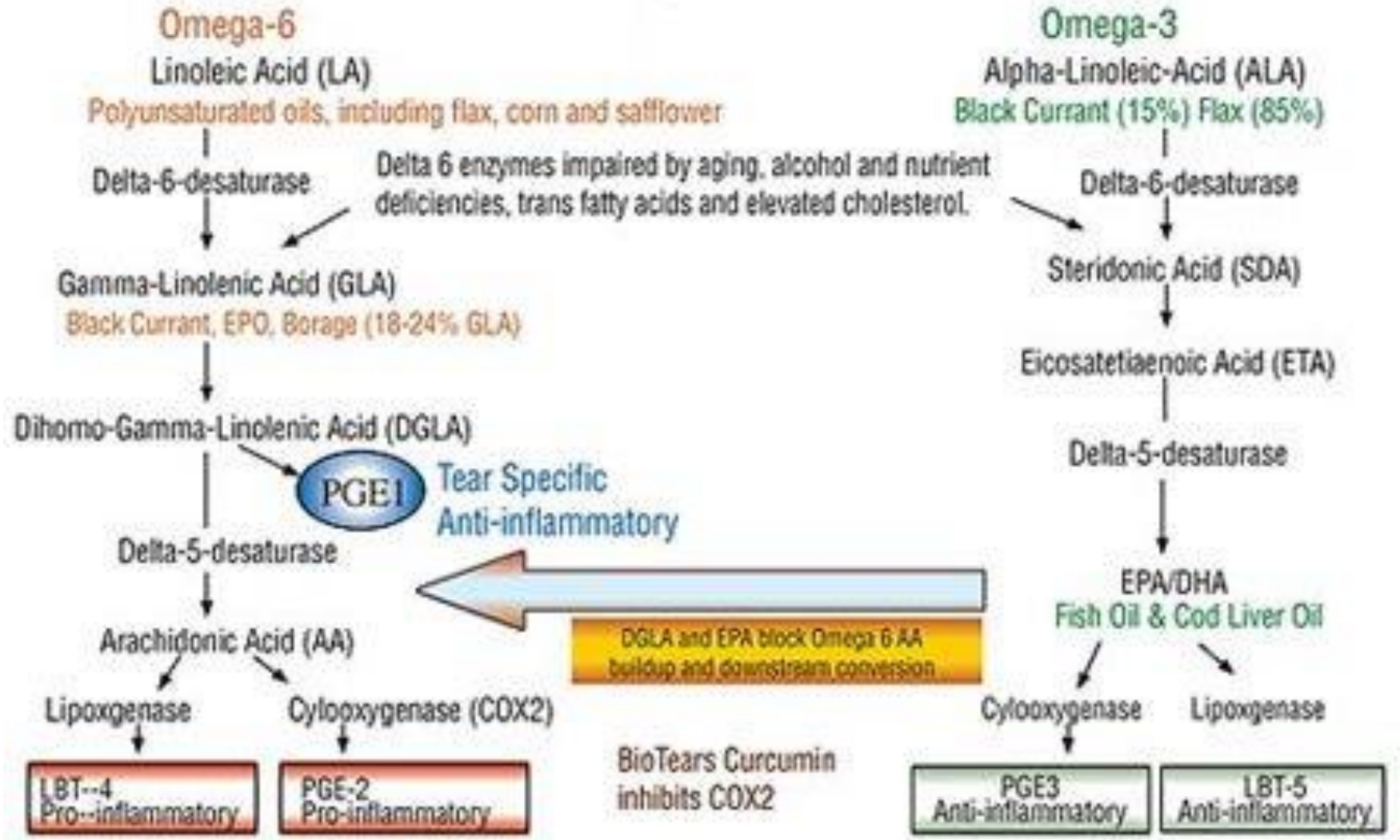
Nutritionnal

- Energy
- Essential Fatty acids
- Precursors of prostaglandins, thromboxans, prostacycline, leucotrienes (= eicosanoids)





Metabolic Pathways of Omega-3 and Omega-6 Fatty Acids

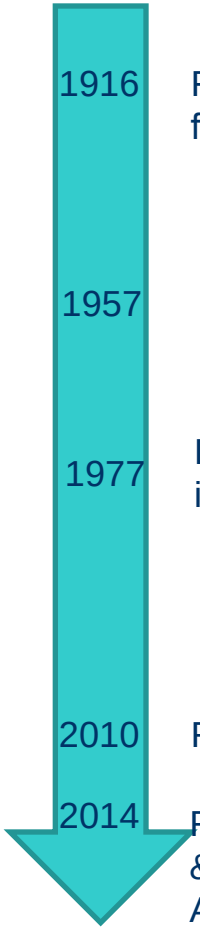


Brief history of lipid nutritionnal recommandations

1957. The '**seven country studies**'. Keys et al. JAMA. 164:1912-1919.

→ apparent link between consumption of saturated fat, cholesterol and CV

Brief history of lipid nutritionnal recommandations



1916 First American food guide 5 groups : 1) meat, milk, other ; 2) cereales, others ; 3) fruits and vegetables ; 4) lipids ; 5) sugar. Lipids ≤ 30 % total

1957 The ‘seven country studies’. Keys et al. JAMA. 164:1912-1919. apparent link between satuated fat consumption and CV pbs

1977 Dietaries goals for the USA. Fat and saturated FA => main nutritionnal risk factors that could induce chronic ilnesses and CV risk (lipides **40 => 30** and AGS de 16 à 10 %)

Substitution of lipids by carbohydate => prevalence of overweight/ obesity in USA 70.7 % (**2013–2014 NHANES Data)**

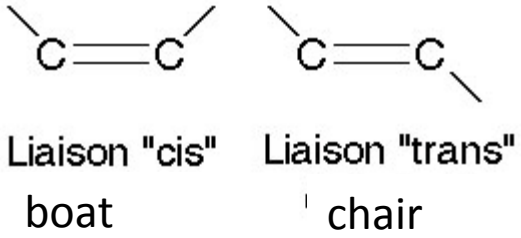
2010 Re-assesment of RDA for lîpids / ANSES

2014 Relative international consensus for total lipids ~ 35 % calories / limits for SFA but (Lamarche & Couture. 2014.39:1409-1411)
ANSES, 2010 : 35-40%

Brief history of lipid nutritionnal recommandations

Fatty acids	RDA (% TEI)		% TFA
essential	LA (C18:2, ω6)	4 %	10-12 %
	ALA (C18:3, ω3)	1 %	2.5-3 %
	Docosahexaenoic acid, DHA (C22:6 ω3)	250 mg	
	Eicosapentaenoic acid, EPA (C20:5 ω3)	250 mg	
Non essential	Lauric + myristic + palmitic FA	≤ 8 %	**20-23 %**
	Total saturated FA	**≤12 %**	**30-34 %**
	Oleic FA (C18:1, ω9)	15-20 %	38-50 %

FA trans < 1% TEI

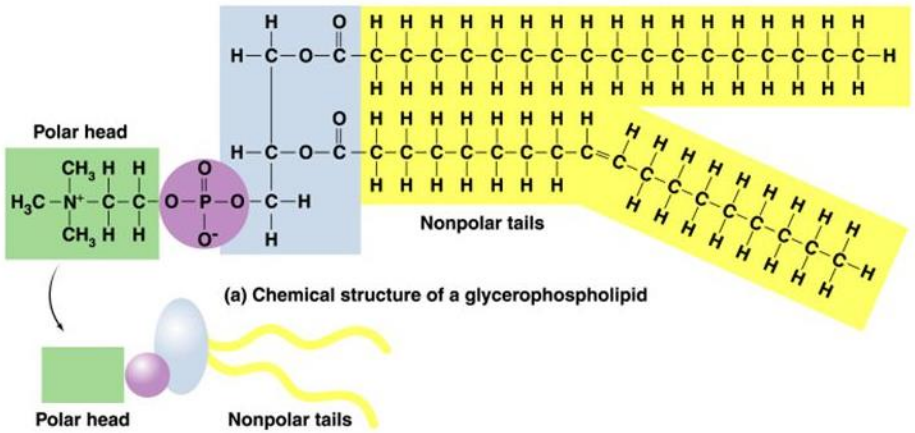


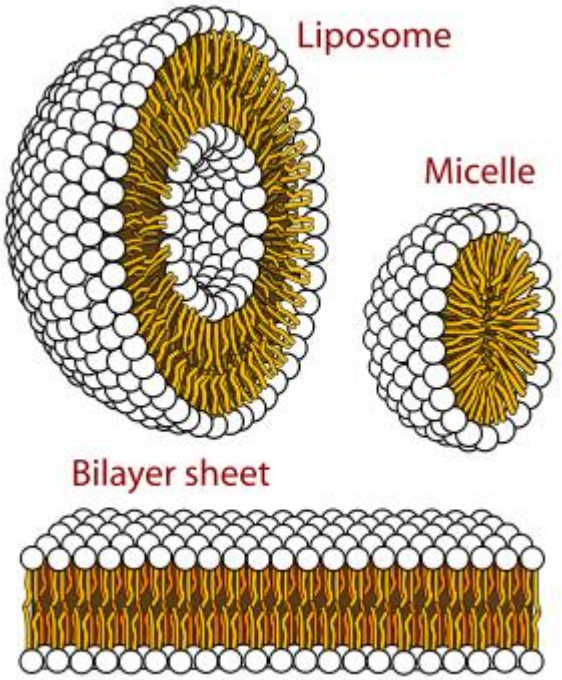
2010. Re-assesment of RDA for FA / ANSES

Main part played by oil in food ?

Nutritionnal

- Energy
- Essential Fatty acids
- Precursors of prostaglandins, thromboxans, prostacycline, leucotrienes (= eicosanoids)
- Membranar constituants





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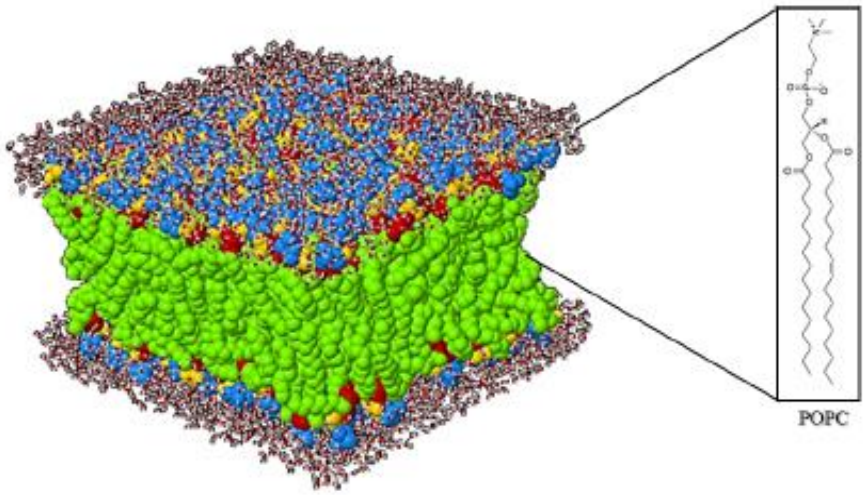

Simulation numérique représentant l'architecture d'une bicouche de 200 molécules de POPC (1-palmitoyl-2-oleoyl-phosphatidylcholine), en présence de molécules d'eau. Les acides gras sont colorés en vert, le glycérol en rouge, la partie phosphate en jaune et la choline en bleu. Les molécules d'eau apparaissent en bâtonnets.

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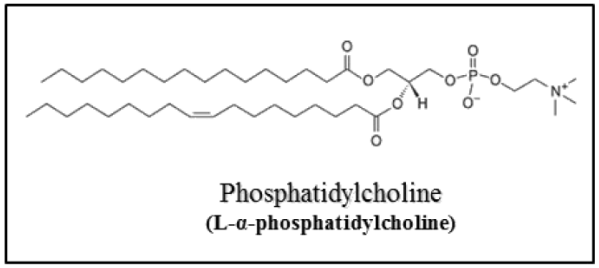
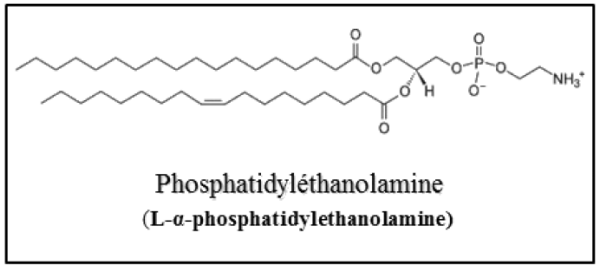
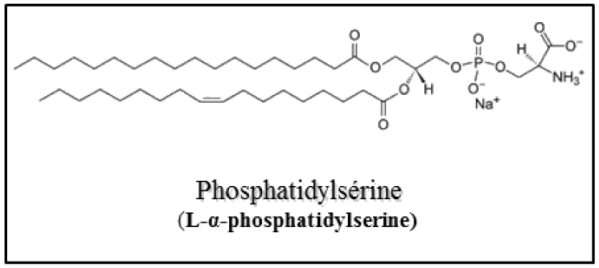


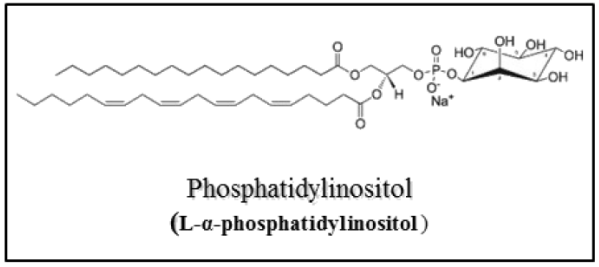
Phosphatidylcholine
(L-α-phosphatidylcholine)



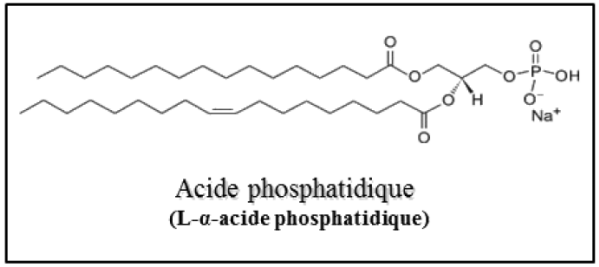
Phosphatidyléthanolamine
(L-α-phosphatidylethanolamine)



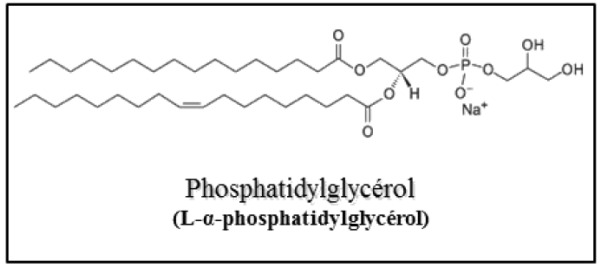
Phosphatidylsérine
(L-α-phosphatidylserine)



Phosphatidylinositol
(L-α-phosphatidylinositol)

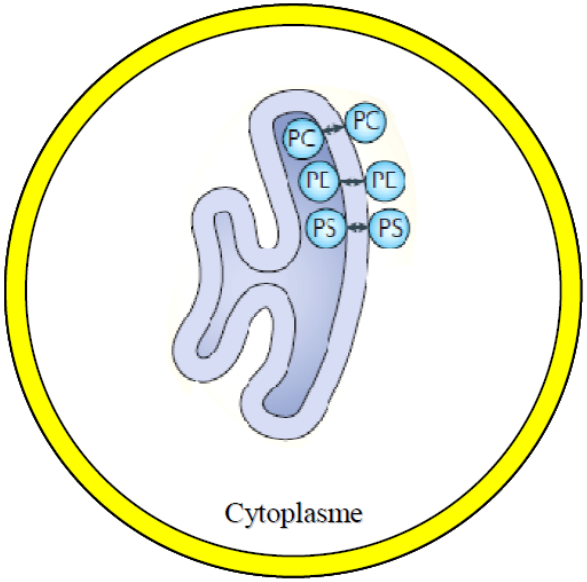


Acide phosphatidique
(L-α-acide phosphatidique)

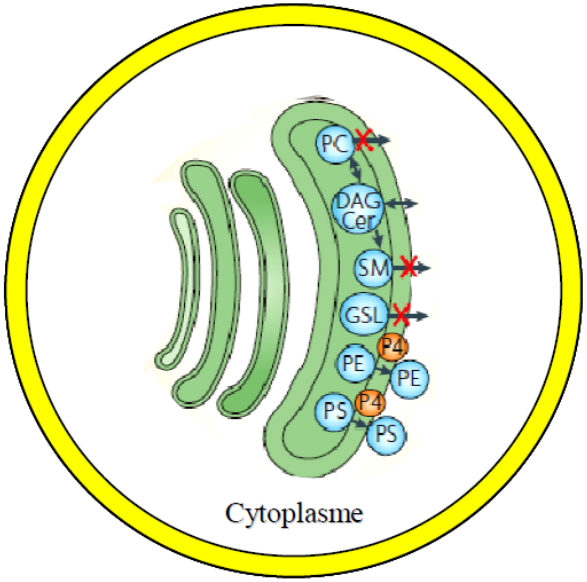


Phosphatidylglycérol
(L-α-phosphatidylglycérol)

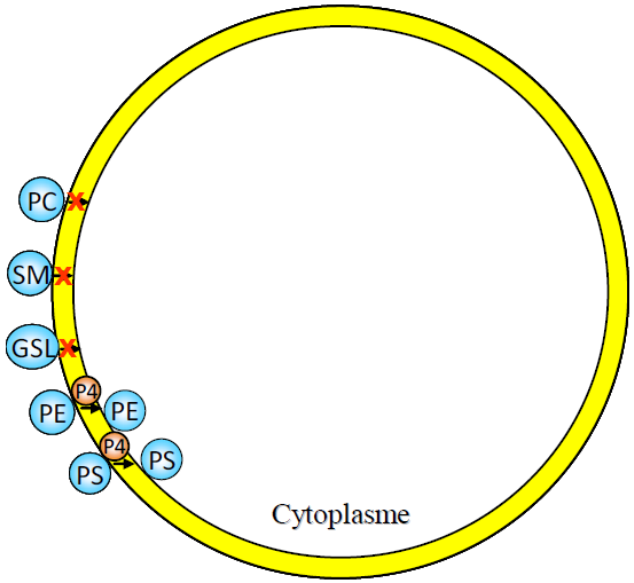
A. Réticulum endoplasmique



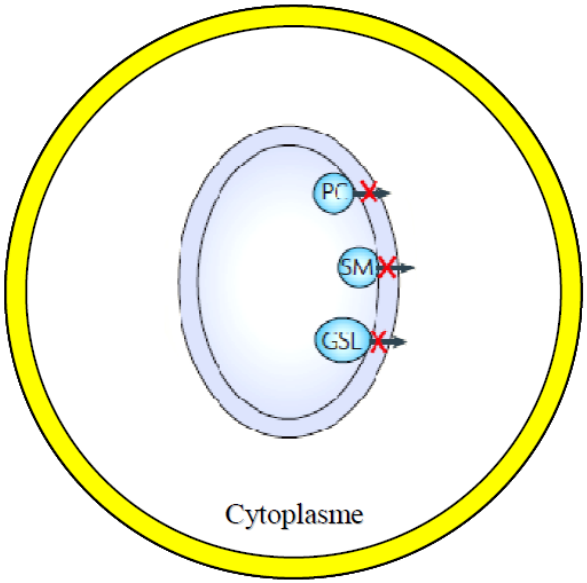
B. Golgi



C. Membrane plasmique



D. Endosomes



- **SOURCES of PL**

TABLE I. *Relative phospholipid composition (%) in different commercial sources of lecithin products*[a]

	Soya	Egg	Milk
PC	34	75	27
PE	21	15	25
PI	18	0,4	8
SM	0	1.5	24
PS	0.5	0	12
PA	9	0	0
Others	17.5	8.1	4

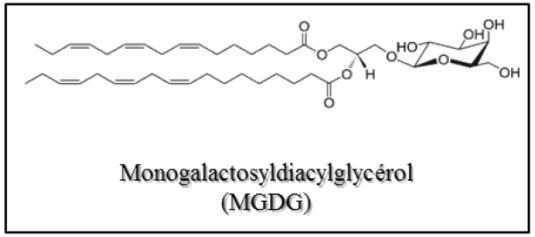
Burling et al. Inform 2009

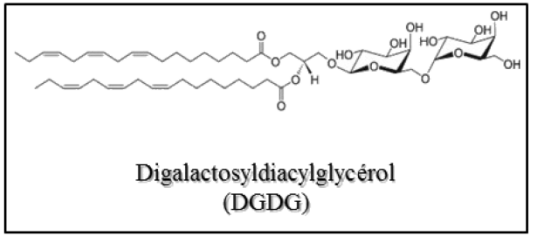
Tons/an : **200 000** **300**

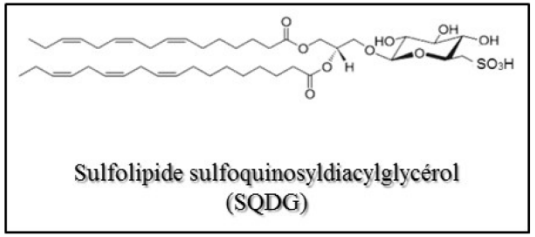
Main part played by oil in food ?

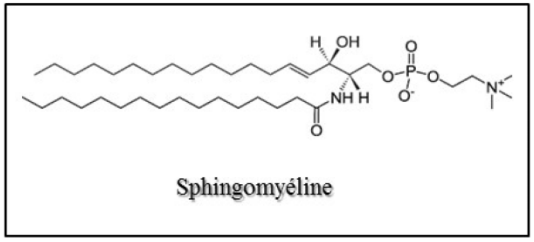
Nutritionnal

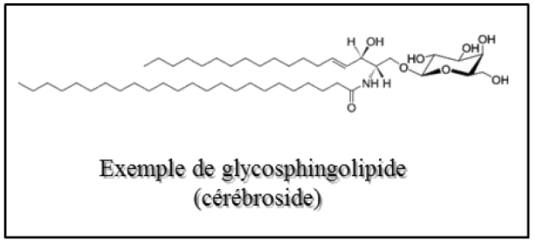
- Energy
- Essential Fatty acids
- Precursors of prostaglandins, thromboxans, prostacycline, leucotrienes (= eicosanoids)
- Membranar constituants

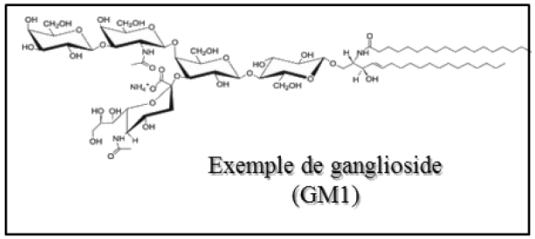

Monogalactosyldiacylglycérol
(MGDG)

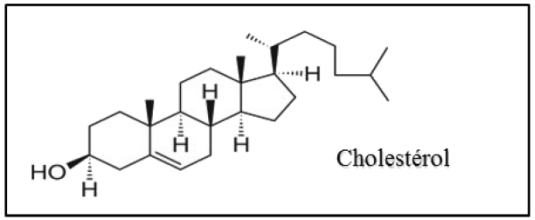

Digalactosyldiacylglycérol
(DGDG)

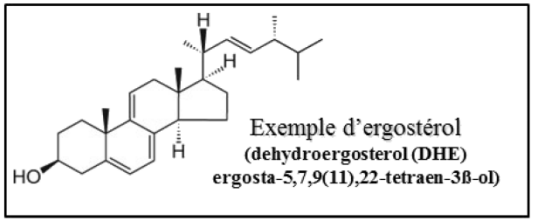

Sulfolipide sulfoquinosyldiacylglycérol
(SQDG)


Sphingomyéline


Exemple de glycosphingolipide
(cérébroside)

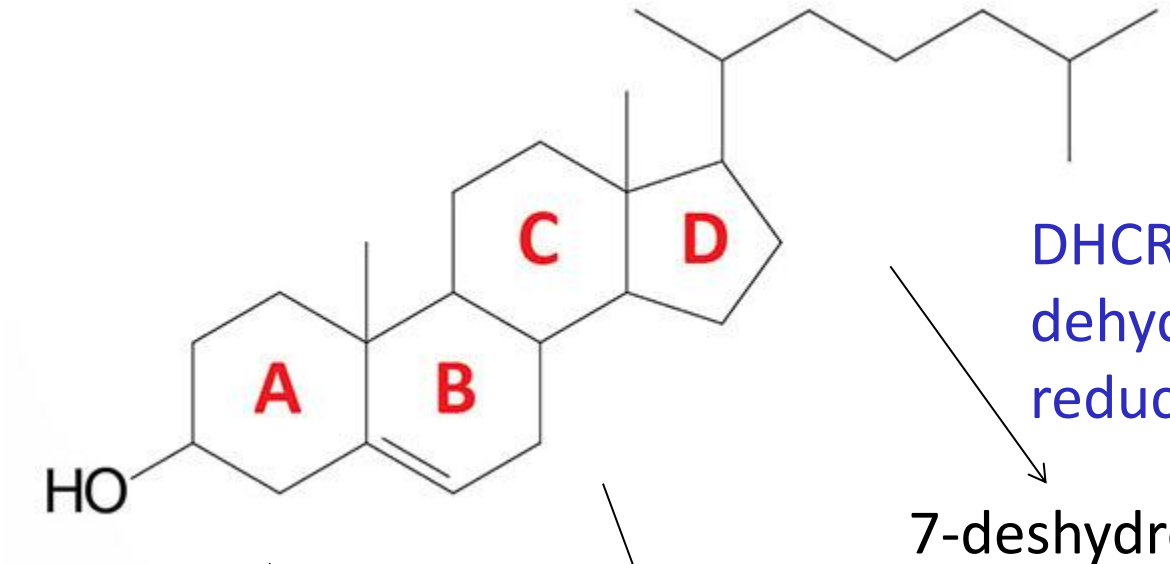

Exemple de ganglioside
(GM1)


Cholestérol


Exemple d'ergostérol
(dehydroergosterol (DHE)
ergosta-5,7,9(11),22-tetraen-3ß-ol)

Cholesterol and cholesterol esters

Cholesterol is an extremely important biological molecule that has roles in membrane structure as well as being a precursor for the synthesis of the steroid hormones, the bile acids, and vitamin D



DHCR7: 7-dehydrocholesterol reductase.

7-deshydrocholesterol

Gonads
adrenals

+++ Biliary salts

Steroids

Vitamine D

Cholesterol and cholesterol esters

De novo biosynsthesis, 2/3 of total (liver and intestine), 1/3 dietary

Healthy adults synthesize cholesterol at a rate of ~1g/day, consumption 0.3 g/day. A relatively constant level of cholesterol in the blood (150–200 mg/dL) is maintained primarily by controlling the level of *de novo* synthesis.

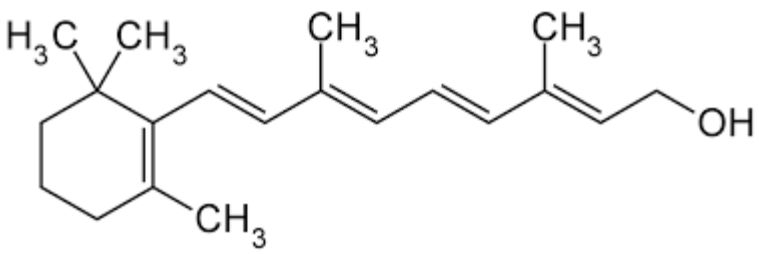
3 distinct mechanisms of regulation:
1. Regulation of Hydroxyméthylglutaryl-CoA réductase activity and levels (oxydoreductase statine target)
2. Regulation of excess intracellular free cholesterol through the activity of sterol O-acyltransferases, SOAT1 and SOAT2
3. Regulation of plasma cholesterol levels via LDL receptor-mediated uptake and HDL-mediated reverse transport (to liver).

Main part played by oil in food ?

Nutritionnal

- Energy
- Essential Fatty acids
- Precursors of prostaglandins, thromboxans, prostacycline, leucotrienes (= eicosanoids)
- Membranar constituants
- Vector of vitamines (A, D, E, K)

Vitamin A



Main functions:

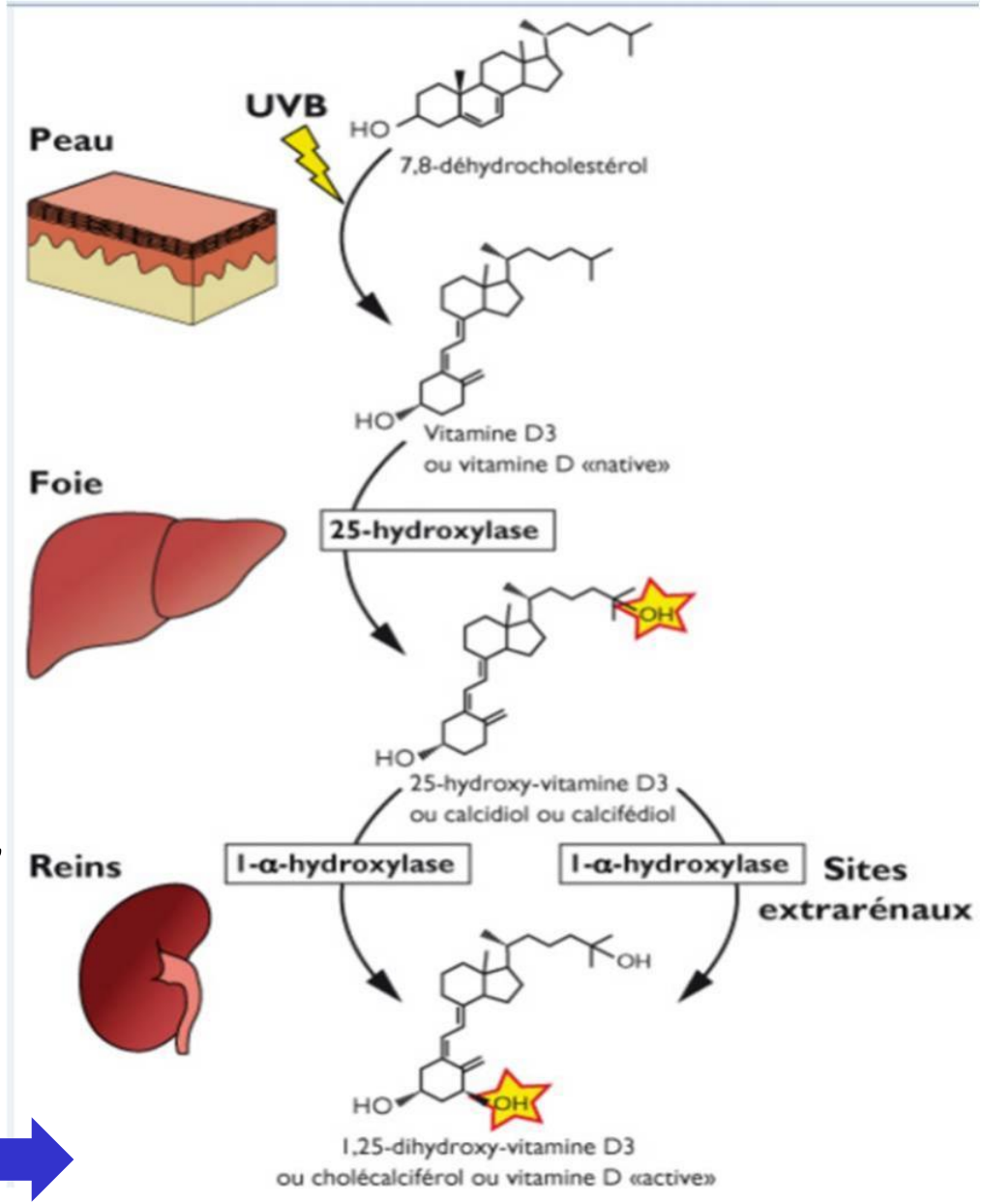
Visual: helping the eyes adjust to light changes, bone growth, tooth development, reproduction, cell division, gene expression, and regulation of the immune system. Hydration of skin, eyes, and mucous membranes of the mouth, nose, throat and lungs prevention of certain cancers.

Recommended Dietary Allowance (RDA): 900 µg/ day for adult males and 700 mcg/day for adult females, expressed µg of retinol activity equivalents (RAE). => body converts only a portion of betacarotene to retinol. 1 RAE = 1 µg of retinol =12 µg beta-carotene.

Vitamin D

Main functions:
- use of calcium and phosphorous. ↗ amount of calcium absorbed from the small intestine and reabsorption by kidneys
-immunity and controlling cell growth.
-Children : bone development, teeth.

90 % of conversion under UVB



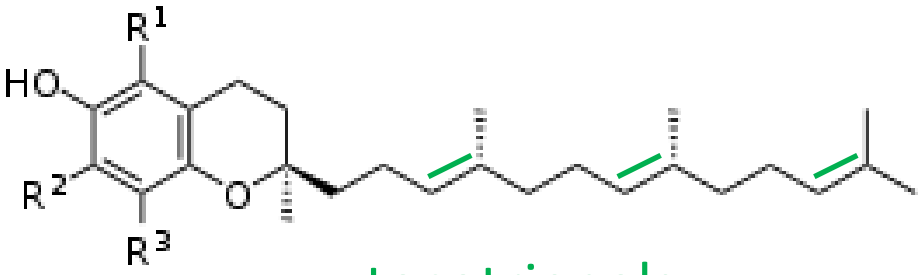
Vitamin D

RDA:
-0-12 months 10 µg cholecalciferol (vitamin D3)
- From 12 months to 50 y =15 µg
-20 µg = 800 International Units (IU), recommendation for maintenance of healthy bone for adults >50
- Special needs: exclusively breast-fed infants: Human milk 25 IU /L, Dark Skin, Covered and protected skin, illnesses (Fat malabsorption syndromes, inflammatory bowel disease (IBD), obesity)

10 % from food

Aliments	Vitamine D (UI)
Huile de foie de morue (une cuillère à soupe)	400 - 1 000
Saumon sauvage (100g)	800
Sardine (100g)	300
Maquereau (100g)	250
Thon (100g)	230
Saumon d'élevage (100g)	200
Lait enrichi en vitamine D (un grand verre)	100
Jaune d'œuf	20

Vitamin E: Tocopherol



tocotrienols

R1	R2	R3	Name
CH3	CH3	CH3	α-tocopherol
CH3	H	CH3	β-tocopherol
H	CH3	CH3	γ-tocopherol
H	H	CH3	δ-tocopherol

Main functions:

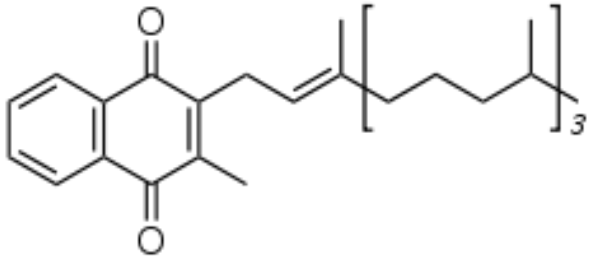
antioxidant, and protecting vitamins A and C, red blood cells, and essential fatty acids from destruction

Recommended Dietary Allowance (RDA):

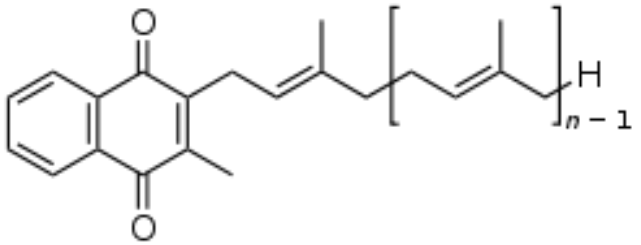
- males and females >14, 15 µg of alpha-tocopherol per day.
- Expressed in the most active and used form => alpha-tocopherol.

1 mg alpha-tocopherol=1.5 International Units (IU).

Vitamin K:



vitamine K1 (phylloquinone)



vitamine K2 (ménaquinones)

Main functions:

- Blood clotting, naturally produced by the bacteria in the intestines,
- bone health
- post-traductional modification of proteins for blood, bones, and kidneys.

Recommended Dietary Allowance (RDA):

- males and females >18, resp. 120 and 90 µg of Vit K
- Highly dependent on age, 0-6 mo 2 µg, 6-12 mo 2.5 µg

A common controversial subject

Nutritionnal aspect of palm OIL

Nutritionnal aspect of palm OIL

- Concrete oil. Solid at ambiant temperature since rich in SFA

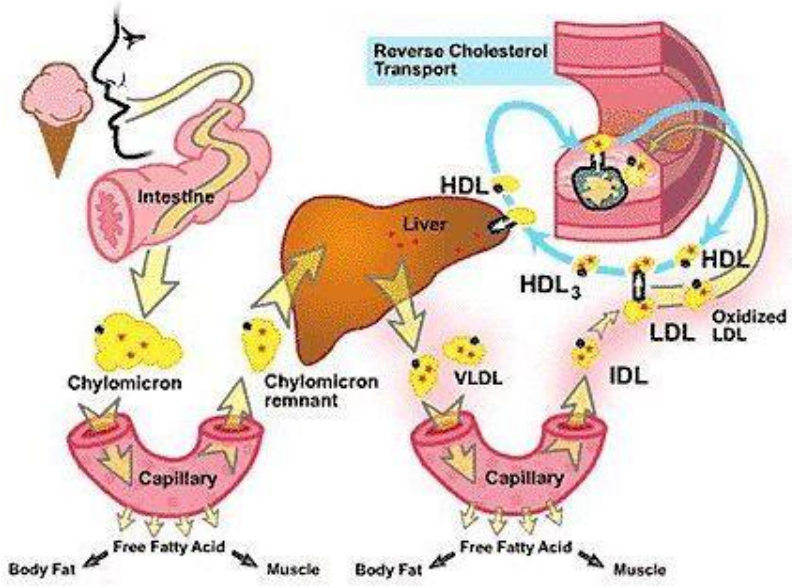
Acides gras saturés	**45-55**
Acide laurique C12:0	< 0,5
Acide myristique C14:0	0,5 – 2
Acide palmitique C16:0	39,5 – 47,5
Acide stéarique C18:0	3,5 – 6
Acides gras monoinsaturés	**38-45**
Acide oléique C18:1n-9	36 – 44
Acides gras polyinsaturés	**9-12**
Acide linoléique C18:2n-6	9 – 12
Acide αlinolénique C18:3n-3	< 0,5

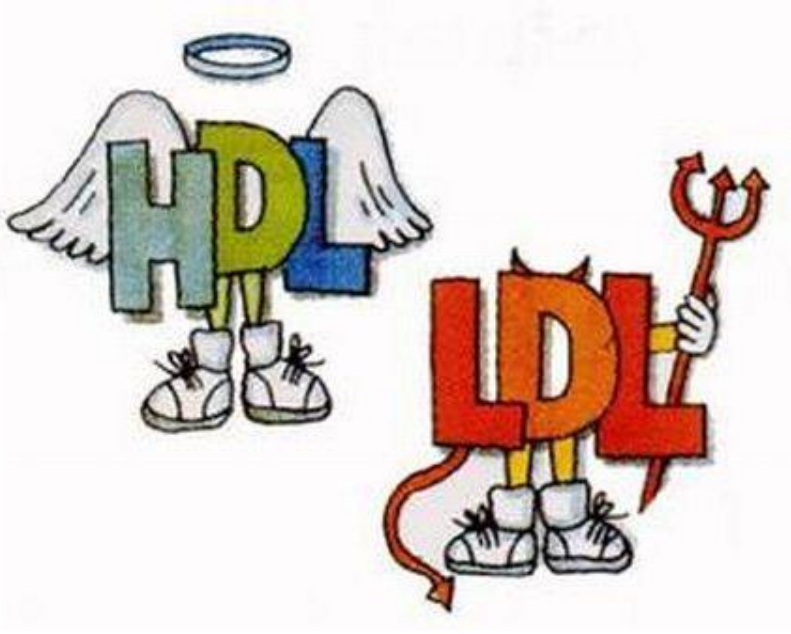
- Palmitic acid dominant : group atherogenic in exces with lauric and myristic ≤ 8 % TEI (total satured ≤ 12 % TEI)
- Only 11 % of palmitic in central sn-2 position, less aborbed in external position

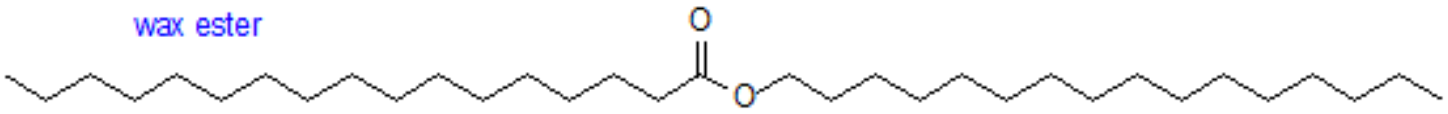
Nutritionnal aspect of palm OIL

- Increase of cholesterol LDL (less than coprah oil) and less of HDL

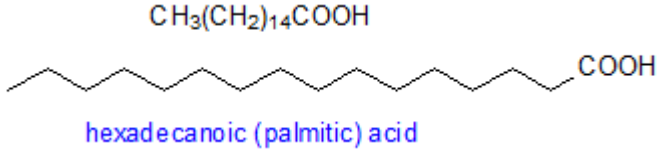
- Moderate effect on plasma lipids can be explained by minor compounds : E vitamin E, carotenoïdes, phytosterols, phenolic compounds.

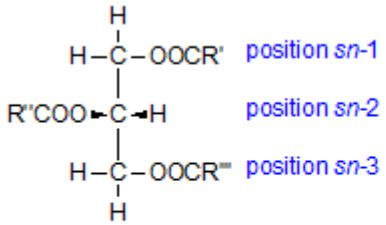




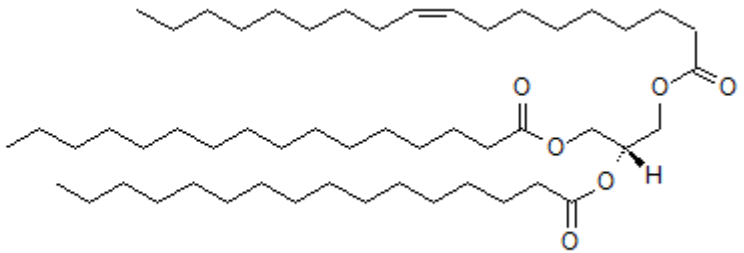


3. BIOCHIMIE and ANALYSIS OF LIPIDS





Fischer projection of a triacyl-*sn*-glycerol

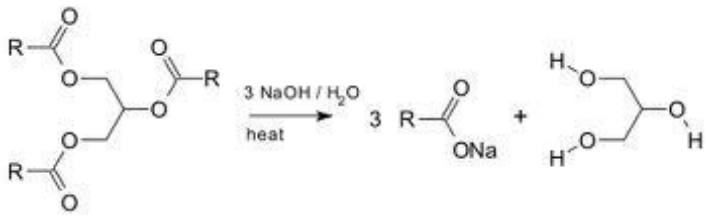


1,2-dihexadecanoyl-3-(9Z-octadecenyl)-*sn*-glycerol

LIPID FRACTION

Lipids —(OH^-)→ Aqueous phase (FA salts, ...)
Lipids —(OH^-)→ Phase insoluble in water

Saponifiables	Unsaponifiables
• Glycerides (>90%) - TAG - DAG - MAG • Free FA • Phospholipids • Waxes, cutins	• Hydrocarbures • Derivés terpeniques (sterols, carotenoïds, liposolubles vitamins) • Pigments (chlorophylles, ...)



Shea butter

→ 90 % saponifiable

→ 10 % unsaponifiable

What about cocoa butter ?

ANNEX I

SALES NAMES, DEFINITIONS AND CHARACTERISTICS OF THE PRODUCTS

A. SALES NAMES AND DEFINITIONS

1. **Cocoa butter**

designates the fat obtained from cocoa beans or parts of cocoa beans with the following characteristics:

— free fatty acid content (expressed as oleic acid):	not more than 1,75 %
— unsaponifiable matter (determined using petroleum ether):	not more than 0,5 %, except in the case of press cocoa butter, where it shall not be more than 0,35 %

MAX 0.5 %

Unsaponifiable concentrate for pharmaceuticals and dermatological applications

VALIDATED HARVESTING AREAS
- Specific quality of fruit
- Continuous quality control

Avocado fruit

PATENTED PROCESS
- Drying technology
- Mechanical extracting process
- Exclusive partnership

Dried fruit

PATENTED TECHNOLOGY
- Mechanical operation
- Controlled and fractionated operation

Avocado oil

Avocado oil concentrate

EXTRACTING PROCESS
- Multi-step purification
- Good manufacturing pratices

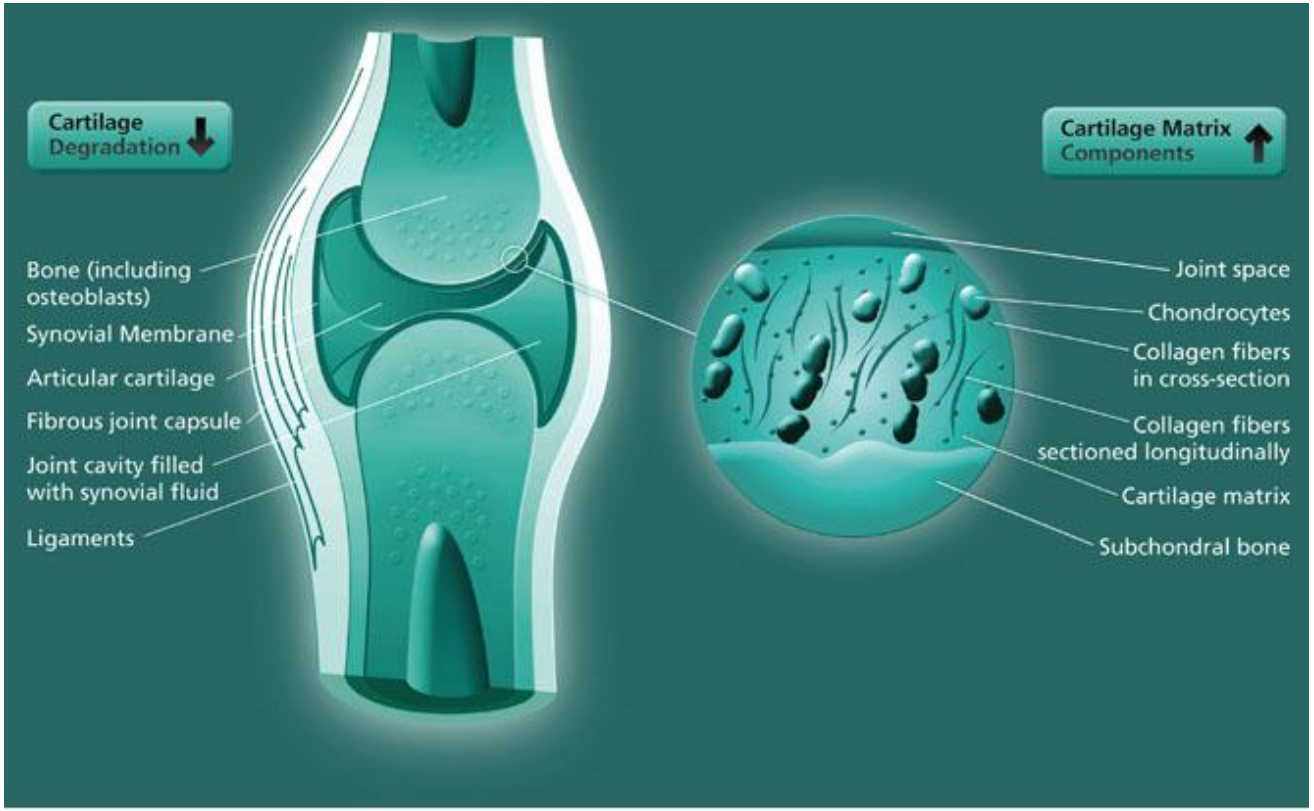
Avocado oil unsaponifiables

EXPANSCIENCE®
LABORATOIRES

Unsaponifiable concentrate for pharmaceuticals and dermatological applications

Very controlled supply chain, green chemistry and bioraffinery

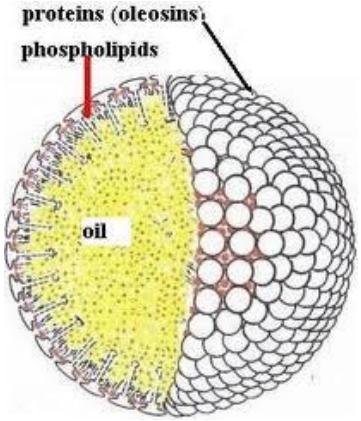
For high VA niche markets



Potential functions of ASU Expanscience on cartilage homeostasis

www.originalasu.com

Triglycerides = triacylglycerols



Naturel state:

Stored under the form of oil inclusion called Oleosomes in seeds or fruits pericarp

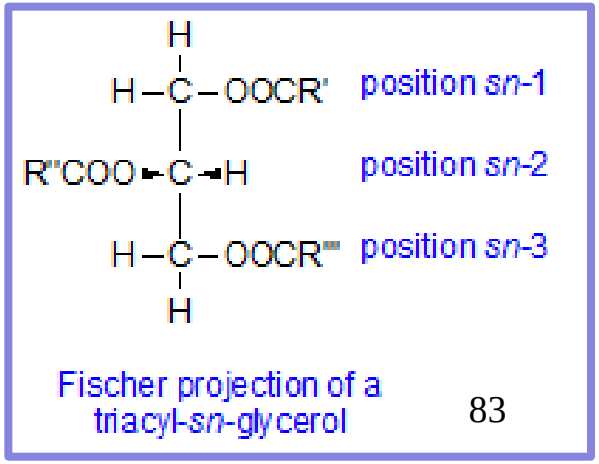
Structure:

triester of glycerol and fatty acids with pair C number

Homogeneous: 3 identical FA
Heterogeneous : 3 different FA

In vegetable oil :

TG heterogeneous, complex blend
saturated FA on primary OH
Unsaturated FA on secondary OH



Fischer projection of a triacyl-*sn*-glycerol

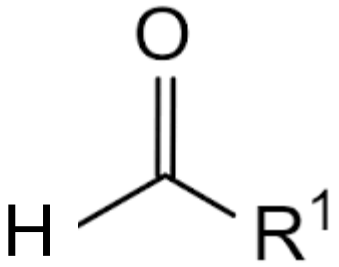
Property of TAG

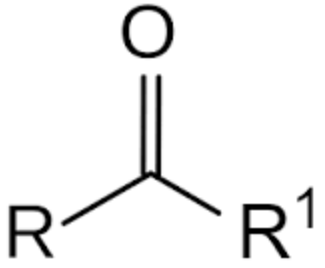
Solubles in organic solvant

release 1 molecule of glycerol and 3 fatty acids when hydrolyzed (alcaline hydroxyde)

Rancidity

- Off flavours can be generated when in contact with air
- Linked to FA peroxydation that get polymerized or broken into aldehydes, cetones or acids





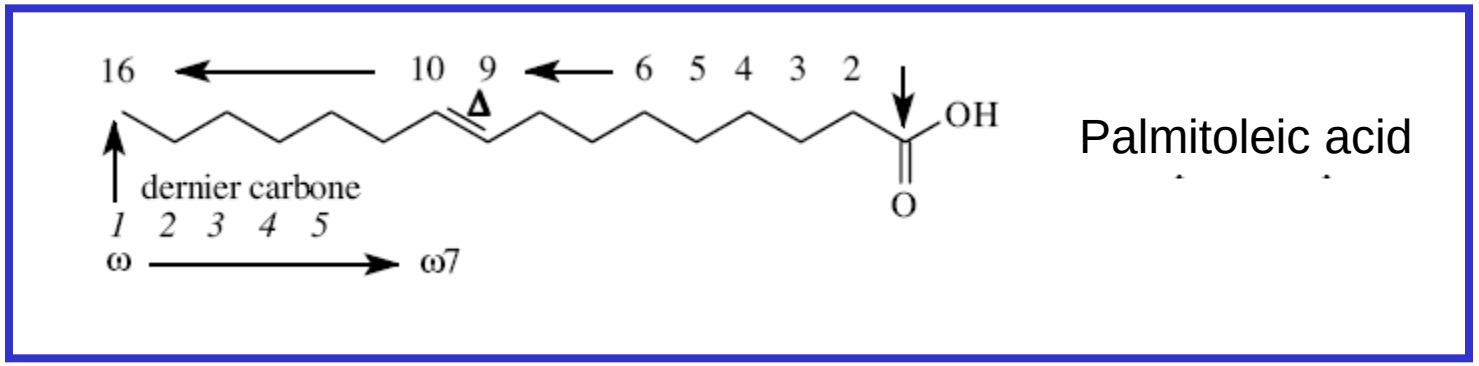
Fatty acids

Nomenclature

Several parallel rules coexist: systematic names often replaced by common names.

2 ways of numbering, one systematic (chemist) and the other often used by dieteticians/ biologists helps separated FA in series

First indicate number of carbons on fatty acid, then indicate number of unsaturation (double bond) (Δ or ω), then their position and configurations (***cis* ou *trans*).**



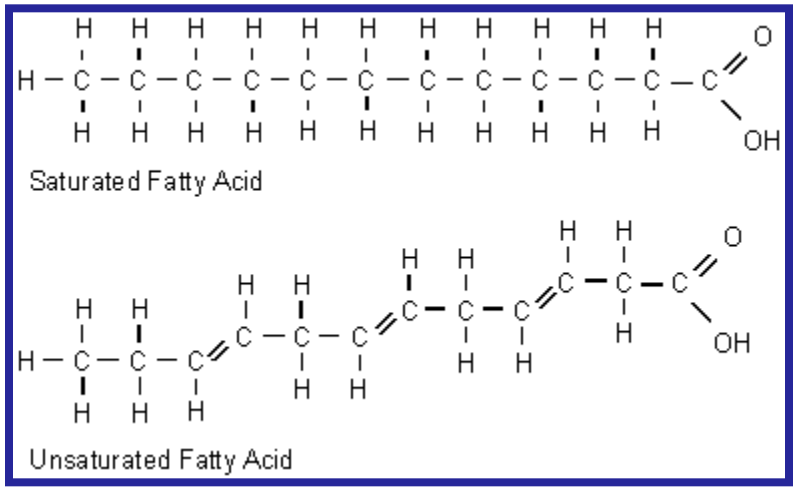
Palmitoleic acid

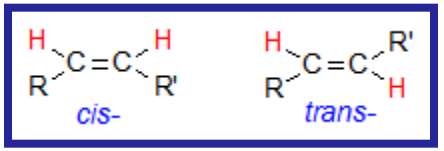
Fatty acids

Saturated:

C8 à C10 in some tropical seed, lauric acid (C12) and myristic acid (C14)
C20 in arachid oil => arachidic acid
Palmitic acid (C16): main saturated fatty acid present in vegetable oils

Unsaturated:





Most unsaturated FA have chain length betweeen 16 to 20 carbons.
Generally: :
- The first or only double bond is located between C9 and C10
- Multiple double bonds are not conjugated but separated by methylene group typical location is thus : in Δ9, Δ12, Δ15…
- Double bonds are in cis configuration mainly

Saturated FA

longueur relative	nC	nom systématique	nom courant de l'acide	
chaîne courte	4	n-butanoique	butyrique	*beurre*
	6	n-hexanoique	caproique	*lait de chèvre*
	8	n-octanoique	caprylique	…
	10	n-décanoique	caprique	…
chaîne moyenne	12	n-dodécanoique	laurique (laurier)	*huile, graisses animales et végétales*
	14	n-tétradécanoique	myristique (muscade)	
	16	n-hexadécanoique	palmitique (palmier)	
	18	n-octadécanoique	stéarique (suif)	
chaîne longue	20	n-icosanoique	arachidique	*graines*
	22	n-docosanoique	béhénique	
	24	n-tétracosanoique	lignocérique	
	26	n-hexacosanoique	cérotique	*cires des plantes bactéries insectes*
	28	n-octacosanoique	montanique	
	30	n-triacontanoique	mélissique	
	32	n-dotriacontanoique	lacéroique	

Unsaturated FA

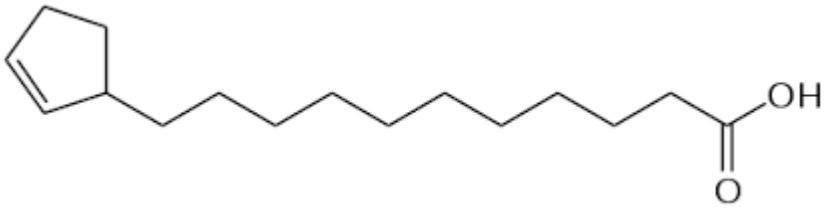
*EPA : EicosaPentaenoic acid

nC	nom systématique	nom courant	symbole	série	
16	cis-9-hexadécénoique	palmitoléique	C16: 1(9)	ω7	*très répandu*
	cis-9-octadécénoique	oléique	C18: 1(9)	ω9	*très répandu*
	cis-11- octadécénoique	vaccénique	C18: 1(11)	ω7	*bactéries*
18	cis, cis-9-12 octadécadiénoique	linoléique	C18: 2(9, 12)	ω6	*graines*
	tout cis-9-12-15 octadécatriénoique	linolénique	C18: 3(9, 12, 15)	ω3	*graines*
	tout cis-5-8-11-14 icosatétraénoique	arachidonique	C20: 4(5, 8, 11, 14)	ω6	*animaux*
20	tout cis-5-8-11-14-17 icosapentaénoique	EPA*	C20: 5(5, 8, 11, 14, 17)	ω3	*huiles de poissons*
24	cis-15-tétracosénoique	nervonique	C24: 1(15)	ω9	*cerveau*

Unusual fatty acids

Oxydized :

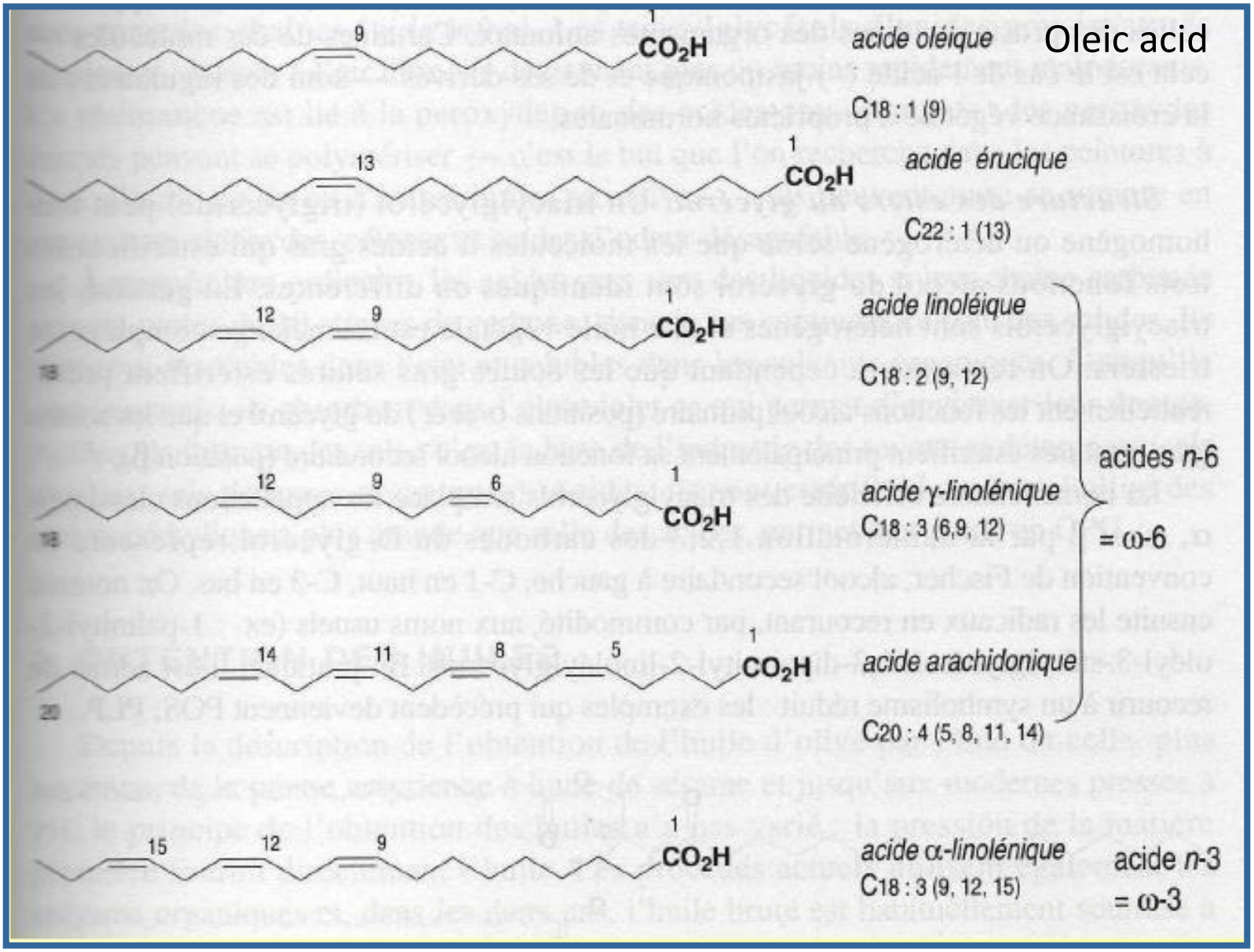
- hydroxylated FA (ricinoleic acid)
- Epoxy FA (vernolic acid)

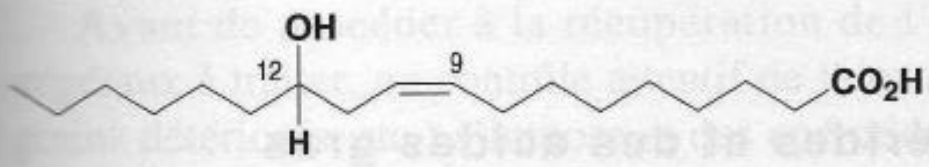


Cyclized :

- cyclopropanic and cyclopropenic from Sterculiaceae (malvalic and sterculic acids) or litchi seed oil (*Litchi sinensis, Sapindacées)*
- cyclopentenic acids from Flacourtiaceae (chaulmoogric, hydnocarpic, gorlic acids)

Common in TAG of *Hydnocarpus wightiana* or *Chaulmoogra* oil used for the treatment of leprosy before sulfones era.


Oleic acid
acide oléique
C18 : 1 (9)
acide érucique
C22 : 1 (13)
acide linoléique
C18 : 2 (9, 12)
acide γ-linolénique
C18 : 3 (6,9, 12)
acide arachidonique
C20 : 4 (5, 8, 11, 14)
acides n-6
= ω-6
acide α-linolénique
C18 : 3 (9, 12, 15)
acide n-3
= ω-3

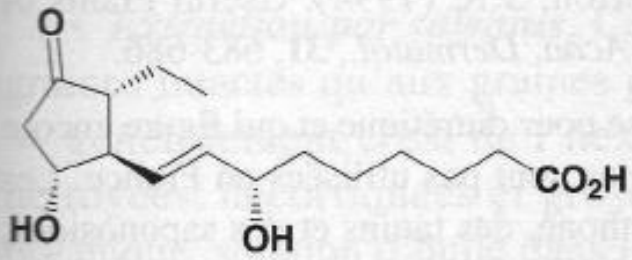


acide ricinoléique

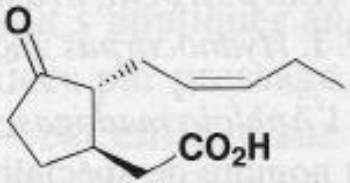
acide chaulmoogrique

acide sterculique

acide crépénynique



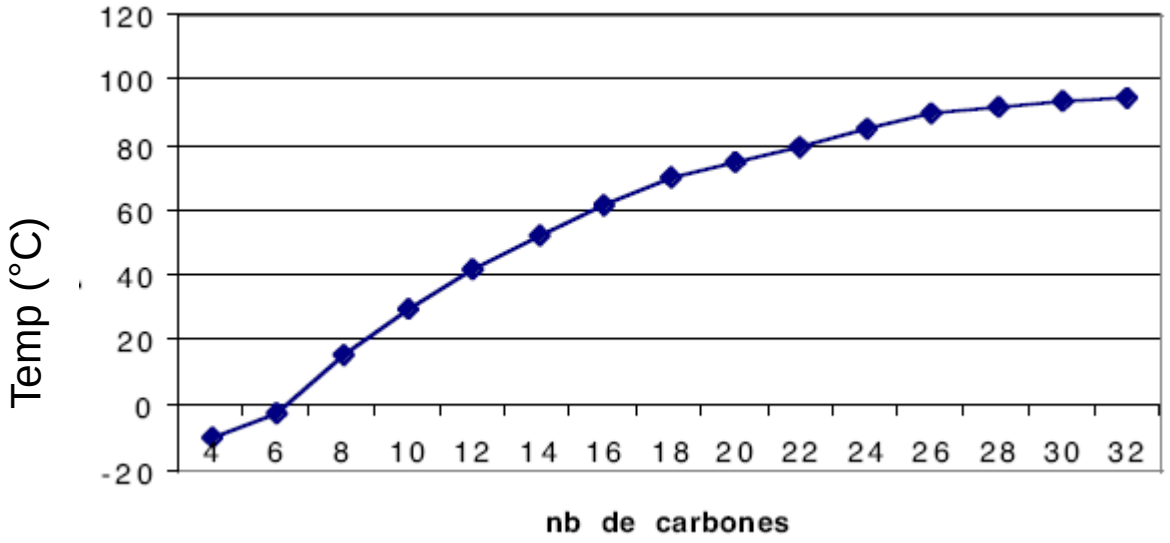
acide cyclopentanique, isolé de Lemna minor



acide jasmonique

Physico-chemical properties of FA:

Liquid at ambiant T°C if C<10
Solid at ambiant T°C if C>10
Unsaturation decrease strongly fusion point



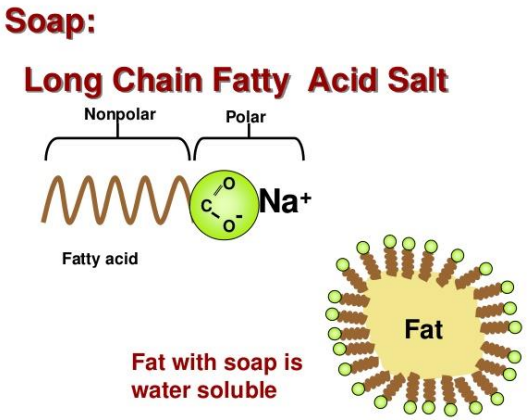
Fusion Point of FA according to chain length

Comun names, symbole and fusion point of most comun FAs

Nom commun	Symbole	Point de fusion
Butyrique	4:0	-7.9
Caproïque	6:0	-3.9
Caprylique	8:0	16.5
Caprique	10:0	31.3
Laurique	12:0	44.1
Myristique	14:0	54
Palmitique	16:0	63
Stéarique	18:0	69.5
Arachidique	20:0	
Béhénique	22:0	84
Palmitoléique	16:1 (9)	-0.5
Oléique	18 : 1 (9)	13.4
Erucique	22:1 (13)	
Linoléique	18:2 (9, 15)	-5
α-Linolénique	18:3 (9, 12, 15)	-11
γ-Linolénique	18:3 (6, 9, 12)	

Physico-chemical properties of FA:

Liquid at ambiant T°C if C<10
Solid at ambiant T°C if C>10
Unsaturation decrease strongly fusion point
Soluble in organic solvant / insoluble in water
unsaturated AG absorbent in UV => UV dosage
Salts formation in acidic conditions => soaps, detergents



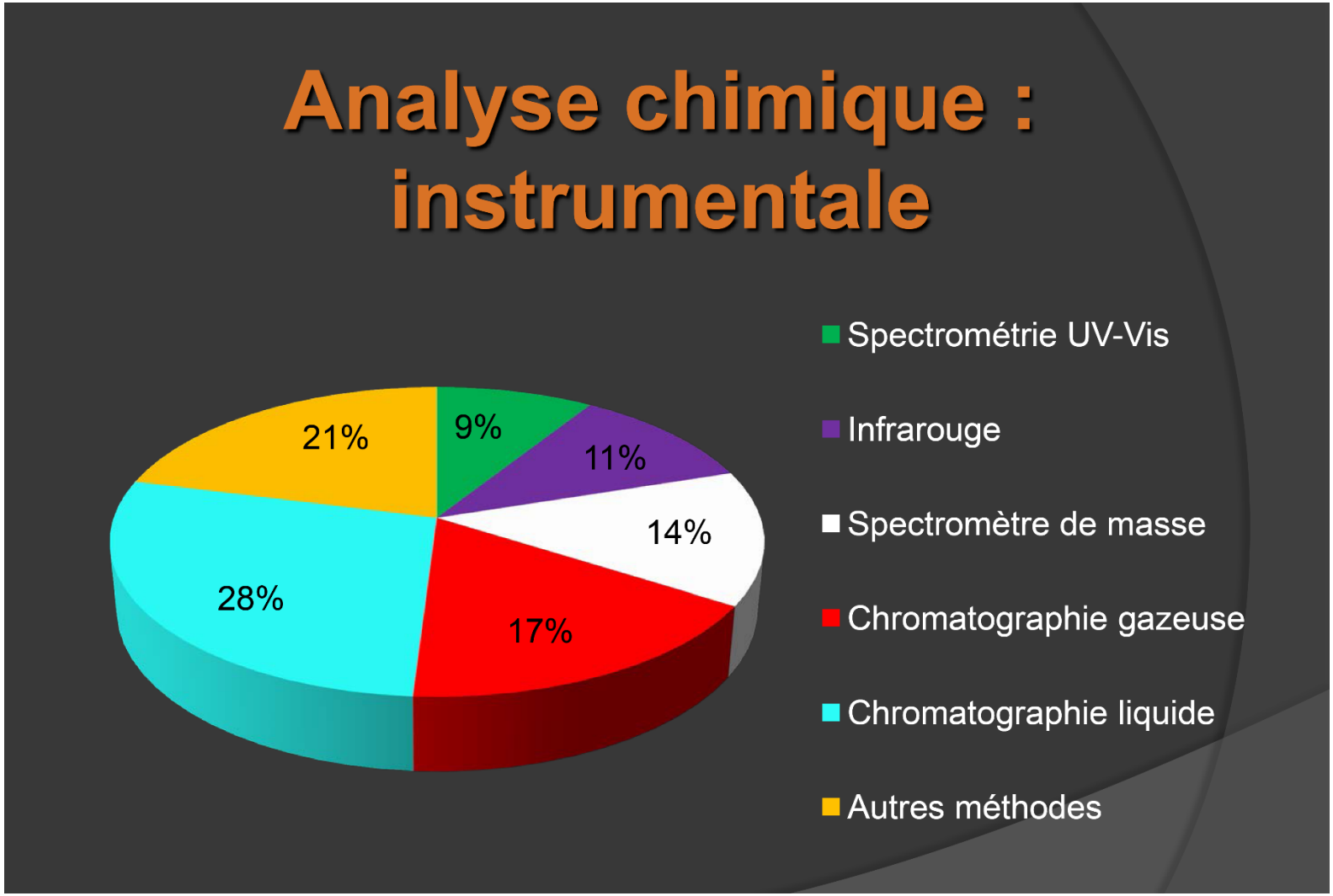
Esterifiable in acidic conditions: increase in volatility, CPG analysis

Analysis of fatty acids composition within fats and oils

- ✓ Transformation into methyl esters
  Basic Methanolysis followed by acid esterification

- ✓ Gaz phase Chromatography

Analysis of fatty acids composition within fats and oils



Analysis of fatty acids composition within fats and oils

- ✓ Physico-chimical processes belonging to fractioning or separative techniques
- ✓ Difference of affinity among compounds to analyze between a stationary phase (sorbant : solid, gel…) and a mobile phase (elution : liquid, gaz…)

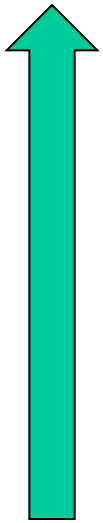
Analysis of fatty acids composition within fats and oils

TYPES OF SEPARATIVE TECHNIQUES

TLC : thin layer chromatography
CPG: Gas phase chromatography
HPLC: high pressure liquid chromatography

Analysis of fatty acids composition within fats and oils

POLAR MOLECULES

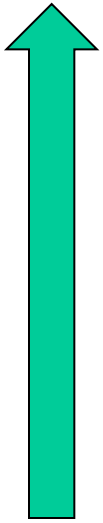


Water
Amine R-NH2
Acid R-COOH
Alcool R-OH
FA
TAG

APOLAR MOLECULES

Analysis of fatty acids composition within fats and oils

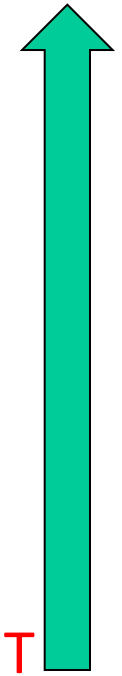
POLAR MOLECULES



Water
Amine R-NH2
Acid R-COOH
Alcool R-OH
FA
TAG

APOLAR MOLECULES

POLAR SOLVANT



Water
Methanol
Ethanol
Acetone
Propanol
Acetonitrile
Diethyl ether
Dichloromethane
Choroform
Benzene
Cyclohexane
Hexane
Heptane

APOLAR SOLVANT

QUALITY OF OIL By TLC

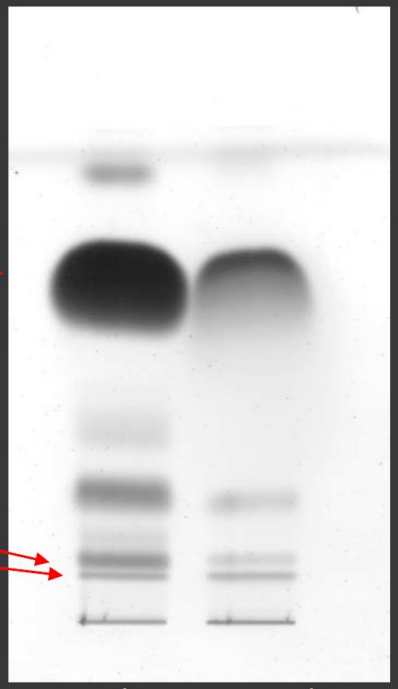
TAG

FFA

DAG 1,3

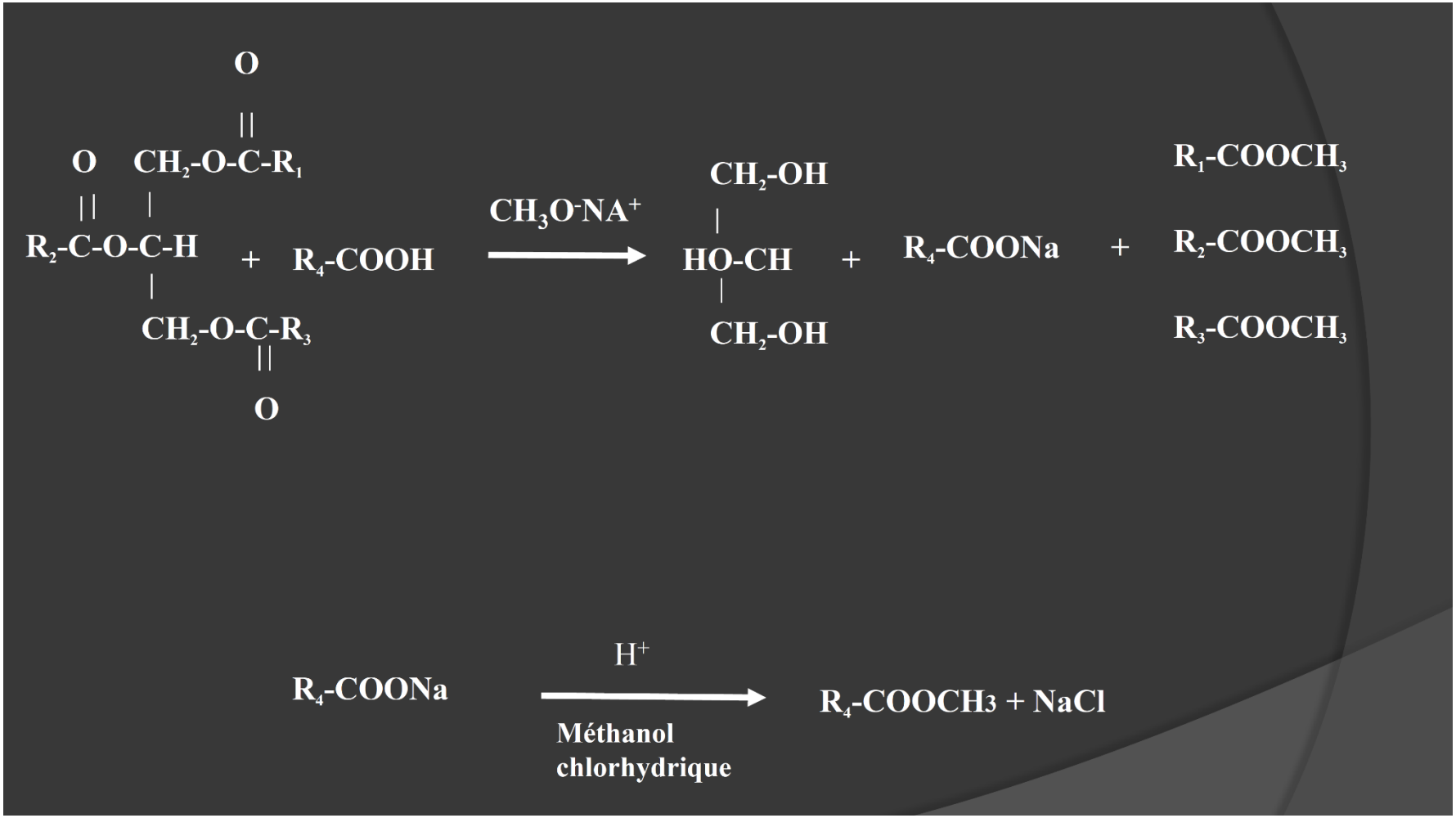
DAG 1,2

MAG

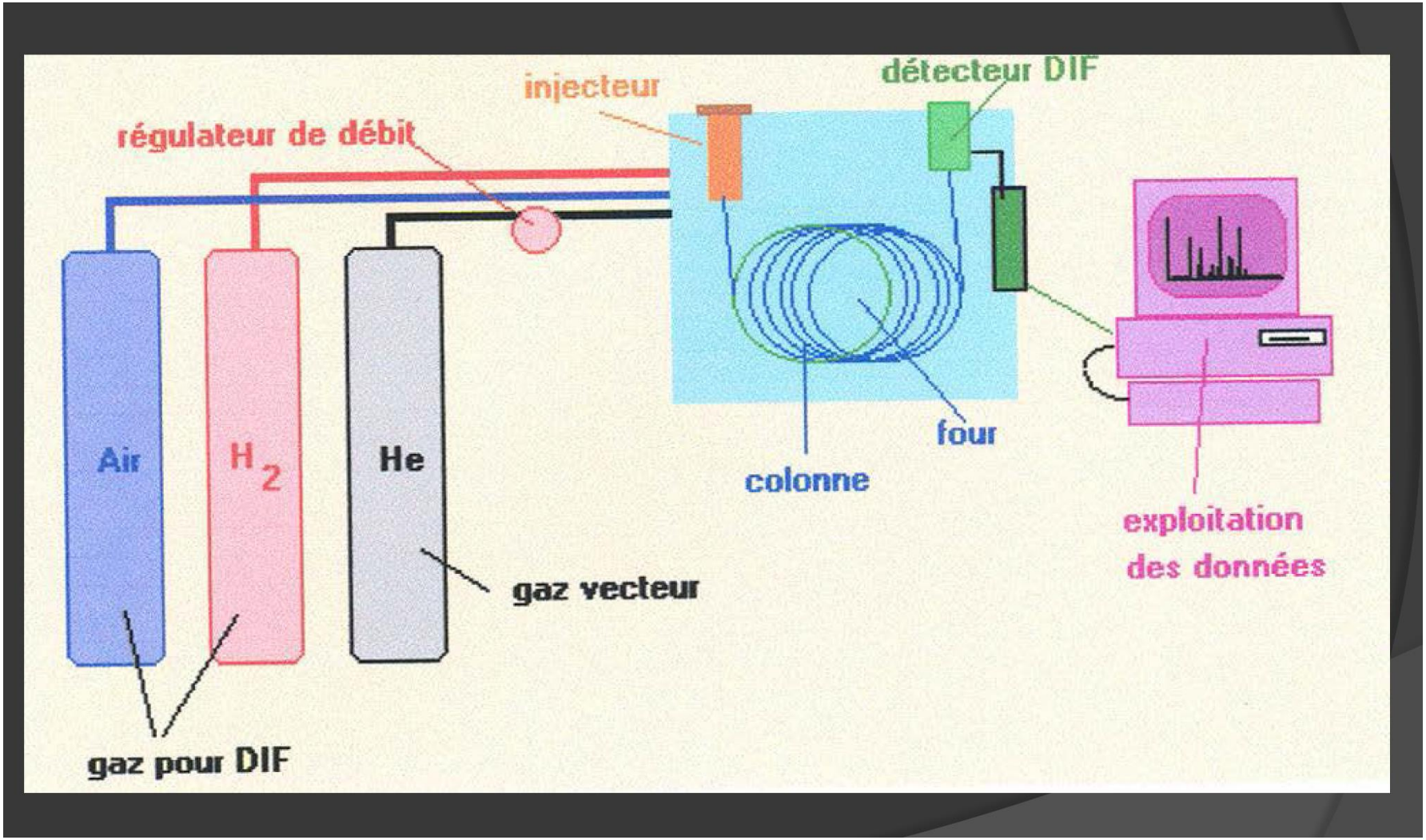


Hexane/ Ether diéthylique /Acide acétique (70/30/1)

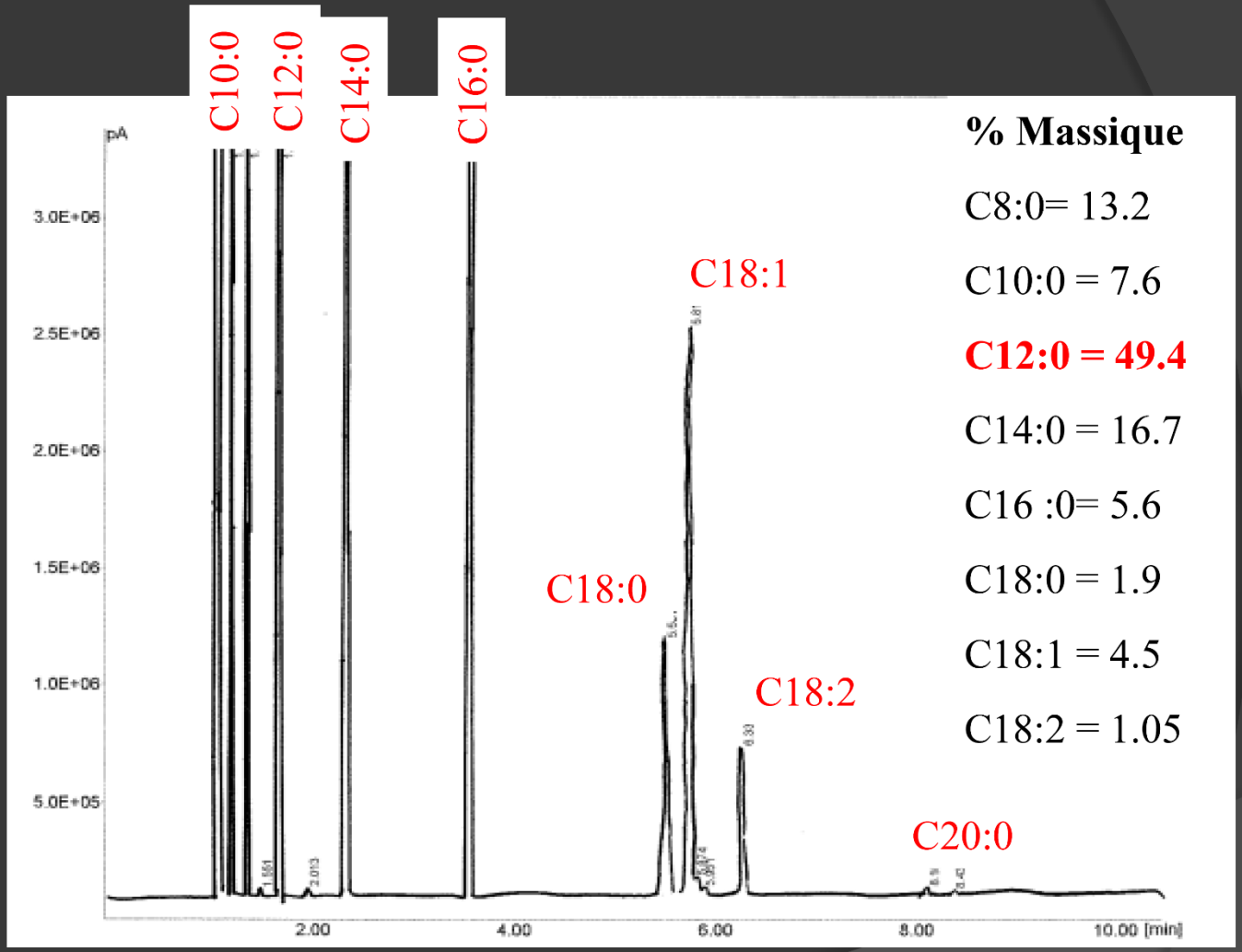
Analysis of fatty acids composition within fats and oils



✓ Gas phase Chromatography



COPRAH OIL



% Massique

C8:0= 13.2

C10:0 = 7.6

C12:0 = 49.4

C14:0 = 16.7

C16 :0= 5.6

C18:0 = 1.9

C18:1 = 4.5

C18:2 = 1.05

Conditions opérationnelles :

Injecteur, diviseur 1/80 t =250° C

Colonne innowax longueur 30 m phase stationnaire polyéthylene glycol 0.25µm

Programmation t = 185 °C+4°C / mn => 220°C

Détecteur ionisation de flamme 270°C

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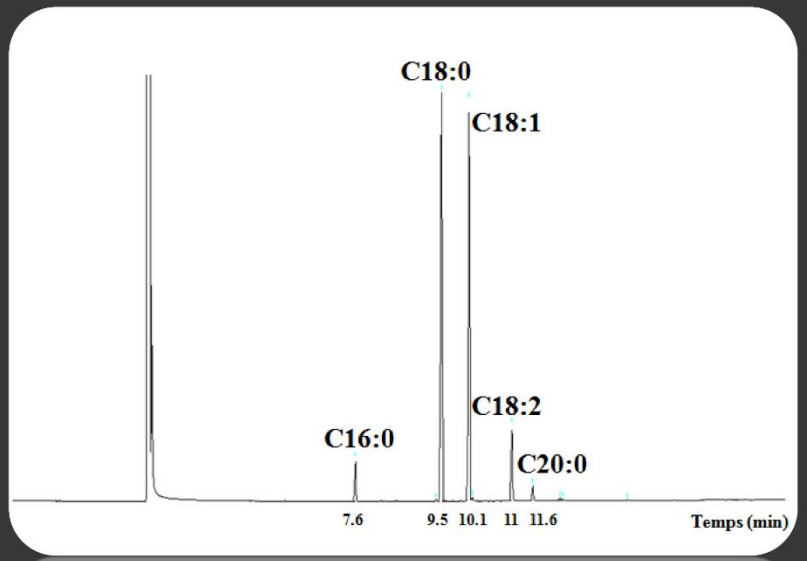
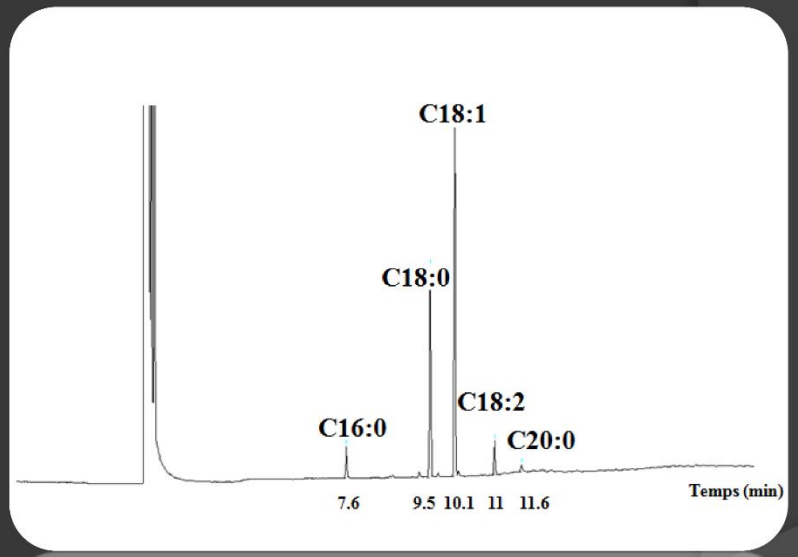


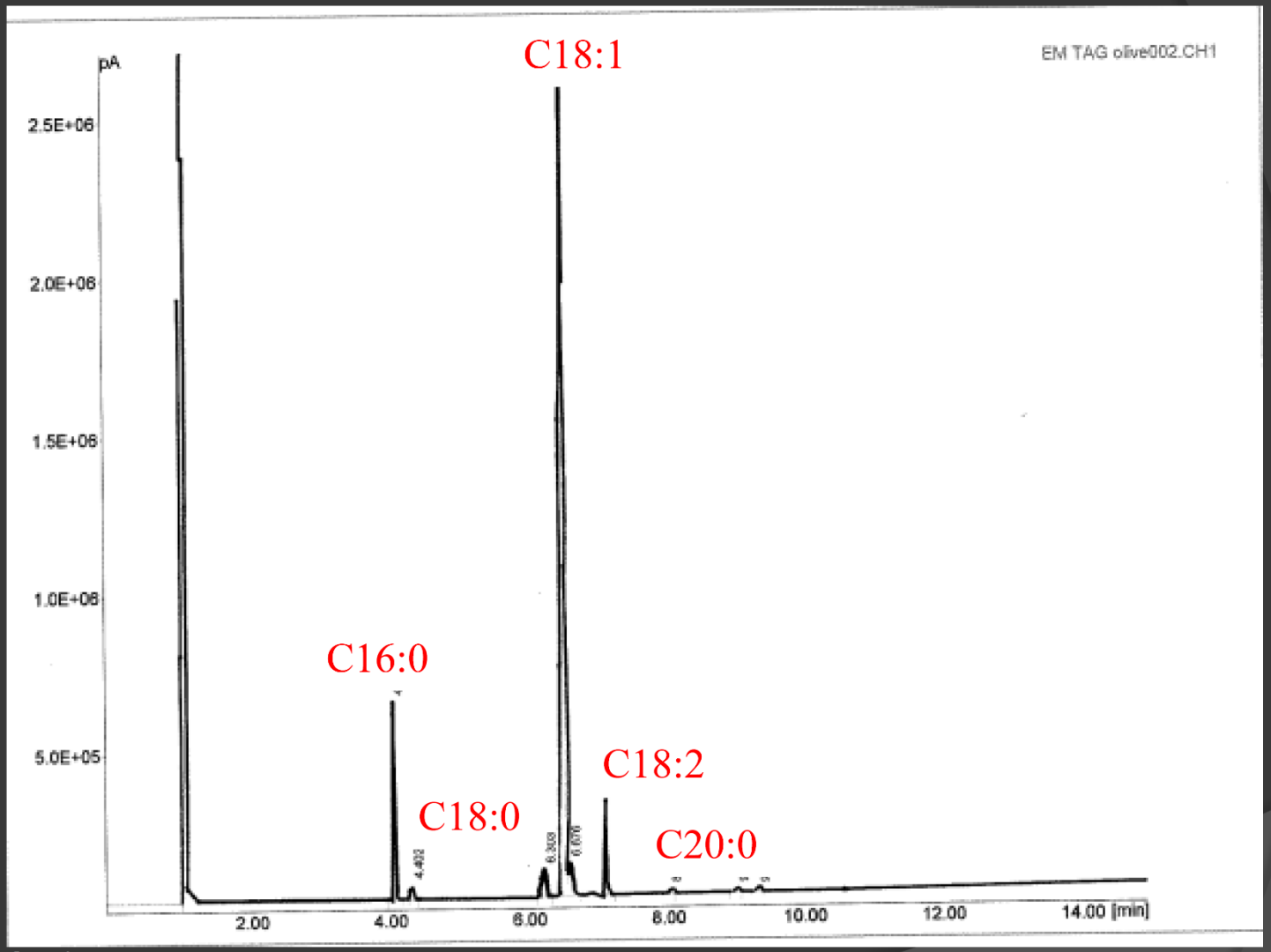
MALI BUTTER



OUGANDA BUTTER

Conditions opératoires :
Gaz vecteur : Hélium; **Colonne** : CP CIL 98, 50m;
Gradient de température : 150°C → 225°C (5°C/min)

OLIVE OIL



Conditions opérationnelles :

Injecteur, diviseur 1/80 t =250° C

Colonne innowax longueur 30 m phase stationnaire polyéthylene glycol 0.25µm

Programmation t = 185°C +4°C / mn => 220°C

Détecteur ionisation de flamme 270°C

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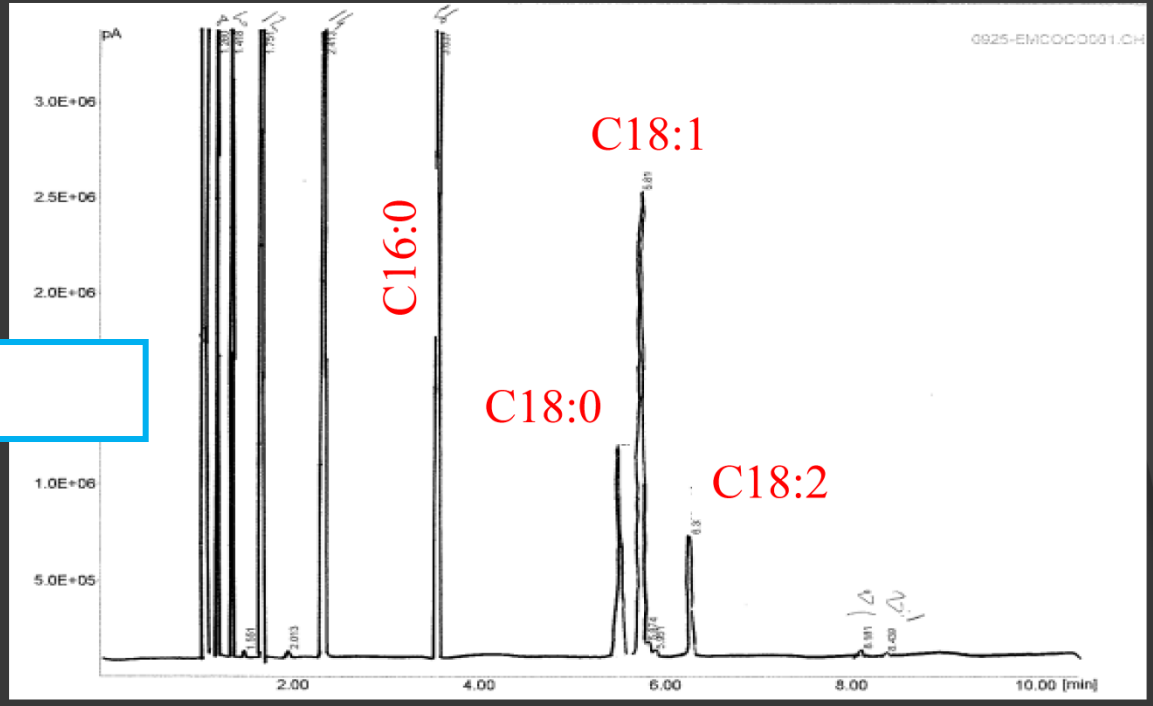
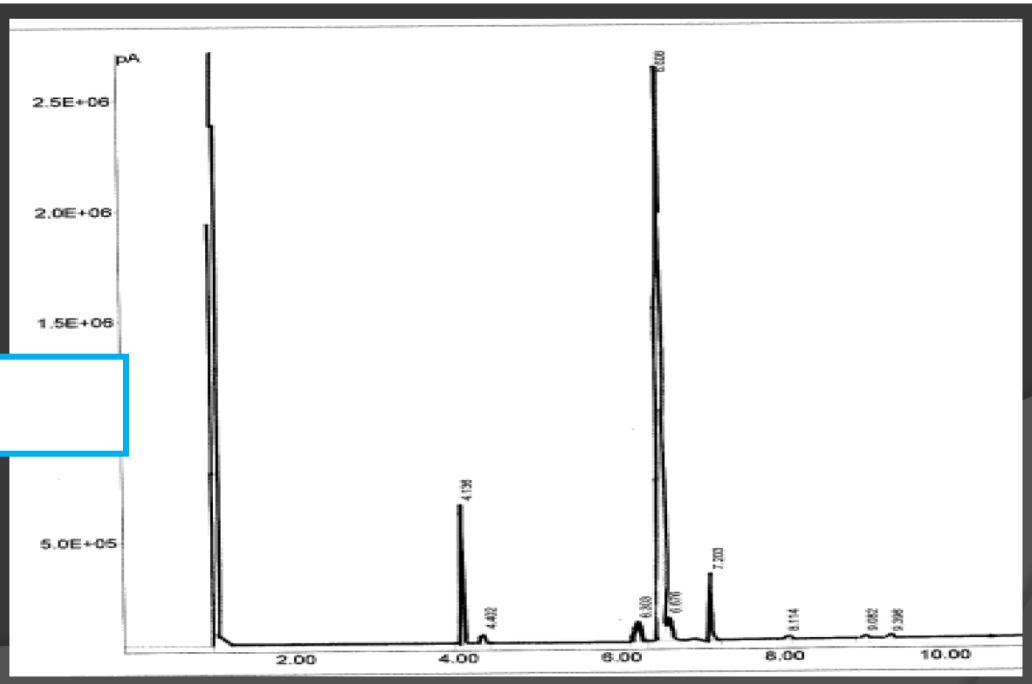
COPRAH OIL



OLIVE OIL



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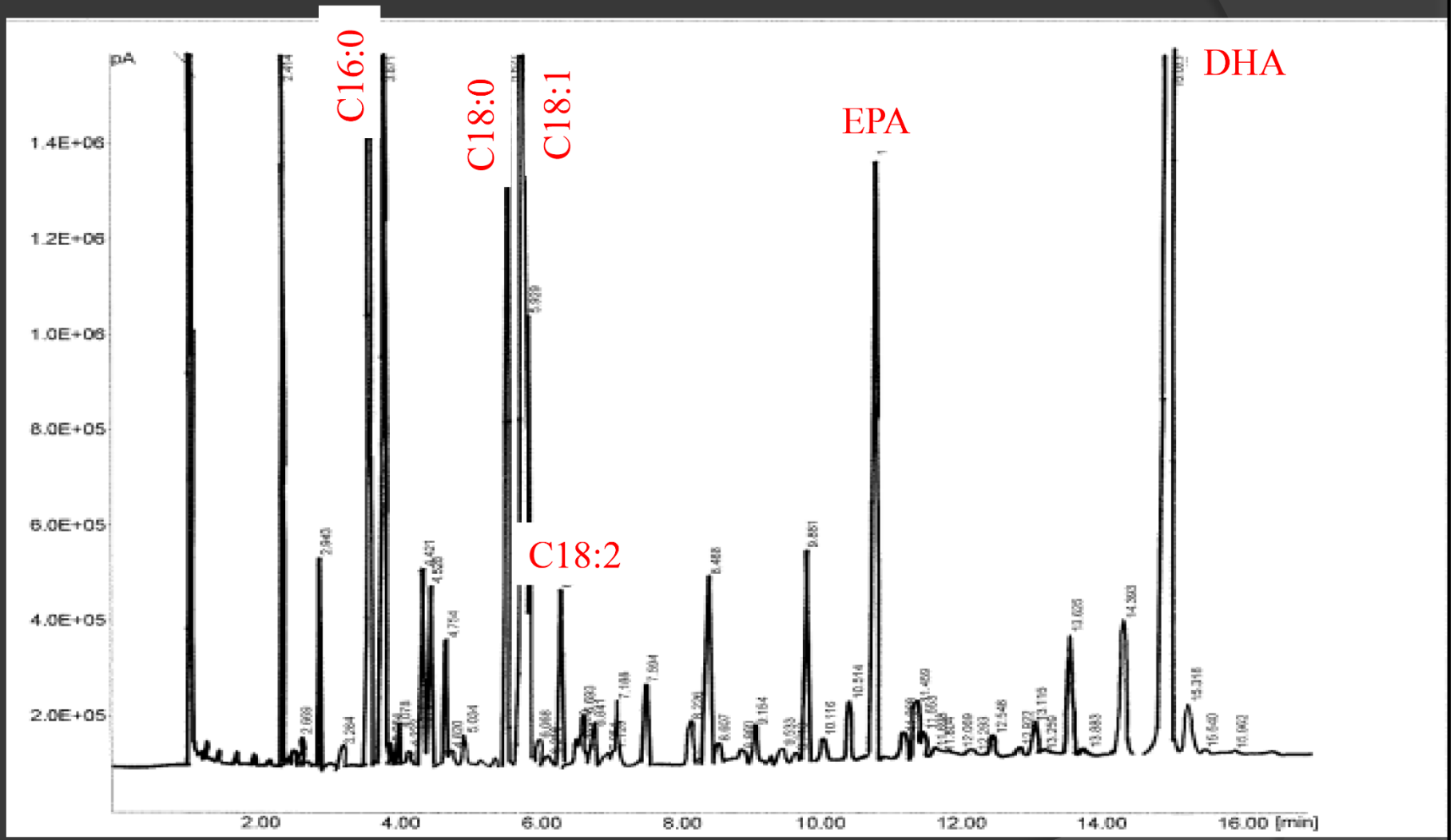
FISH OIL



Conditions opérationnelles :

Injecteur, diviseur 1/80 t =250° C

Colonne innowax longueur 30 m phase stationnaire polyéthylene glycol 0.25µm

Programmation t = 185°C +4°C / mn => 220°C

FID : 270°C

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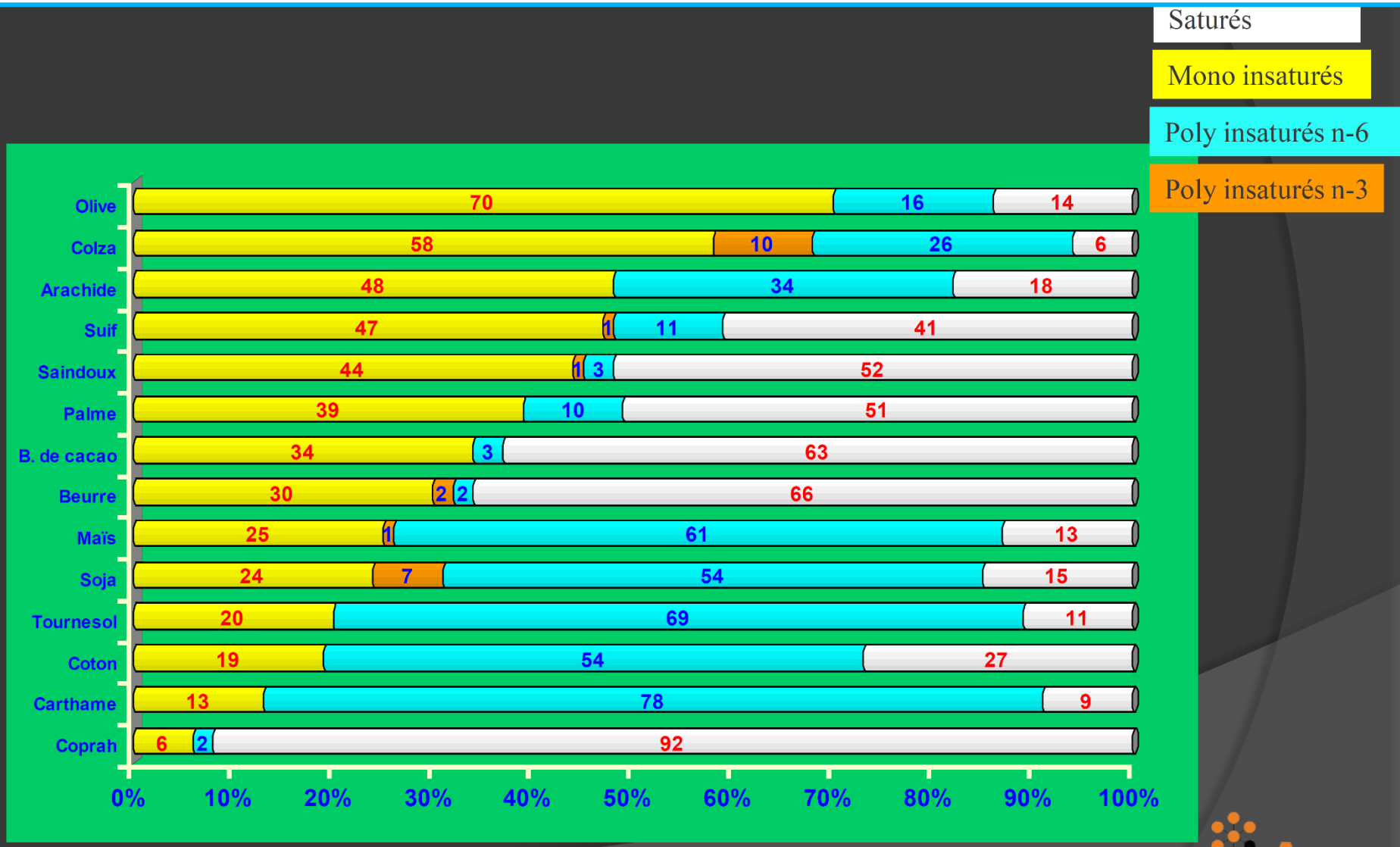
COMPARATIVE FA COMPOSITION OF DIFFERENT VEGETABLE FATS/OILS



ANALYSIS OF OIL

PHYSICAL CARACTERISATION

(plastic properties)

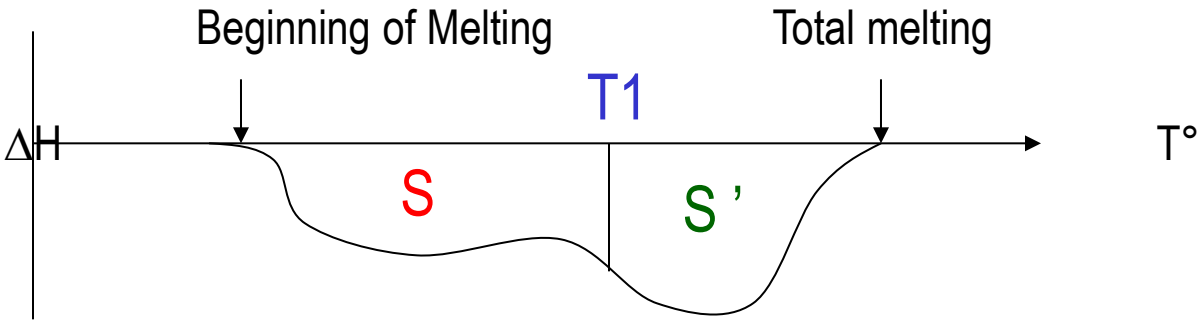
- Melting point: function of FA composition, regiodistribution of these FA and cristallines forms

- % Solid - liquid

PHYSICAL CHARACTERISATION

- *Melting point*
- *% solid/liquid*

  - Differential enthalpy analysis



% solide = S ’/(S + S ’)

  - Proton Relaxation

% solide = $1 - I_{70ms}/I_0$

PHYSICAL CHARACTERISATION

- *Melting point*
- *% solid/liquid*

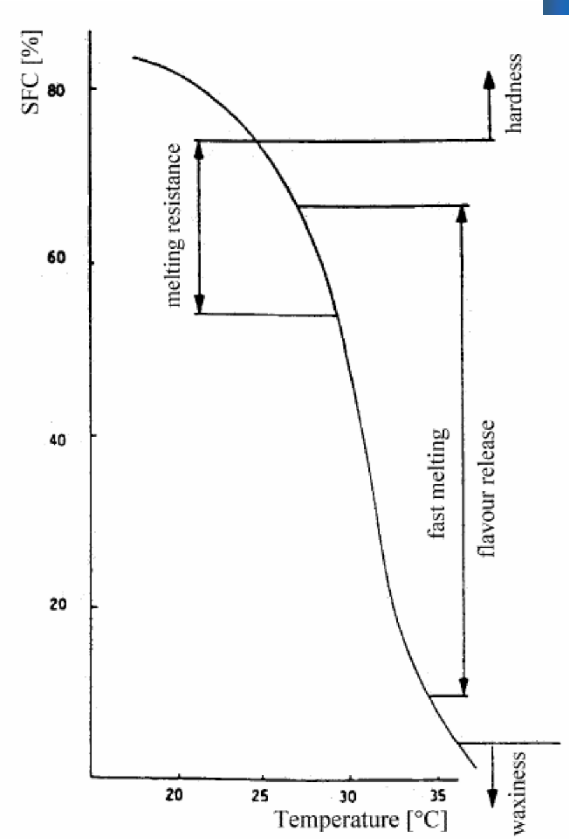


Figure 1.2. Solid fat content of cocoa butter measured by pNMR (from Foubert, 2003).

Table 1.1. Overview of the CBAs.

	CBE	CBR	CBS
Origin	Illipe butter Palm oil Sal fat Shea butter kokum butter Mango kernel fat	Palm oil Soybean oil Rapeseed oil Cottonseed oil	Palm kernel oil Coconut oil
Processing	Hydrogenation Fractionation	Hydrogenation Fractionation	Hydrogenation Fractionation Interesterification
TAG composition	Similar to CB	Different from CB	Different from CB
Lauric acid	Non lauric	Non lauric	Lauric (45-55% lauric acid)
Compatibility to CB	Compatible	Compatible in small ratios	Incompatible
Crystallization	Tempering to obtain stable polymorphic form	Crystallize directly from the melt in the stable polymorphic form	Crystallize directly from the melt in the stable polymorphic form
Application	* 5% replacement on total product * compound	Compound	Compound
Remark	*Subgroups:* * cocoa butter extender (CBEX) * cocoa butter improver (CBI)	High level of trans fatty acids	

(Stewart & Timms, 2002; Talbot, 2009b; Norberg, 2006; Timms, 2003)

ANALYSIS OF OIL

CHEMICAL CHARACTERISATION

(stability, nutritionnal properties, cristallisation properties)

- General index (iode, acid, peroxyde)
- Fine Analyses (triglycerides, FA, unsaponifiable)

Iode index:

Quantity of halogene (iode) fixed in specific conditions by 100g of substances.
Allow assessing global usaturation of TAG.

Acidity:

Quantity (in mg) of potassium hydroxyde necessary to neutralize 1g of substance.
Use to measure alteration state of oil, raffinery quality.

Peroxyde index:

Quantity (in milli-equivalent d'O_2) of peroxyde contained in 1000g of substance.

ANALYSIS OF OIL

CHEMICAL CHARACTERISATION

Unsaponifiable :
Non volatile substances at 100-105 °C, obtained by extraction, with an organic solvant, from a solution of the substance to analyse after saponification
Extraction of the aqueous saponification media with ethyl dioxyde.
Washing and solvant elimination. Weighting of residu (=unsaponifiable)
Refractive index: of a media compared to air is equal to the ratio of the sinus of the incident angle of the light on the sinus of the refracted angle of the refracted light in the considered media.
Saponification index :
Quantity of potassium hydroxyde (en mg) necessary to neutralize FFA and to the saponification of esters present in 1 g of substance. All the most elevated as FA chains are short.
Water content (determined by semi-microtitration) very important when oil are destinated to pharmaceutical applications.
Sterols : Separation of sterol fraction. Titration of sterols : By GC or GC/MS.

ACIDITY
ESSENTIAL QUALITY CRITERIA IN SHEA BUTTER

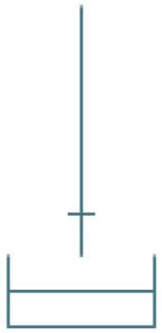
Les normes de l'UEMOA relatives au beurre de karité non raffiné

Ces normes sont adoptées le 1 janvier 2006 par tous les huit pays membres de l'UEMOA

Usages	Cosmétique pharmaceutique	FOOD	SOAP
AGL (%)	0 - 1	1,1 - 3	3,1 - 8

NORMALIZED METHOD ISO 660

$$ROOH + K^+OH^- \longrightarrow ROO^-K^+ + H_2O$$



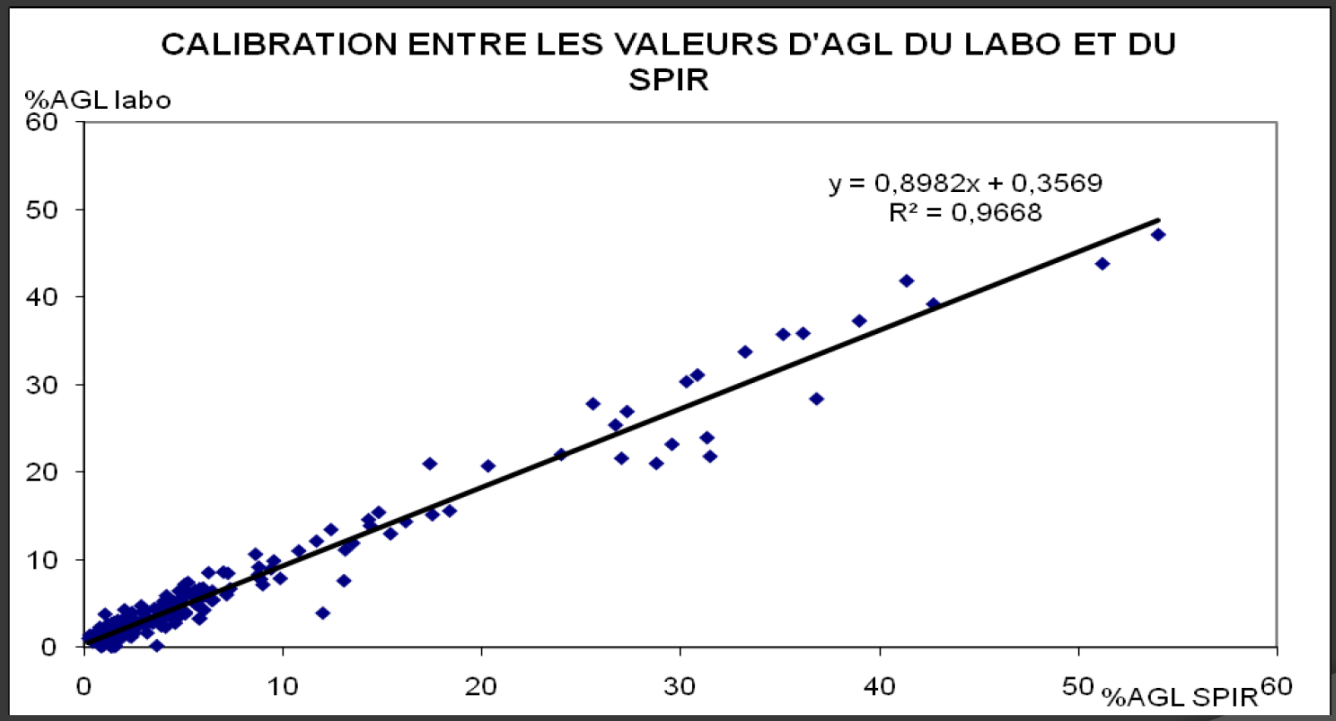
KOH à 0.01988 N

Beurre de Karité + 40 ml d'EtOH/EtO_2
+ 2 à 3 gouttes de phénolphtaléine

Acidity is expressed in % oleic acid

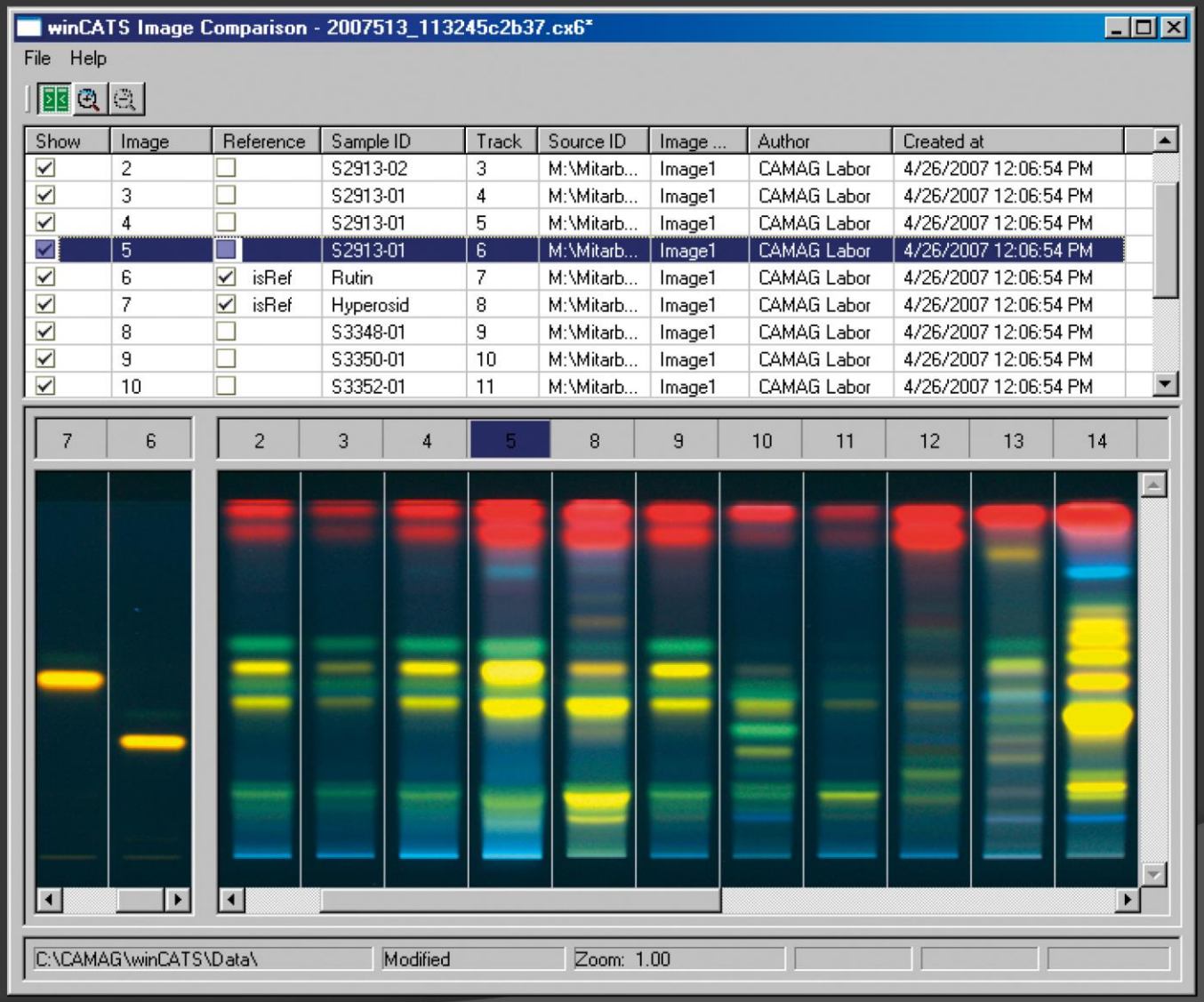
CORRELATION TITRIMETRY / IR

Droite de calibration obtenue :

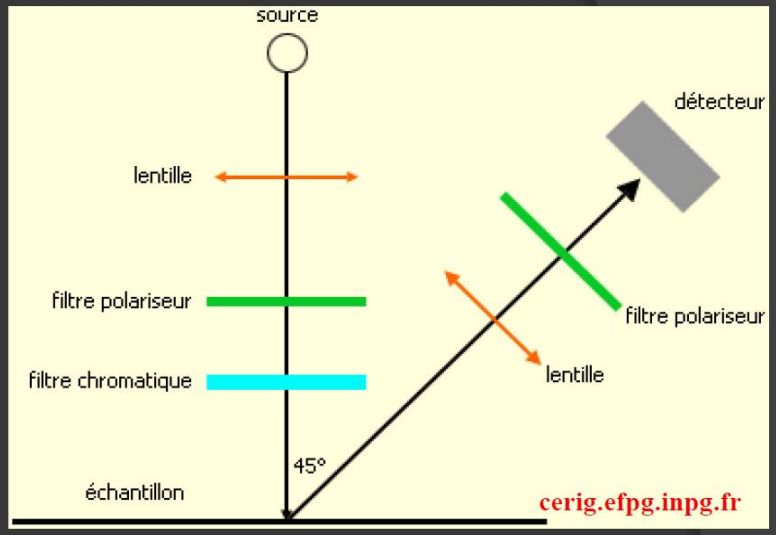


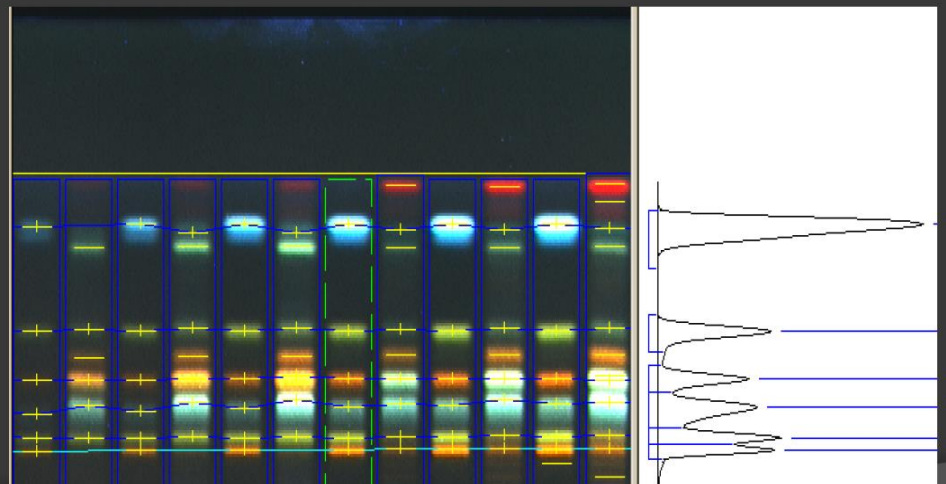
Variable	Observations	Minimum	Maximum	Moyenne	Ecart-type
Labo	205	0,2	54,0	7,0	10,0
SPIR	205	-0,9	47,2	6,7	9,1

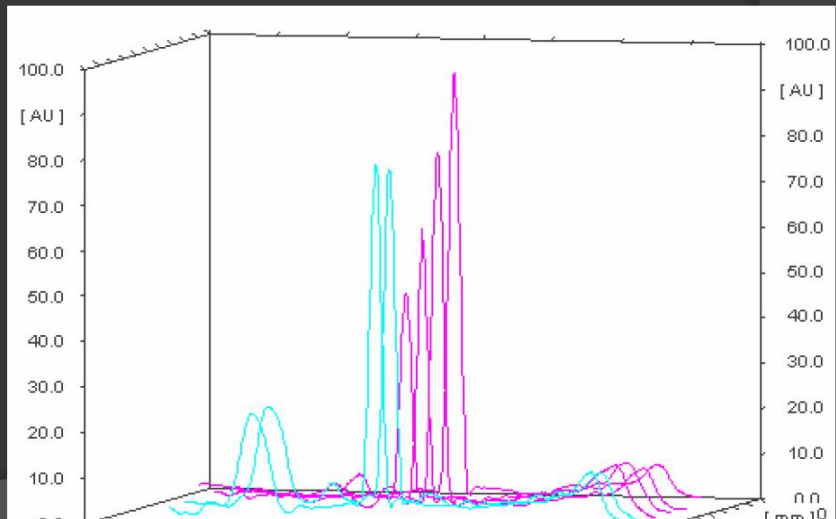
TLC alternative METHOD



DENSITOMETRY

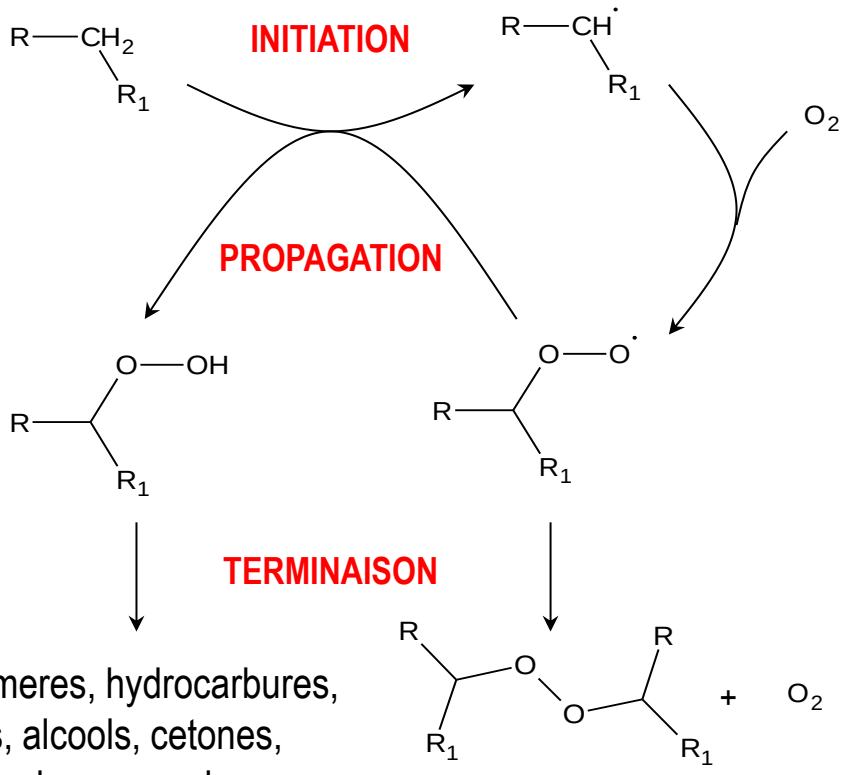






OXIDATION OF LIPIDS

Mechanism :



Lipidic Substrates :

- PUFA

Catalysts :

- Metallic ions
- Lipoxygenase
- Electromagnetic radiations
- Elevated Temperatures

Inhibitors :

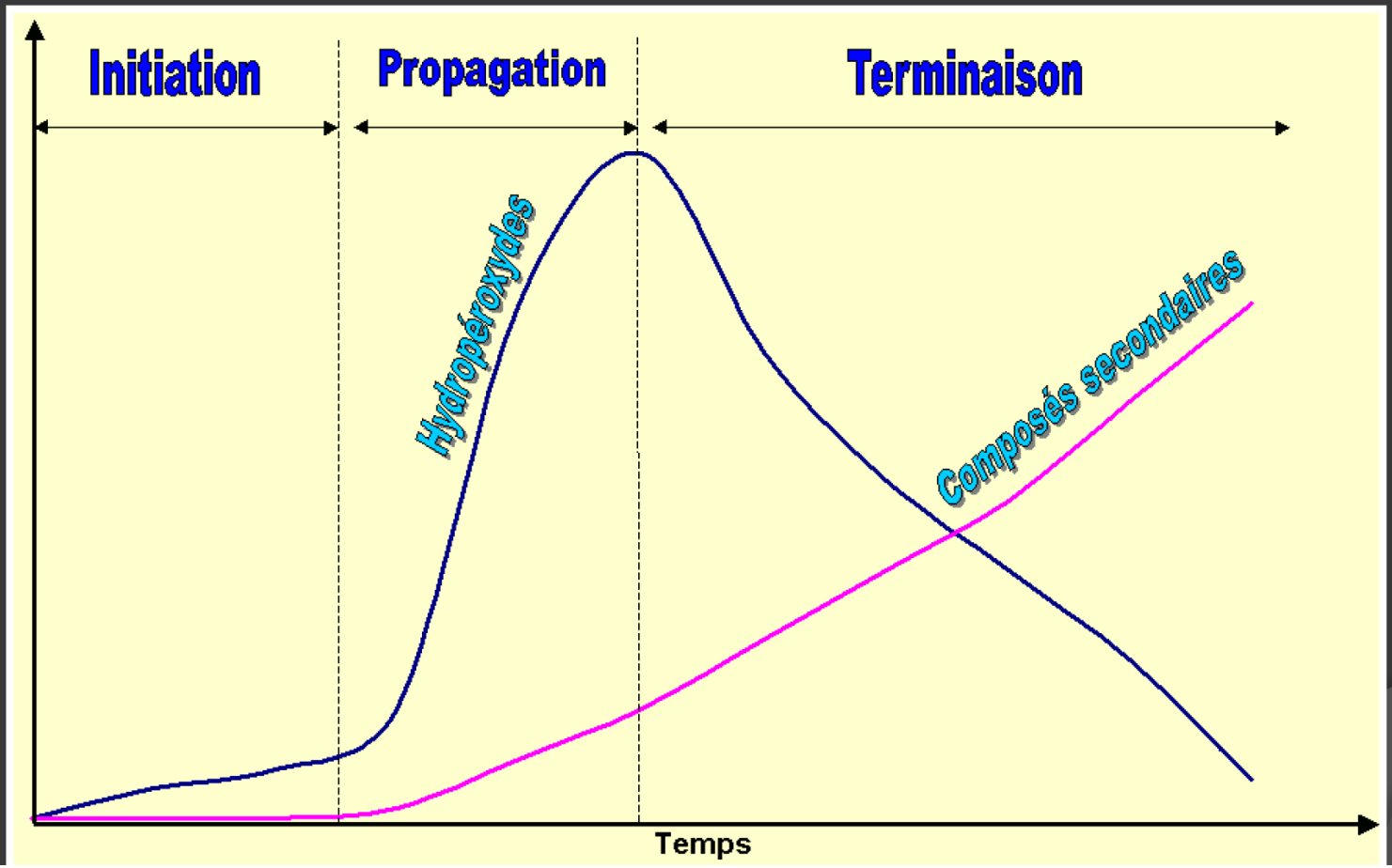
- Antioxidants

- **Organoleptic defects** → rancidity (from 2-3% of oxidized chains) – colour
- **↘ nutritionnal value** → ↘ essential FA
- **↘ technological properties** → ↘ storage stability, ↗ loss during oil refining process, inactivation of hydrogenation catalysts

Alteration of lipids / oxidation

Primary oxidation compounds
Secondary oxidation compounds

PRIMARY OXIDATION COMPOUNDS



PEROXIDE DETERMINATION

Méthode iodométrique : NF T 60-220

Schéma réactionnel :

- **Oxydation de l'iodure de potassium en excès par le corps gras peroxydé (ROOH) :**

$$ROOH + 2H^+ + 2e^- \rightarrow ROH + H_2O$$

$$2I^- \rightarrow I_2 + 2e^- + \text{excès de } I^-$$

$$ROH + 2H^+ + 2I^- \rightarrow ROH + I_2 + \text{excès de } I^- + H2O$$

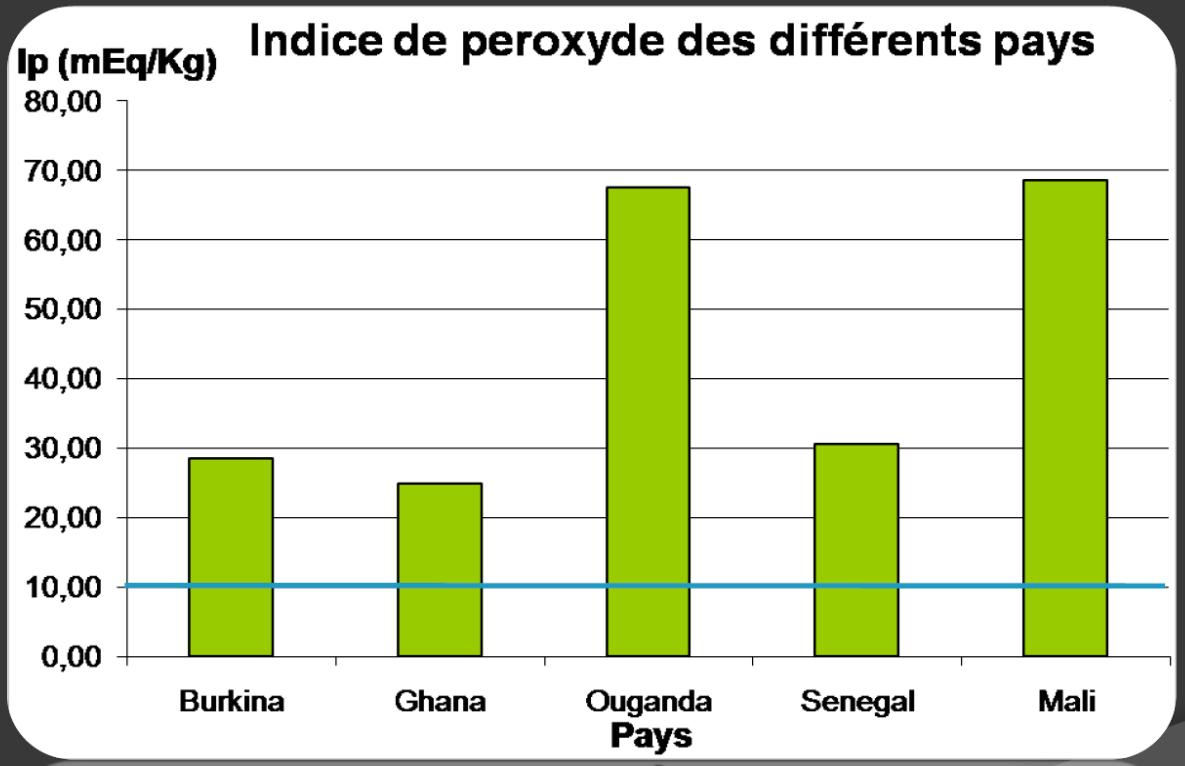
- **Titration de l'iode libérée par S_2O_3Na**

$$I_2 + \text{excès de } I^- + 2^{e-} \rightarrow 2I^- + \text{excès de } I^-$$
$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2^{e-}$$

$$I_2 + \text{excès de } I^- + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^- + \text{excès de } I^-$$

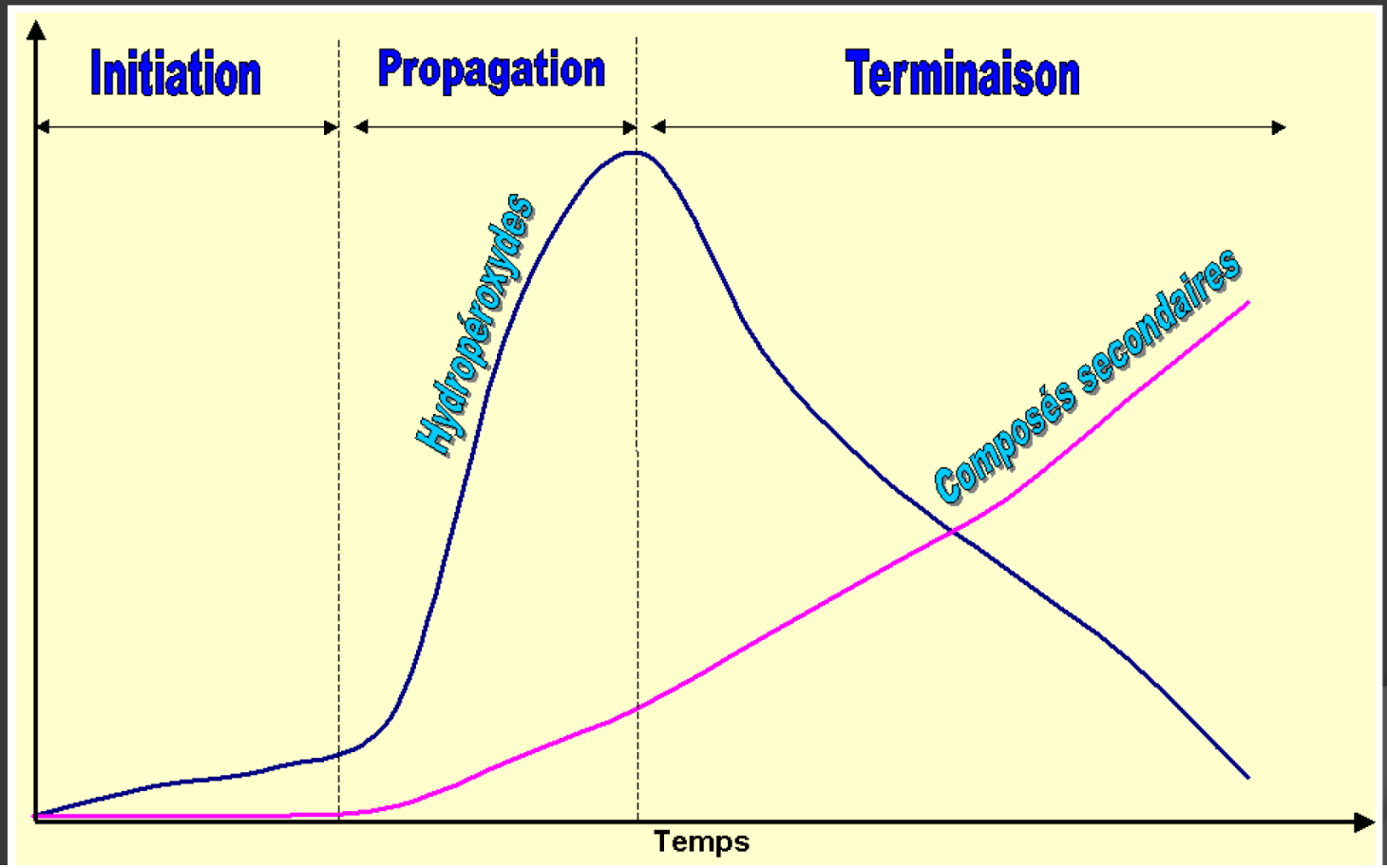
Couleur de : $I_2 + I^-$ couleur de I^-

Oxydation des beurres

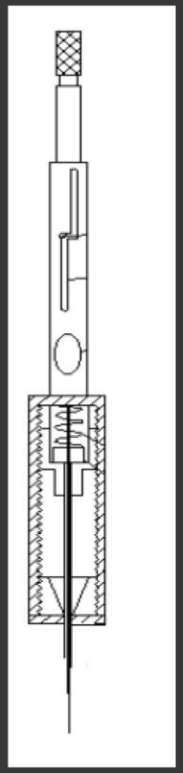


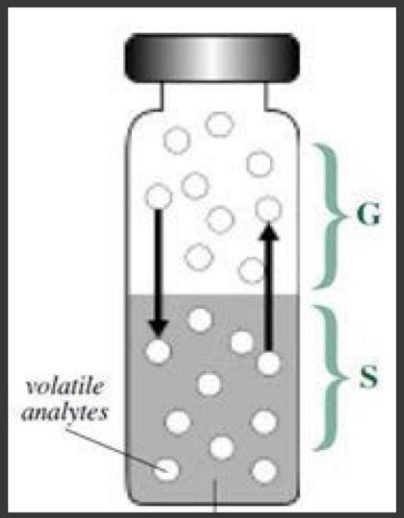
Limite cosmétique

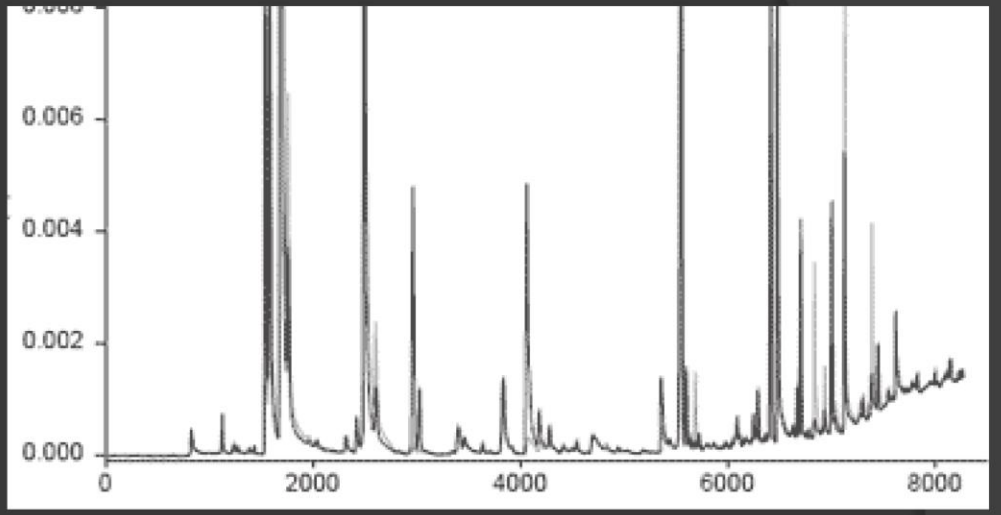
SECONDARY OXIDATION COMPOUNDS

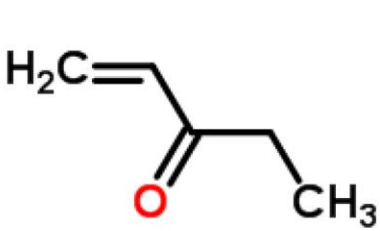


GC-head space

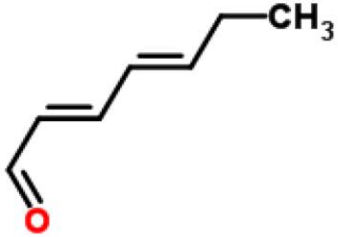




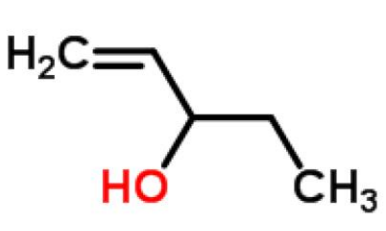




1 penten-3-one

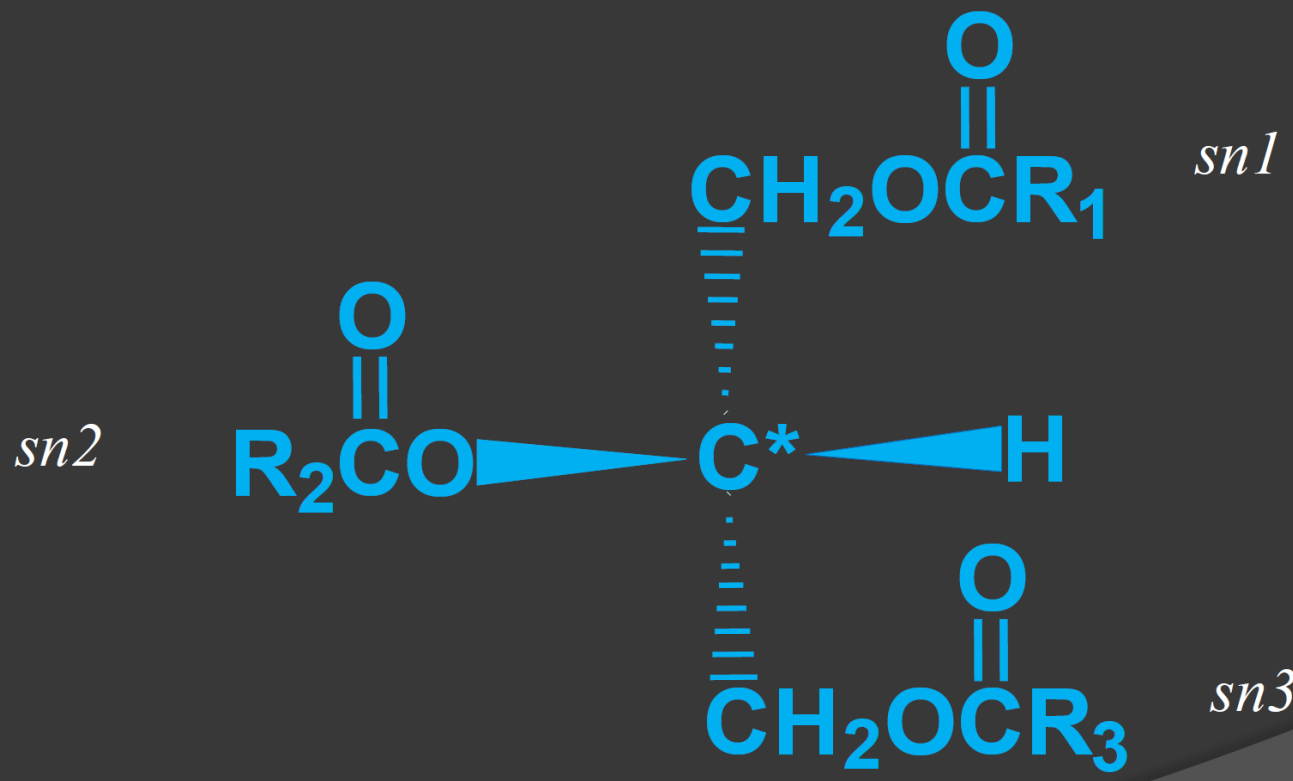


2,4 heptadienal

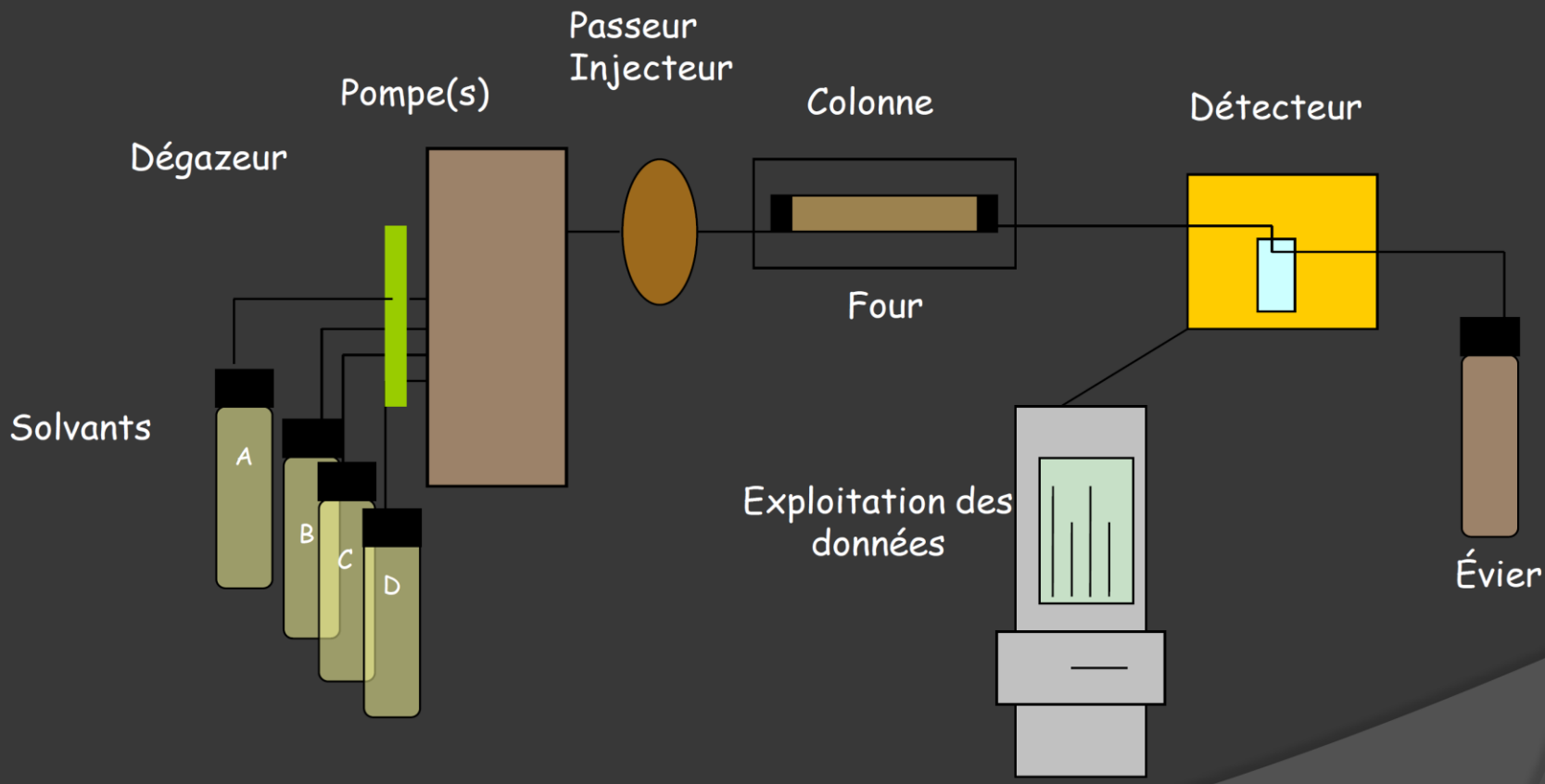


1-penten-3-ol

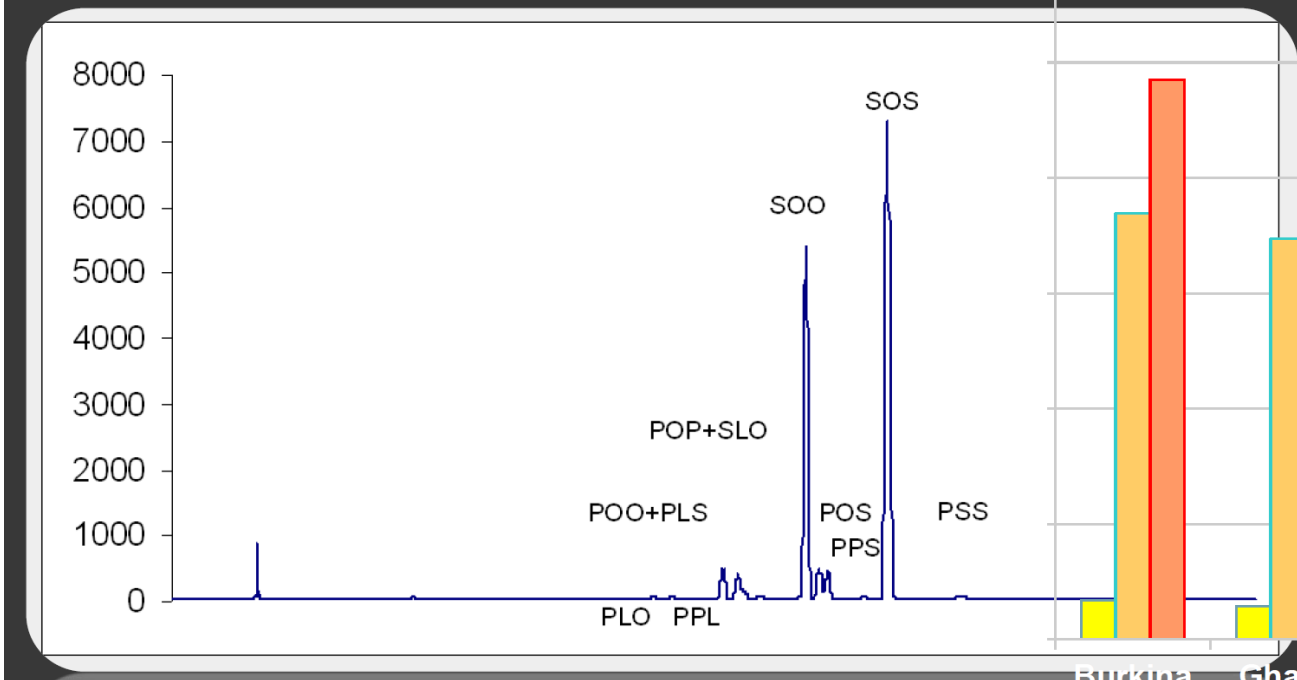
TAG PROFILE

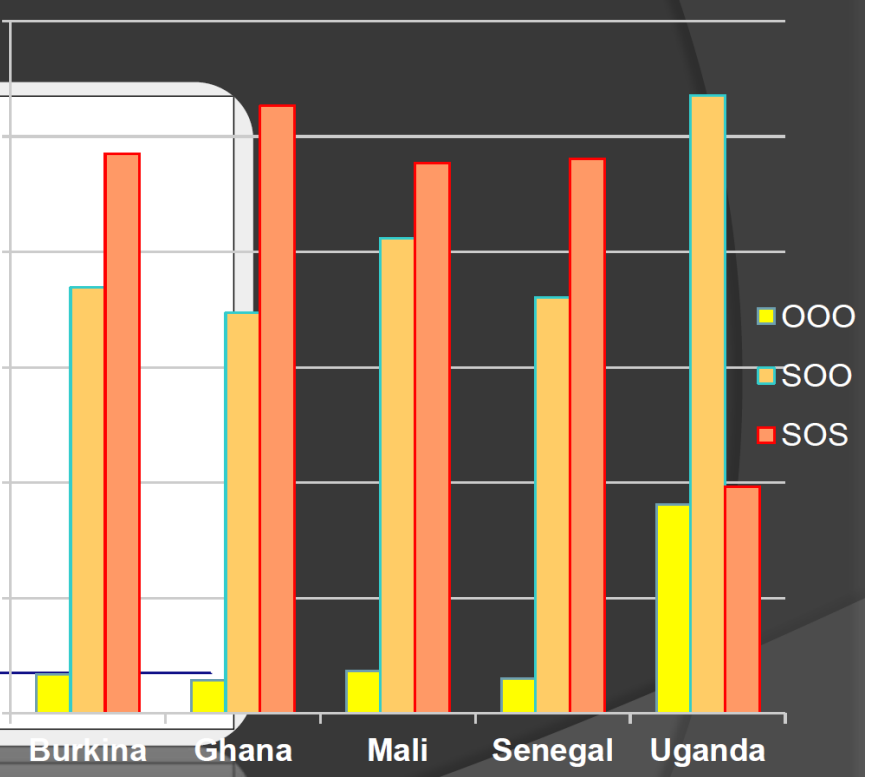


HPLC


Passeur
Injecteur
Pompe(s)
Colonne
Détecteur
Dégazeur
Four
Solvants
A
B
C
D
Exploitation des
données
Évier

TAG PROFILE





Conditions opératoires :
Phase mobile : (A) Acétone/ Acétonitrile 50/50 (B) Chloroforme
Colonne : Silice greffée C18
Détecteur : DDL

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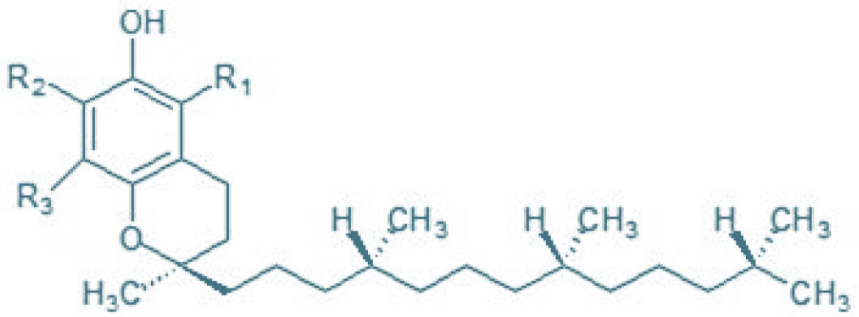
Table 5. Typical triglyceride composition (area %) of cocoa butter (Podlaha *et al.*, 1984)

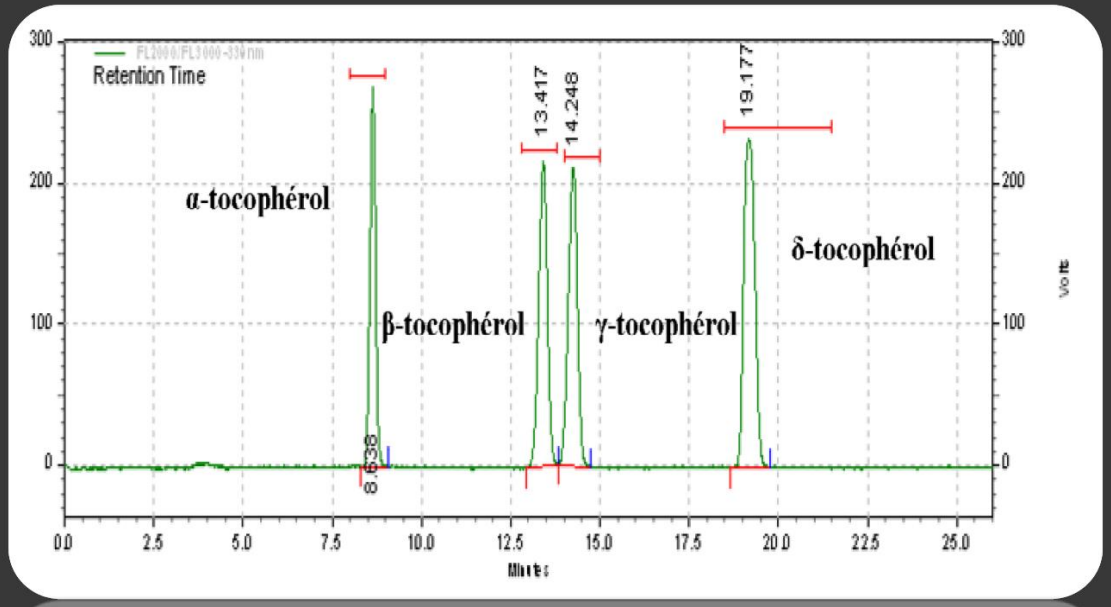
Country of origin	Samoa	Ivory Coast	Ecuador	Malaysia	Ghana	Nigeria	Bahia
POL	0.8	0.6	0.7	0.6	0.6	0.8	1.1
MOO, MMP	0.3	0.2	0.3	0.5	0.2	0.2	0.2
PPL	1.6	1.9	1.9	1.5	1.9	1.9	1.7
OOO	0.2	0.8	0.8	0.8	0.5	0.4	0.9
SOL	0.5	0.9	0.8	0.7	0.4	0.8	1.0
POO	2.2	4.4	3.5	2.7	2.6	3.2	5.5
PSL	2.8	3.6	2.8	2.8	3.2	3.4	3.4
PPO	16.4	15.9	15.3	13.8	15.2	14.8	14.0
SOO, PPP	3.7	6.0	4.8	3.8	4.5	5.1	8.4
SSL	2.1	1.8	1.5	2.0	2.1	1.9	2.1
PSO	38.3	36.6	36.3	36.6	37.3	37.4	34.6
OOA	1.6	1.0	1.2	1.6	1.4	1.2	1.5
PPS	0.4	0.4	0.3	0.6		0.7	0.3
SSO	26.8	23.8	26.9	28.4	26.8	26.4	23.7
SSP	0.7	0.8	0.9	1.0	1.3	0.4	0.2
SOA	2.2	1.6	2.1	2.5	2.2	1.9	1.6

TOCOPHEROL CONTENTS



	R1	R2	R3
α-tocophérol	CH_3	CH_3	CH_3
β-tocophérol	CH_3	H	CH_3
γ-tocophérol	H	CH_3	CH_3
δ-tocophérol	H	H	CH_3

TOCOPHEROL CONTENTS



Conditions opératoire HPLC :

Phase mobile : Hexane/dioxane 97/3

Colonne : Silice

Détecteur : Fluorimètre
λexcitation = 290 nm
λémission = 330 nm