BIOLOGICAL AND CHEMICAL ASPECTS OF SEED OILS AS BIODIESEL SOURCES

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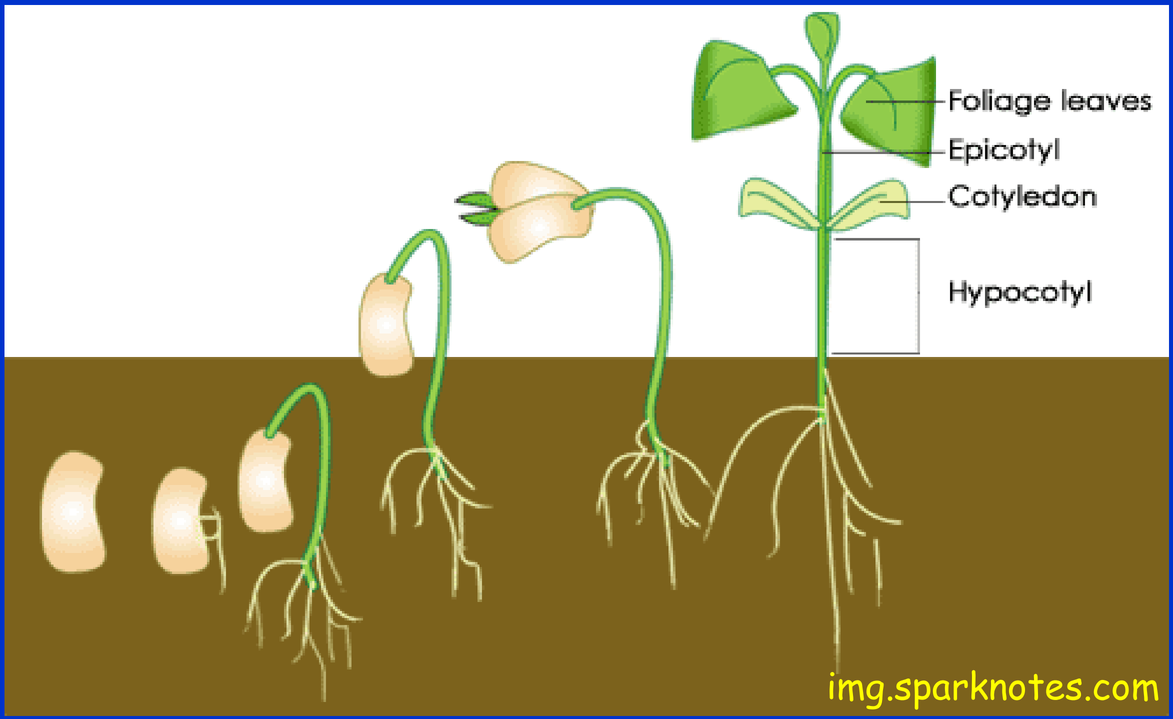
SEEDS CONTAIN RESERVE SUBSTANCES WHICH ARE USED BY THE SEEDLING UNTIL CONDITIONS FOR SELF SUSTENANCE ARE ACHIEVED.

IN ADDITION TO ENERGY, SEED RESERVES PROVIDE CARBON AND OTHER ELEMENTS TO THE SEEDLING GROWING BODY.



MOST ANGIOSPERM SPECIES, ACCUMULATE MAINLY STARCH AS SEED RESERVES.

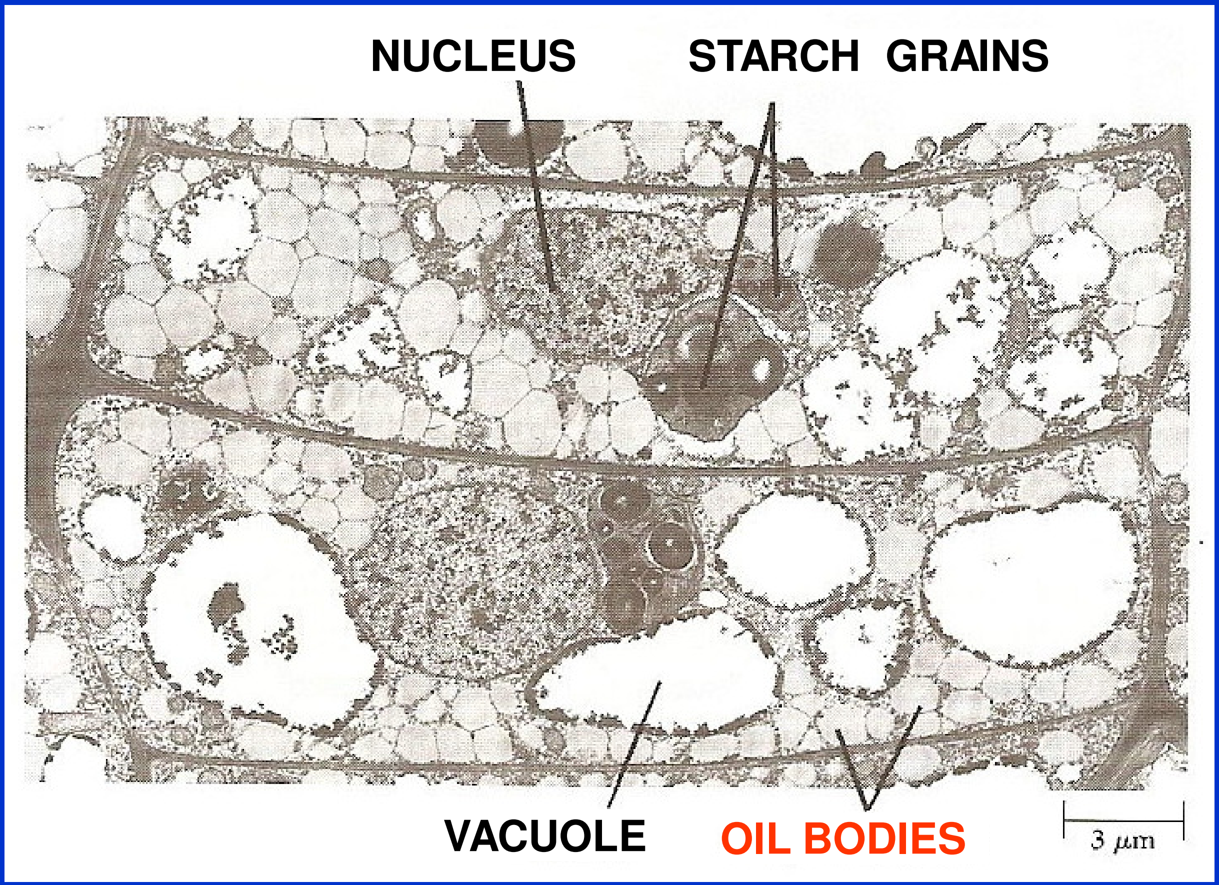
SOME SPECIES, NOTABLY FROM THE LEGUME FAMILY, ACCUMULATE PROTEIN, IN ADDITION TO STARCH.

SOME SPECIES ACCUMULATE PREFERENTIALLY OIL IN THEIR SEEDS.

WELL KNOWN SPECIES OLEAGINOUS SPECIES:

1. *RICINUS COMMUNIS* (EUPHORBIACEAE) – CASTOR OIL PLANT;
2. *COCOS NUCIFERA* (ARECACEAE) – COCONUT PLANT;
3. *ARACHIS HYPOGAEA* (LEGUMINOSAE) – PEANUT PLANT.

OILS ARE ACCUMULATED AS OIL BODIES, EITHER IN THE ENDOSPERM OR IN THE COTYLEDONS.



OIL BODIES ARE SURROUNDED BY PHOSPHOLIPIDS AND ALKALINE PROTEINS.

OIL BODIES OF UNDERGOUND STEM OF *ISOETES MURICATA*

COMPOSITION OF SEED OILS

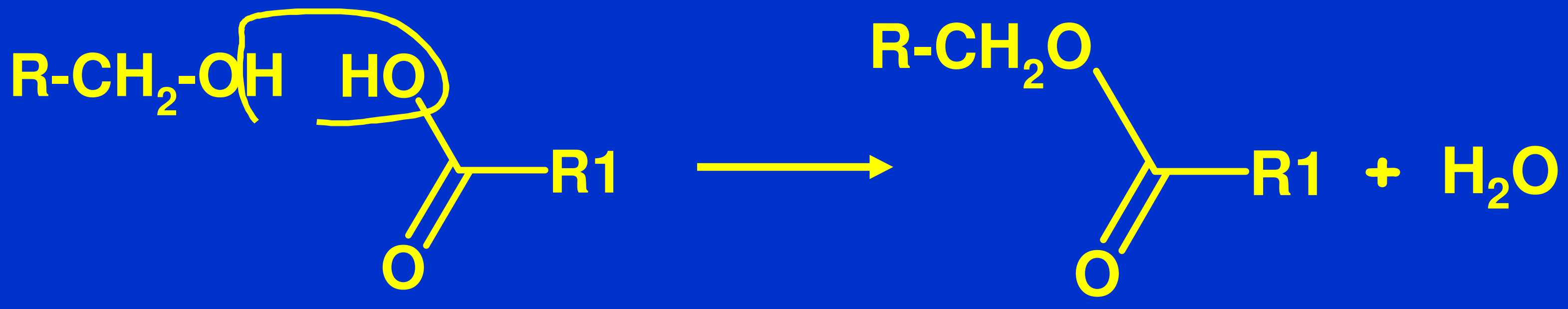
SEED OILS ARE MOSTLY TRIGLYCERIDES.

UNREFINED SOYBEAN OIL CONTAIN MOSTLY TRIGLYCERIDES AND PHYTOSTEROLS (SITOSTEROL, STIGMASTEROL), TOCOPHEROL (VITAMIN E), LECITHIN, WAXES, ETC.

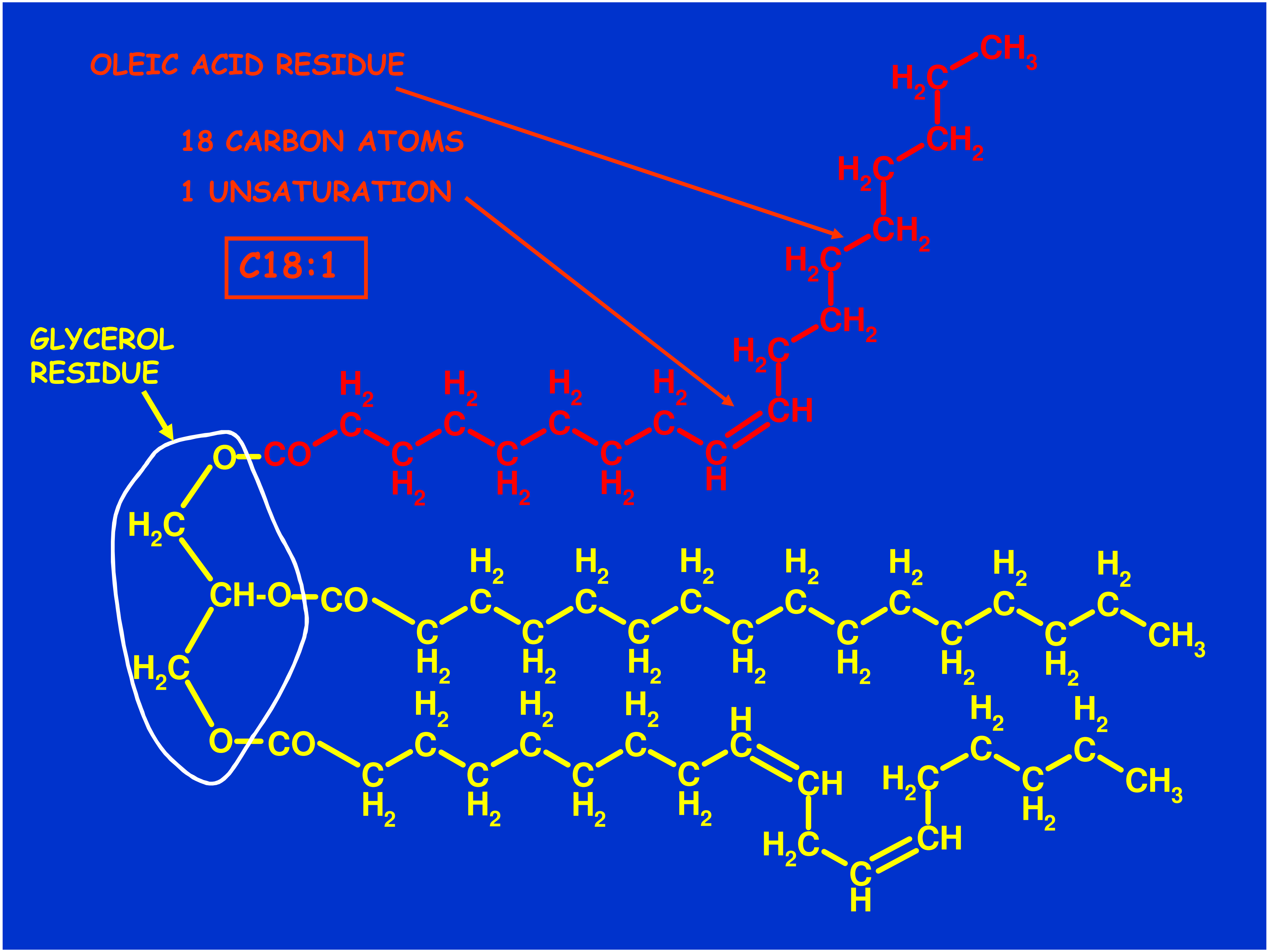
REFINED SOYBEAN OIL IS ALMOST EXCLUSIVELY TRIGLYCERIDES.

TRIGLYCERIDES

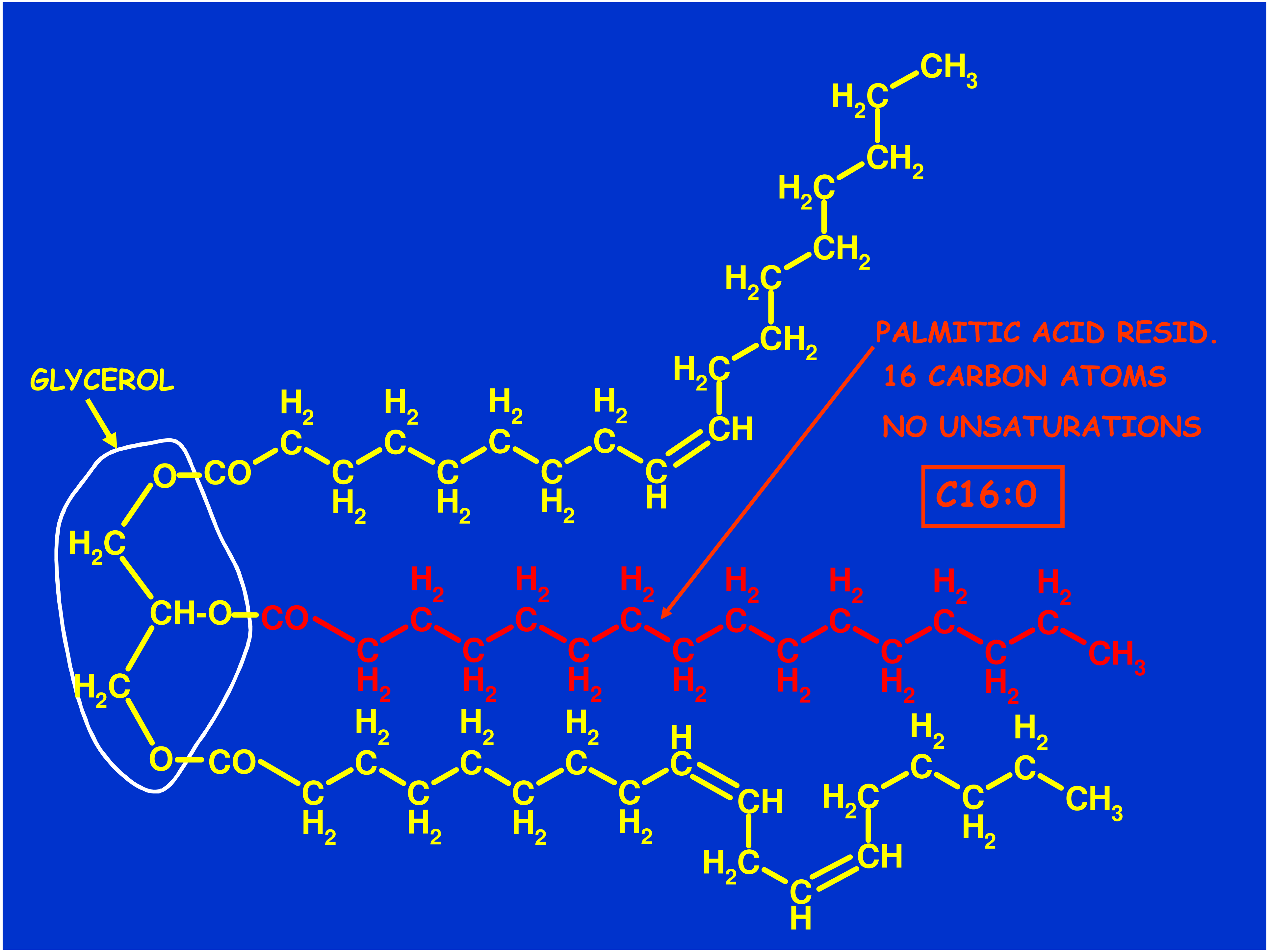
ESTERS COMPOSED BY A RESIDUE OF GLYCEROL (A TRIHYDROXYLIC ALCOHOL) AND THREE RESIDUES OF FATTY ACIDS.



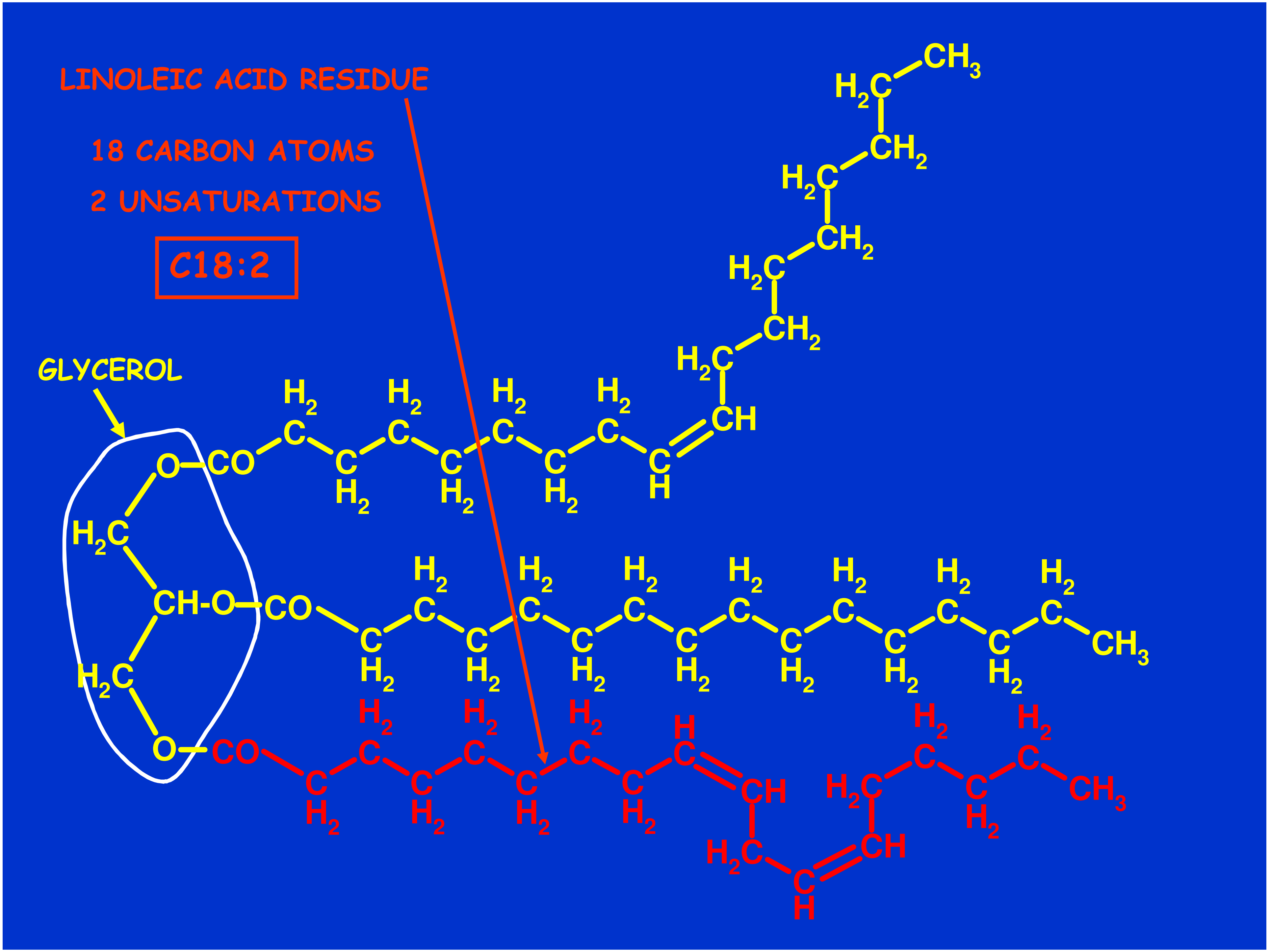
A GENERIC REACTION OF ESTERIFICATION



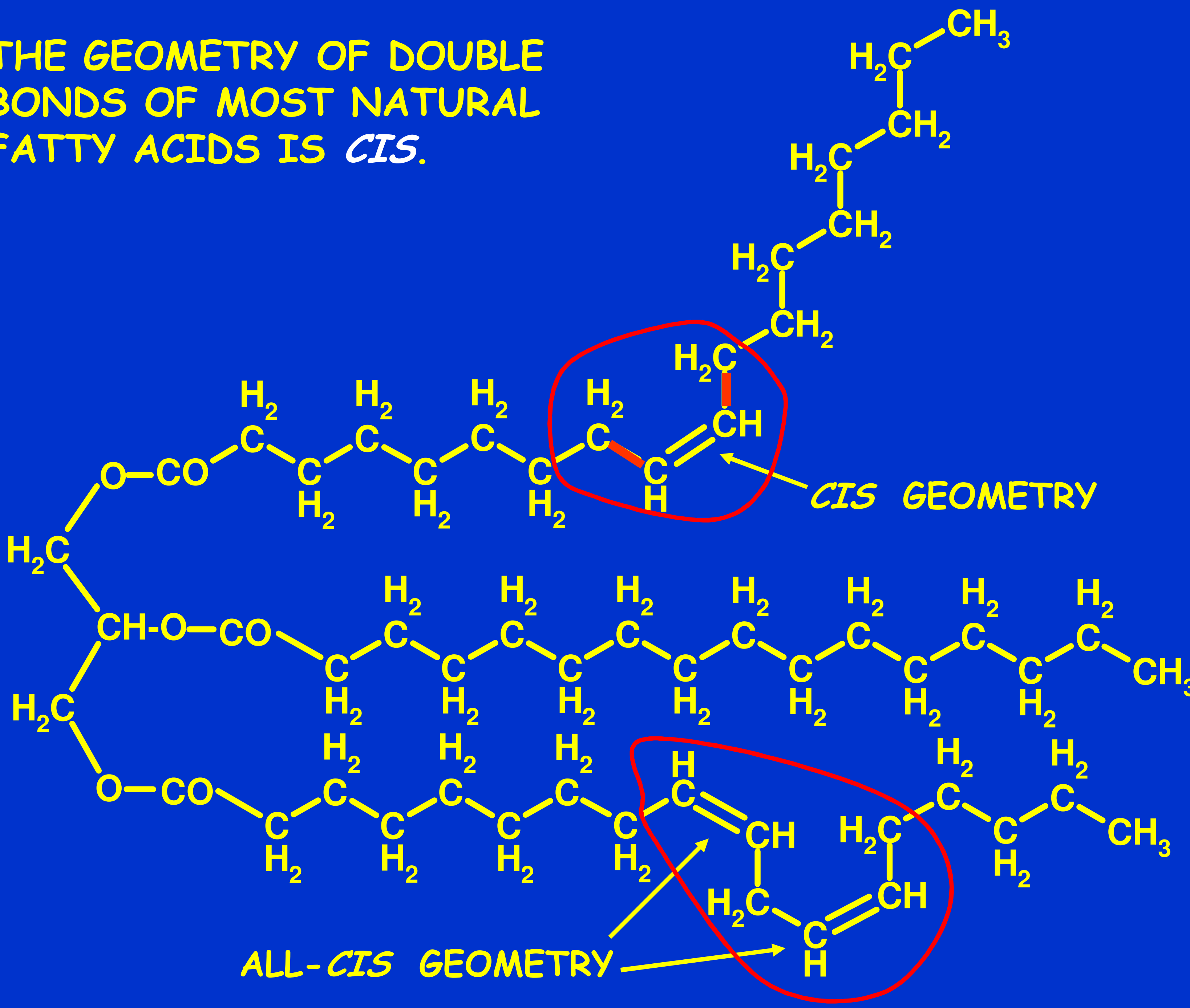
OLEIC ACID RESIDUE
18 CARBON ATOMS
1 UNSATURATION
C18:1
GLYCEROL RESIDUE



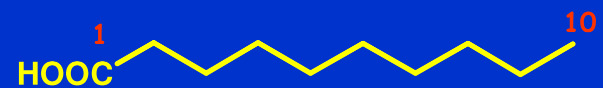
GLYCEROL
PALMITIC ACID RESID.
16 CARBON ATOMS
NO UNSATURATIONS
C16:0


LINOLEIC ACID RESIDUE
18 CARBON ATOMS
2 UNSATURATIONS
C18:2
GLYCEROL

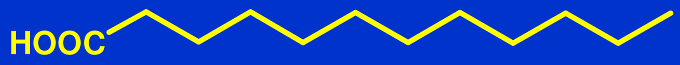
THE GEOMETRY OF DOUBLE BONDS OF MOST NATURAL FATTY ACIDS IS *CIS*.



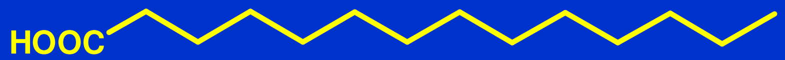
SOME FATTY ACIDS FOUND IN TRIGLYCERIDES



CAPRIC ACID – C10:0 GOAT MILK, *CUPHEA*



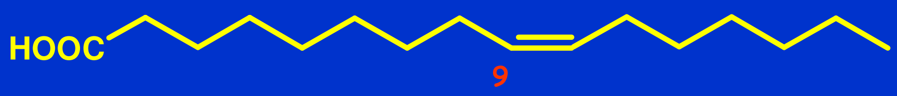
LAURIC ACID – C12:0 COCONUT



MYRISTIC ACID – C14:0 NUTMEG

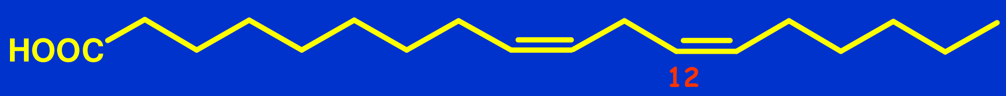
PALMITIC ACID – C16:0 PALM

STEARIC ACID – C18:0 CHOCOLATE

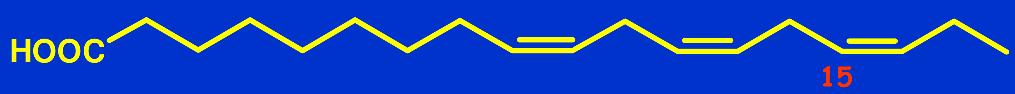


PALMITOLEIC ACID – C16:1 MACADAMIA

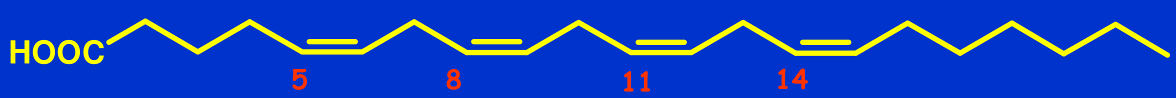
OLEIC ACID – C18:1 OLIVE



LINOLEIC ACID – C18:2 SOYBEAN



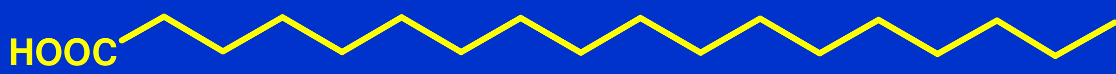
LINOLENIC ACID – C18:3 LINSEED



ARACHIDONIC ACID – C20:4

COD LIVER OIL

CIS-DOUBLE BONDS HAVE STRIKING EFFECTS ON MELTING POINTS OF FATTY ACIDS



STEARIC ACID

MP = 69 °C

OLEIC ACID

MP = 4 °C

LINOLEIC ACID

MP = -12 °C

THE FIRST DOUBLE BOND HAS THE STRONGEST EFFECT.

TRANS-DOUBLE BONDS HAVE WEAKER EFFECTS

STEARIC ACID

MP = 69 °C

ELAIDIC ACID

MP = 45 °C

FATS CONTAINING *TRANS*-DOUBLE BONDS ARE CALLED TRANS FATS.

REGARDED AS HIGHLY NOXIOUS IN NUTRITION AND MEDICINE.

TRIGLYCERIDES WITH PREDOMINANCE OF SATURATED FATTY ACIDS ARE SOLID (FATS) AT ROOM TEMPERATURE.

- MAMMAL AND BIRD TRIGLYCERIDES -

TRIGLYCERIDES WITH PREDOMINANCE OF UNSATURATED FATTY ACIDS ARE LIQUID (OILS) AT ROOM TEMPERATURE.

- FISH AND MANY PLANT TRIGLYCERIDES -

SATURATION ADDS VISCOSITY TO TRIGLYCERIDES.

UNSATURATION ADDS FLUIDITY.

VISCOSITY AND FLUIDITY ARE OPPOSED CHARACTERISTICS

FATTY ACIDS	LINSEED	SOYBEAN	CORN	SUNFLOW.	SESAME	COTTON	PEANUT	OLIVE	COCONUT
<14:0									59
14:0						1			18
16:0	6	11	13	11	10	29	6		10
18:0	4	4	4	4	5	4	5	5	2
20:0							2		
22:0							3		
16:1						2		2	
18:1	22	25	29	29	40	24	61	60	8
18:2	16	51	54	52	45	40	22	45	1
18:3	52	9							
I_2 VALUE	185	130	118	128	110	98	90	83	8

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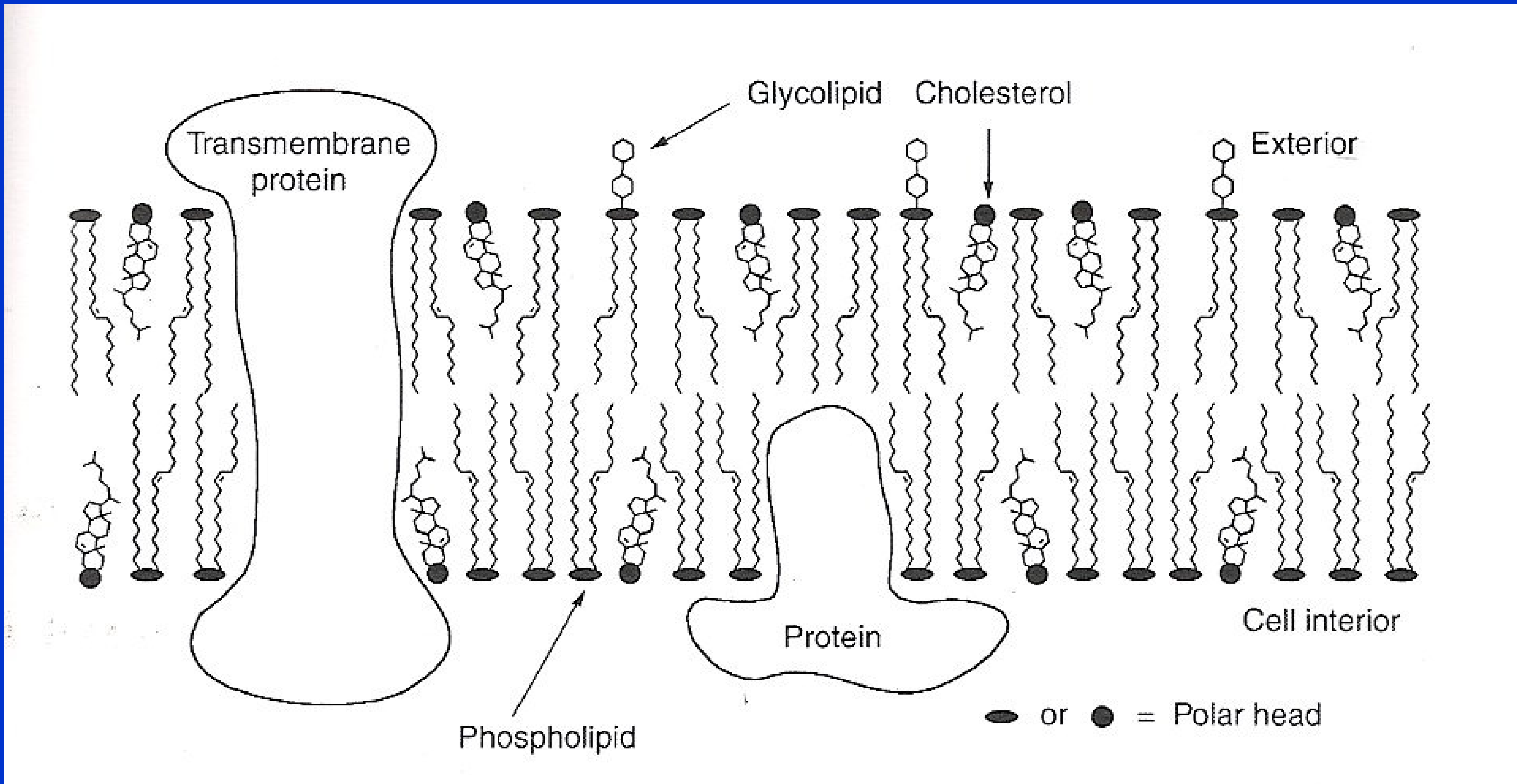
20:0							2		
22:0							3		
16:1						2		2	
18:1	22	25	29	29	40	24	61	60	8
18:2	16	51	54	54	45	40	22	45	1
18:3	52	9							
I_2 VALUE	185	128	118	130	110	98	90	83	8

HIGHER MELT. POINT & VISCOSITY →

FATTY ACIDS ARE ALSO CONSTITUENTS OF CELL MEMBRANES

- CELL MEMBRANES ARE LIPOPROTEIC -



MEMBRANE STRUCTURE OF MAMMALIAN CELLS

FATTY ACID COMPOSITION DETERMINES THE DEGREE OF MEMBRANE RIGIDITY OR FLUIDITY.

A RELATIONSHIP EXISTS BETWEEN FATTY ACID PROFILES AND BODY TEMPERATURE.

TO A CERTAIN DEGREE, IT IS POSSIBLE TO PREDICT CHARACTERISTICS OF FATTY ACID PROFILES ORGANISMS

BIRDS AND MAMMALS HAVE CONSTANT HIGH BODY TEMPERATURE.

THEIR FATTY ACIDS ARE PREDOMINANTLY SATURATED (IMPORTANT FATTY ACID - C16:0). THEIR TRIGLYCERIDES ARE SOLID AT ROOM TEMPERATURE.

FISHS AND PLANTS HAVE NO CONTROL OVER BODY TEMPERATURE. THEIR BODY TEMPERATURES ARE USUALLY BELOW THOSE OF BIRDS AND MAMMALS.

FATTY ACIDS OF MANY PLANTS AND FISHS ARE PREDOMINANTLY UNSATURATED AND THEIR TRIGLYCERIDES ARE LIQUID. FATTY ACIDS OF FISH FROM COLD WATERS (E.G. COD, SALMON) ARE POLYUNSATURATED.

OTHER FACTOR AFFECTING MELTING POINTS OF TRIGLYCERIDES

LENGTH OF CARBON CHAINS

A FACTOR NOT AS STRONG AS UNSATURATION, BUT ALSO DESERVING CONSIDERATION.

FATTY ACID	MELT. POINT	
C18:0	70 °C	LONG CARBON CHAINS
C16:0	63 °C	LONG CARBON CHAINS
C14:0	58 °C	MEDIUM CARBON CHAINS
C12:0	44 °C	MEDIUM CARBON CHAINS
C10:0	31 °C	MEDIUM CARBON CHAINS

WHY ARE TRIGLYCERIDES CONVENIENT RAW MATERIALS FOR BIODIESEL PRODUCTION?

A VERY IMPORTANT REASON: THEY ARE RICH ENERGY SUBSTANCES.

OILS AND FATS HAVE THE HIGHEST CALORIE CONTENT PER UNIT MASS, AMONG THE MAIN CLASSES OF FOODS.

CALORIC CONTENTS OF FOODS – Amount of energy released by totally burning the food

Fat: 1 gram = 9 calories
Protein: 1 gram = 4 calories
Carbohydrates: 1 gram = 4 calories
Alcohol: 1 gram = 7 calories

WHY IS THAT SO?

FATTY ACIDS CONTAIN LOW PERCENT OF OXYGEN IN THEIR MOLECULES.

THE HIGHER THE OXYGEN CONTENT, THE LOWER THE CALORIC VALUE.

$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$

COMPOUNDS WITH LONG METHYLENIC CHAINS, WITH MANY

C-C AND C-H BONDS, *ARE HIGHLY CALORIC.*

CO_2 - CARBON COMPOUND WITH THE HIGHEST OXYGEN CONTENT

PRACTICALLY IMPOSSIBLE TO OBTAIN ENERGY THEREFROM.

HEAT OF COMBUSTION OF SOME COMMON FUELS

FUEL	% OXYGEN	KJ/mol	kJ/g
n-C_8H_{18}	0	-5,508	-48
n-C_4H_{10}	0	-2,881	-49
C_4H_9OH	21	-2,712	-37
C_2H_5OH	35	-1,407	-30

THE HIGHER THE OXYGEN CONTENT THE LOWER THE AMOUNT OF ENERGY RELEASED BY COMBUSTION

IS IT POSSIBLE TO BURN TRIGLYCERIDES IN DIESEL ENGINES?

TRIGLYCERIDES ARE NOT ADEQUATE FOR DIRECT USE IN DIESEL ENGINES.

IMPORTANT PARAMETER TO BE CONSIDERED: VISCOSITY.

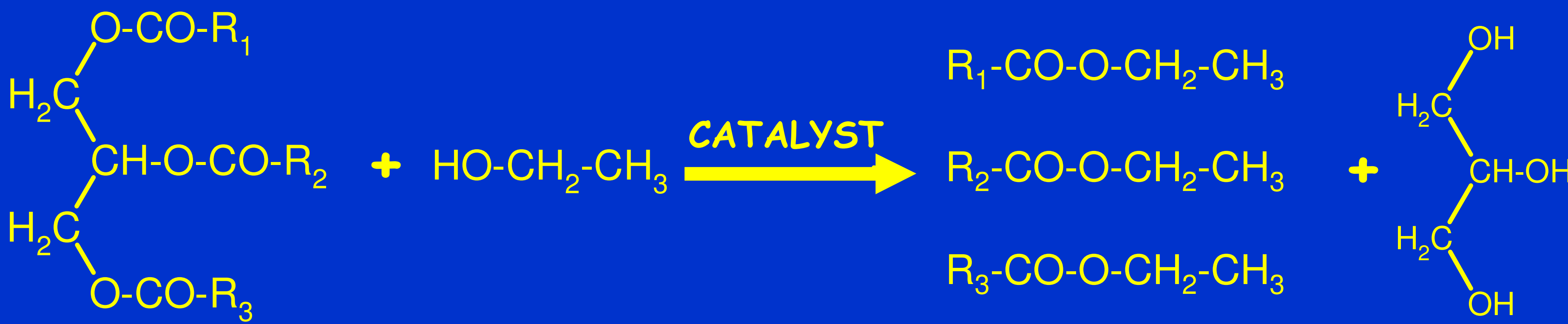
VISCOSITIES OF TRIGLYCERIDES ARE TOO HIGH (OFTEN 10 TIMES ABOVE THE MAXIMUM RECOMMENDED).

TRIGLYCERIDES ARE CONVERTED INTO METHYL OR ETHYL ESTERS OF FATTY ACIDS.

THE REACTION IS CALLED *TRANSESTERIFICATION*.

BIODIESEL IS THE PRODUCT THUS OBTAINED.

THE PROCESS OF TRANSESTERIFICATION

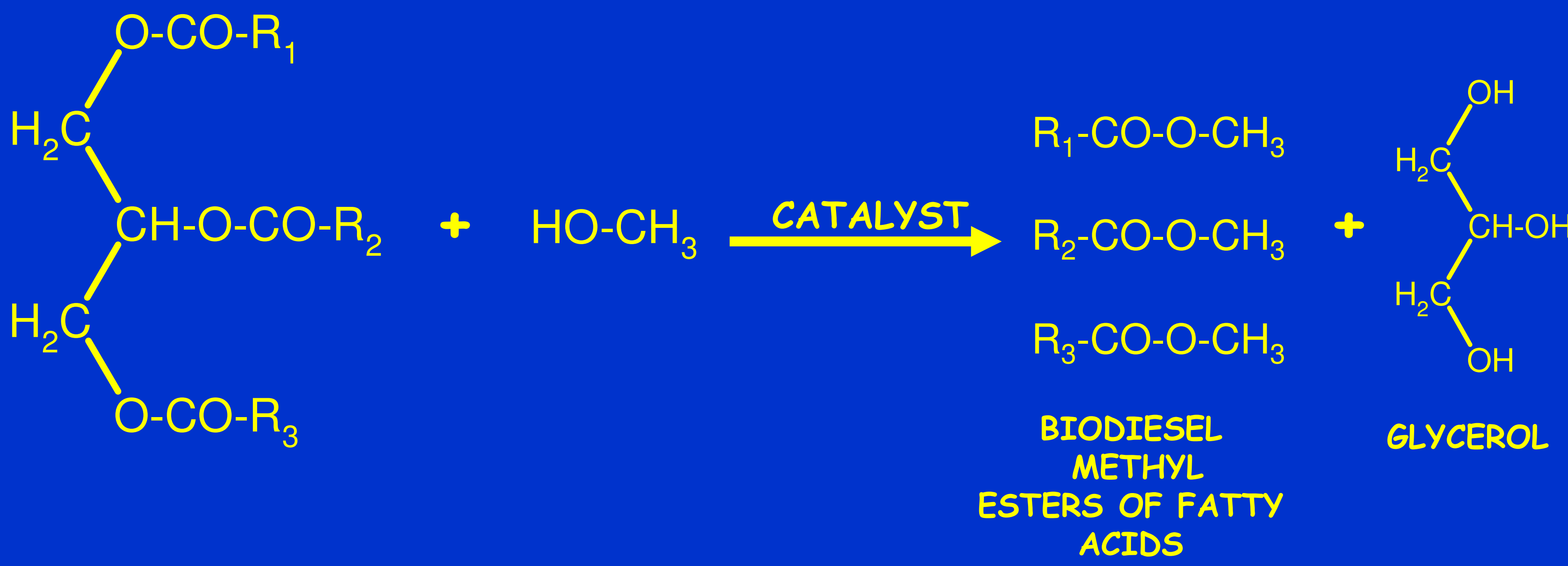


BIODIESEL
ETHYL
ESTERS OF FATTY
ACIDS

GLYCEROL

TRANSESTERIFICATION USING ETHANOL

CATALISTS MAY BE H_2SO_4, NaOH, KOH OR $NaOCH_3$.



TRANSESTERIFICATION USING METHANOL

GLYCEROL IS OBTAINED AS BY-PRODUCT.

FINDING USES FOR GLYCEROL COULD LOWER BIODIESEL COSTS.

INFLUENCE OF CHEMICAL CHARACTERISTICS ON BIODIESEL QUALITY

1. *LENGTH OF CARBON CHAIN*

LONG CHAINS: A. INCREASE CALORIFIC VALUES (GOOD)

B. INCREASE VISCOSITY AND CLOUD POINT (BAD)

2. *UNSATURATION* : A. DECREASES CALORIFIC VALUES (BAD)

B. DECREASES VISCOSITY (GOOD)

POLYUNSATURATION : A. ENHANCES FLUIDITY (GOOD)

B. REDUCES FUEL STABILITY (BAD)

FATTY ACID CHARACTERISTICS AND BIODIESEL QUALITY

1. *UNSATURATED LONG CHAIN ACIDS*

MONOUNSATURATION: GIVES FLUIDITY TO BIODIESEL AND DOES NOT IMPART INSTABILITY.

POLYUNSATURATION: EXCELENT TO IMPROVE FLUIDITY.
INCONVENIENT: TURNS BIODIESEL PRONE TO OXIDATION AND ACCUMULATION OF POLYMERS WHICH DEPOSIT INSIDE THE ENGINE CYLINDERS.

2. *SATURATED MEDIUM CHAIN ACIDS*

ALLOW PRODUCTION OF FLUID BIODIESEL, WITH MAXIMUM STABILITY TO OXIDATION.
INCONVENIENT: HIGH OXYGEN CONTENT – REDUCES CALORIFIC VALUE, WHICH DEMANDS HIGHER FUEL CONSUMPTION.

DESIRABLE CHARACTERISTICS OF PLANT SOURCES OF TRIGLYCERIDES FOR BIODIESEL PRODUCTION

1. NON-EDIBLE OILS – THERE IS STRONG OPPOSITION AGAINST DEVIATION OF EDIBLE COMMODITIES TO FUEL PURPOSES;

2. FAST GROWTH RATE, HIGH PRODUCTIVITY;

3. RESISTANCE TO HARSH GROWING CONDITIONS – DROUGHT, HUMIDITY, SALINITY, PLAGUES, ETC.

4. CAPACITY OF GROWING IN MARGINAL HABITATS.

70-80% OF BIODIESEL COST IS ACCOUNTED FOR COSTS OF RAW MATERIALS.

FATTY ACID PROFILES (%) OF SOME NON EDIBLE SEED OILS

SPECIES	16:0	18:0	18:1	18:2	18:3	OTHER
Azadirachta indica	20	20	42	15		
Brassica carinata	5	1	16	21	13	C22:1 45
Jathropha curcas	14	6	38	38	1	
Ricinus communis	2	1	7	3		C18:1(OH) 87
Terminalia catappa	35	5	32	28		

Ai: Neem; Bc: rapeseed related; Jc: pinhão manso; Rc: castor oil bean; Tc: sea almond, chapéu-de-sol, castanheira

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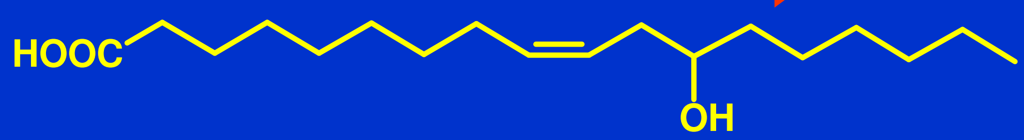
Content of long chain saturated acids too high, particularly for use in temperate countries.

Degree of polyunsaturation too high – brings about oxidative instability



RICINOLEIC ACID – HYDROXYL INCREASES VISCOSITY AND MELTING POINTS.

TURNS CASTOL OIL INADEQUATE AS RAW MATERIAL FOR BIODIESEL PRODUCTION.

JATROPHA CURCAS

PINHÃO-MANSO

IN BRAZIL, THE PLANT WITH THE STRONGEST POTENTIAL AS BIODIESEL SOURCE.

OFFICIAL SUPPORT FOR PLANTATIONS IN THE NORTH OF MINAS GERAIS.
PETROBRAS PLANT SOON IN OPERATION IN MONTES CLAROS.

TERMINALIA CATAPPA

CHAPÉU-DE-SOL, CASTANHEIRA

CAATINGA (*WHITE FOREST*)

~10% OF BRAZILIAN TERRITORY – SEMI-ARID CLIMATE.

REGION WITH SEVERE SOCIAL AND ECONOMICAL PROBLEMS.

SOME OLEAGINOUS EUPHORBIACEAE NATIVE IN THE CAATINGA

EUPHORBIACEAE – PLANT FAMILY WITH MANY XEROPHYTIC REPRESENTATIVES.

SEVERAL EUPHORBIACEAE HAVE OLEAGINOUS SEEDS. EXAMPLES: CASTOR OIL PLANT, BRAZILIAN RUBBER TREE, TUNG OIL PLANT, *JATROPHA CURCAS*.

SOME *JATROPHA* SPECIES FROM THE CAATINGA.

SPECIES	OIL YIELD (%)	MAIS FATTY ACIDS	
J. MOLLISSIMA	22-37	18:2	18:1
J. MUTABILIS	20-39	18:2	18:1
J. RIBIFOLIA	21-34	16:0	18:1

OTHER EUPHORBIACEAE GENERA NATIVE IN THE CAATINGA, WITH OLEAGINOUS SEEDS: *CROTON*, *CHAMAESYCE*, *EUPHORBIA*, *MANIHOT* (CASSAVA GENUS), *SAPIUM*, *SEBASTIANA*.

BRAZIL HAS THE WORLD'S LARGEST PLANT DIVERSITY – ABOUT 50,000 ANGIOSPERM SPECIES (20% OF THE WORLD'S SPECIES).

IT IS IMPORTANT TO MAKE INVENTORIES OF CERTAIN PLANT TAXA WITH NOTORIOUS POTENTIAL AS BIODIESEL SOURCES (E.G. PALMS, EUPHORBIACEAE), THEIR SEED AND SEED OIL YIELDS, FATTY ACID PROFILES AND QUALITY OF DERIVED BIODIESELS.

PRIORITIES SHOULD BE GIVEN TO PLANTS WHICH ARE CURRENTLY NOT AIMS OF ECONOMICAL EXPLOITATION AND ARE TOLERANT TO EDAPHIC AND CLIMATIC CONDITIONS OF MARGINAL HABITATS.

THANK YOU