Introduction to Lipid Chemistry

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Ontario SCC Education Day

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Lipid knowledge for the personal care industry

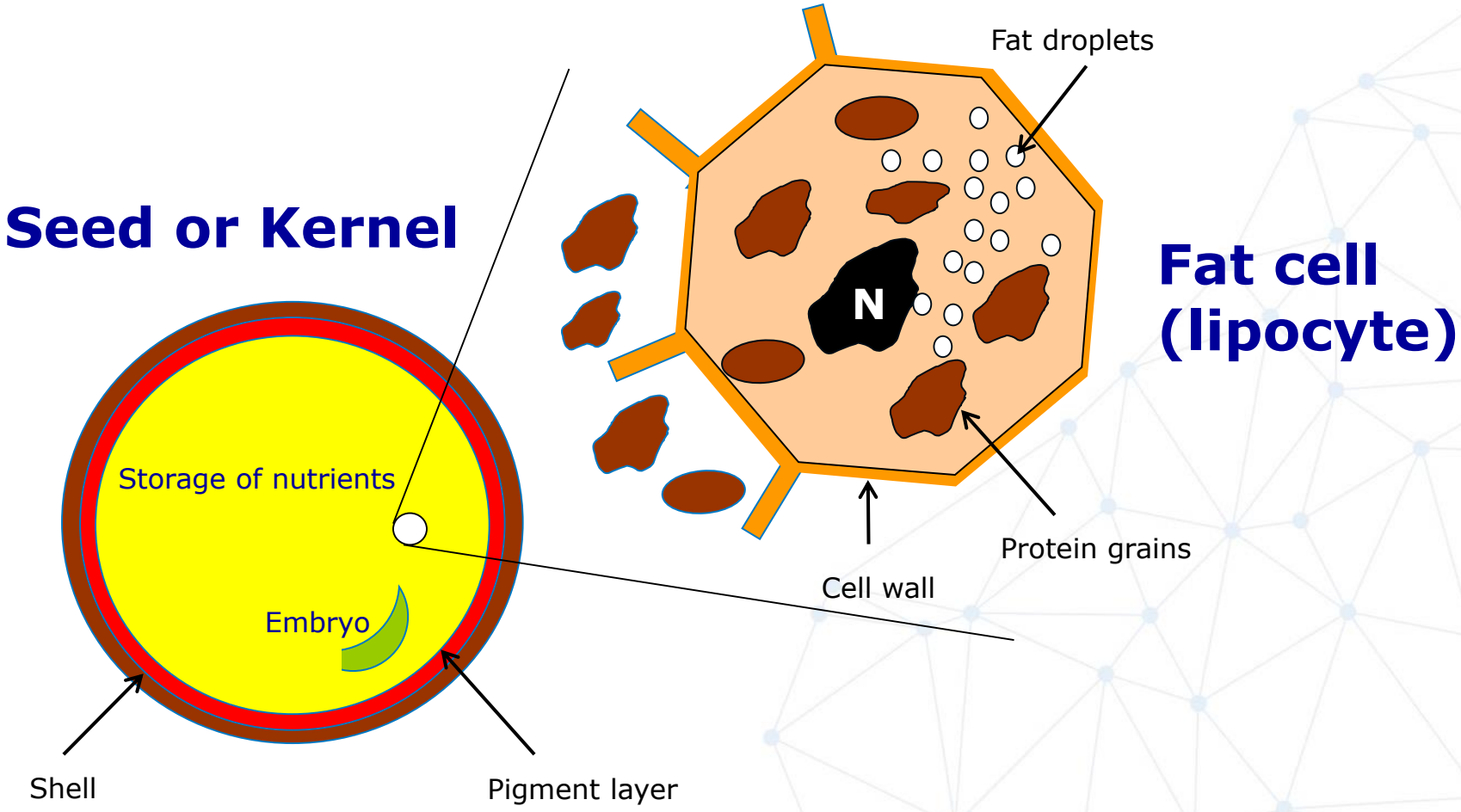
What is a Lipid?

"Lipids are fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds"
(According to W.W. Christie, http://lipidlibrary.aocs.org)

Including:

- Fatty acids and their esters with simple alcohols
- Glycerides (mono-, di- and tri-acylglycerols)
- Sterols and sterol esters (incl. cholesterol, phytosterols etc.)
- Waxes and wax esters (incl. lanolin, bees wax etc.)
- Tocopherols (Vitamin E)
- Complex lipids (phospholipids and glycolipids)

Where do plant lipids come from?



What are vegetable oils & fats?

Major

Component	Content	Function in plant
Triglycerides	90 – 100 %	Energy source
Di- and monoglycerides	0 – 5 %	Breakdown products
Fatty acids	0 – 1 %	Breakdown products

Minor

Component	Content	Function in plant
Aldehydes, ketones, hydrocarbons	ppb – ppm levels	Oxidation products
Phospholipids	0 - 1 %	Membrane lipids
Sterols, sterol esters	500 - 15000 ppm	Membrane lipids
Tocopherols, tocotrienols	0 – 3000 ppm	Antioxidants
Other unsaponifiables	0 – 10 %	

Esters are formed from fatty acids and alcohols

Alcohol

Fatty acid

Esters are formed from fatty acids and alcohols

Alcohol

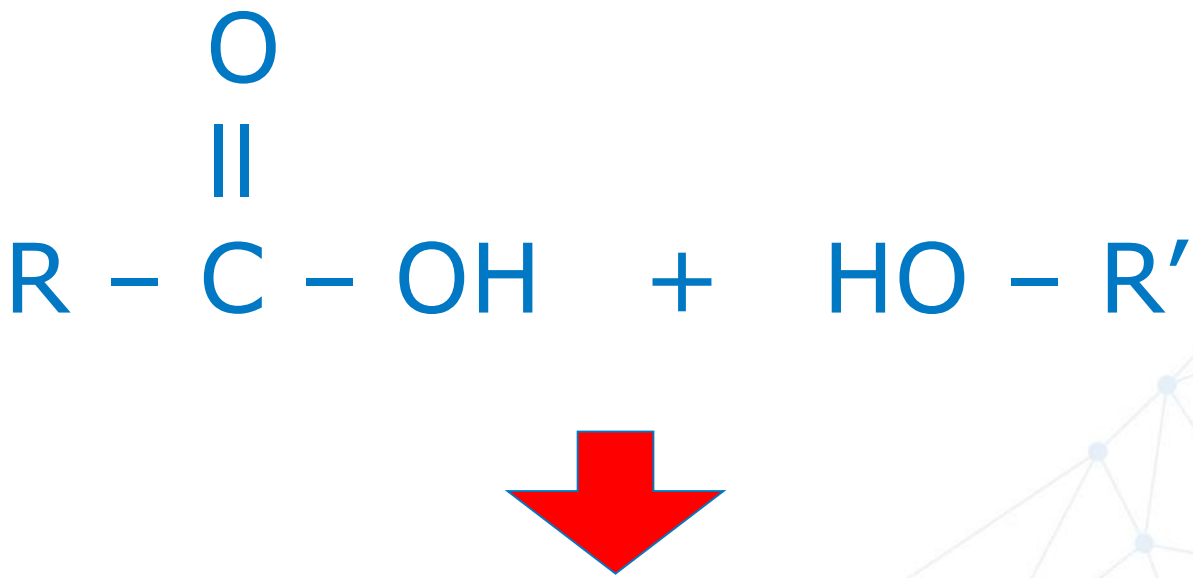
Fatty acid

Ester bond

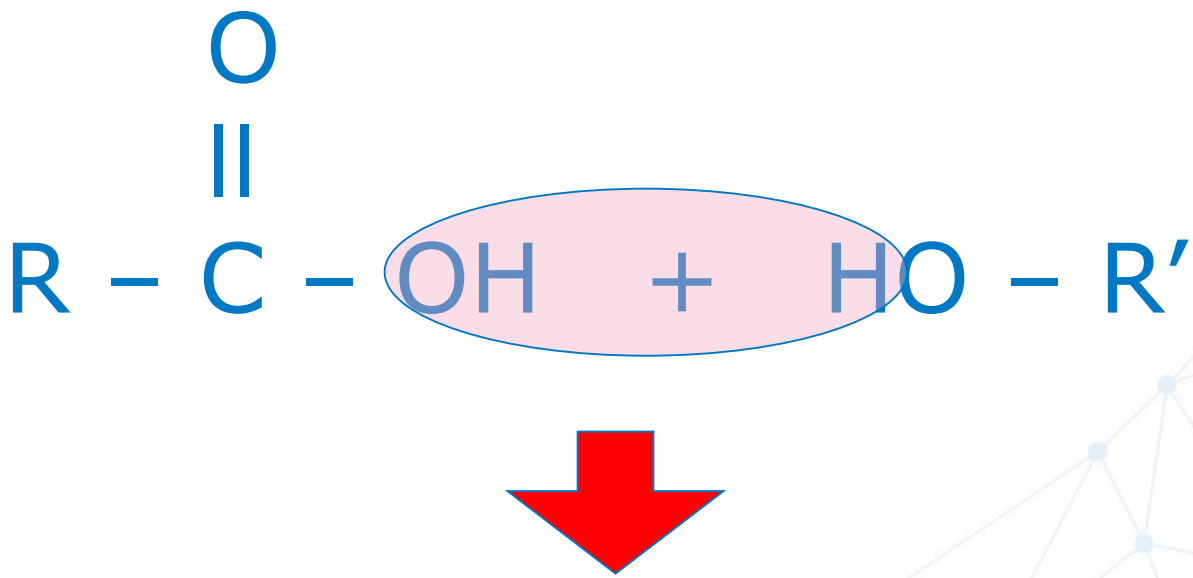
(Formed by dehydration synthesis)

H – from alcohol
OH – from acid

Esters are formed from fatty acids and alcohols



Esters are formed from fatty acids and alcohols



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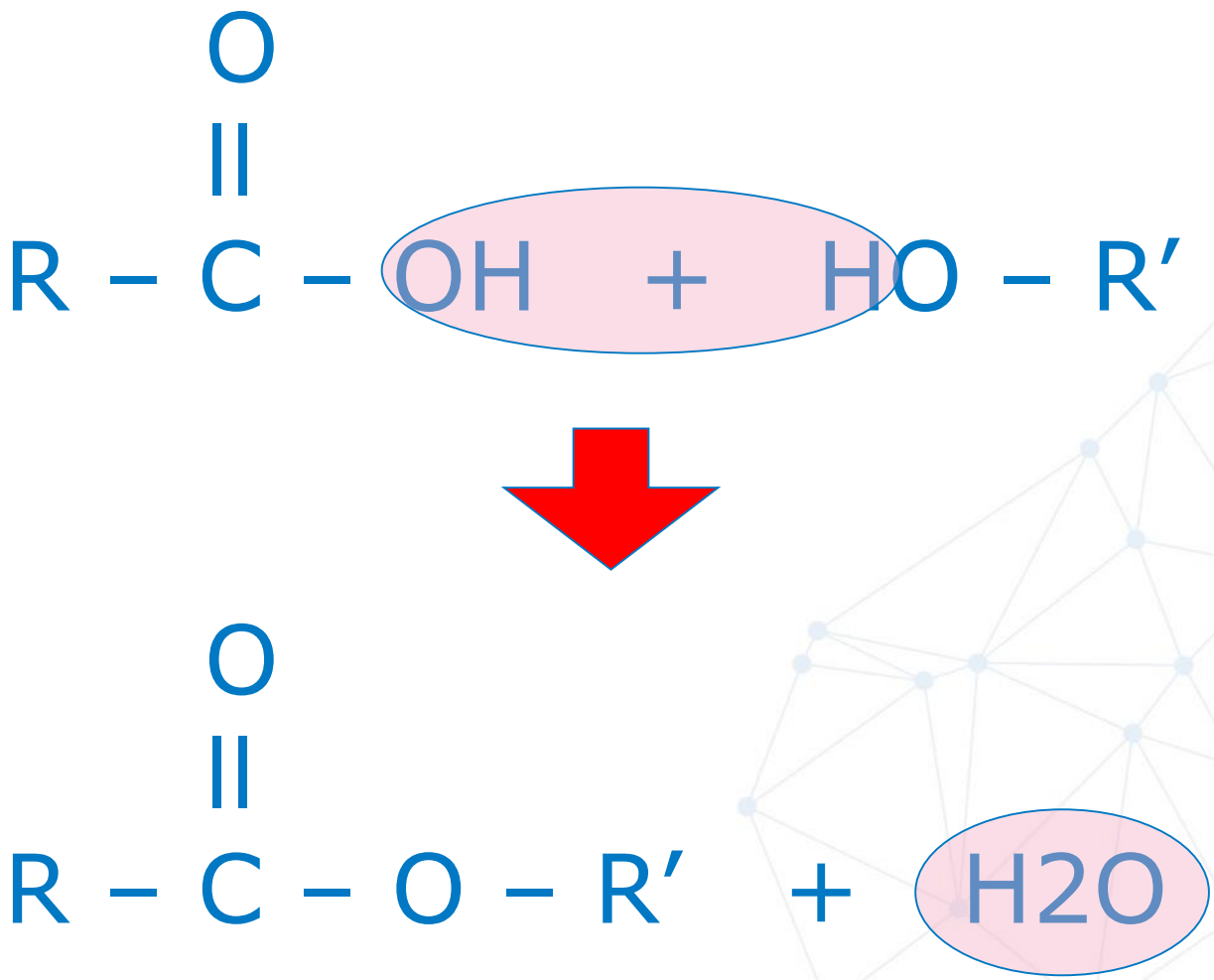

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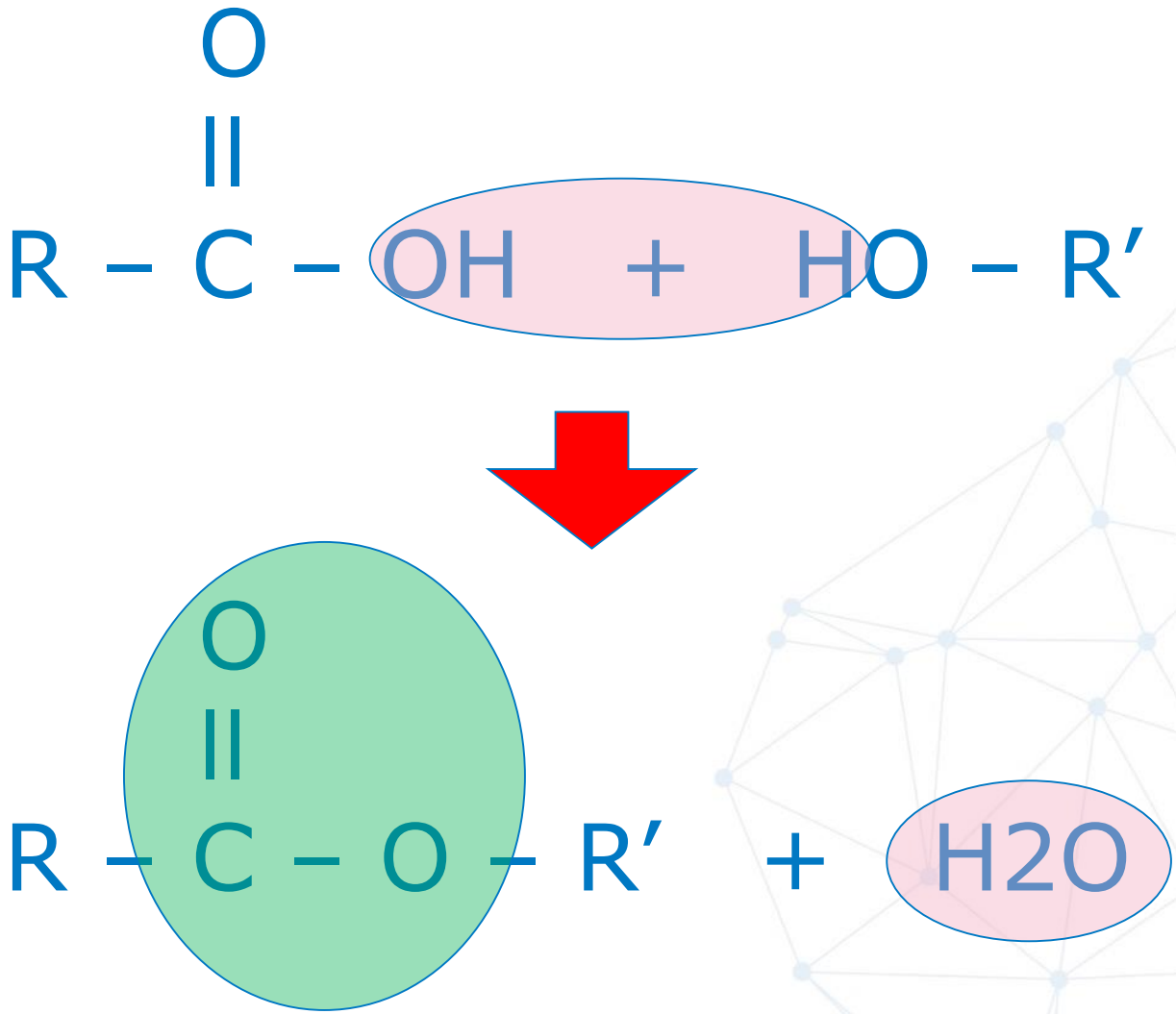
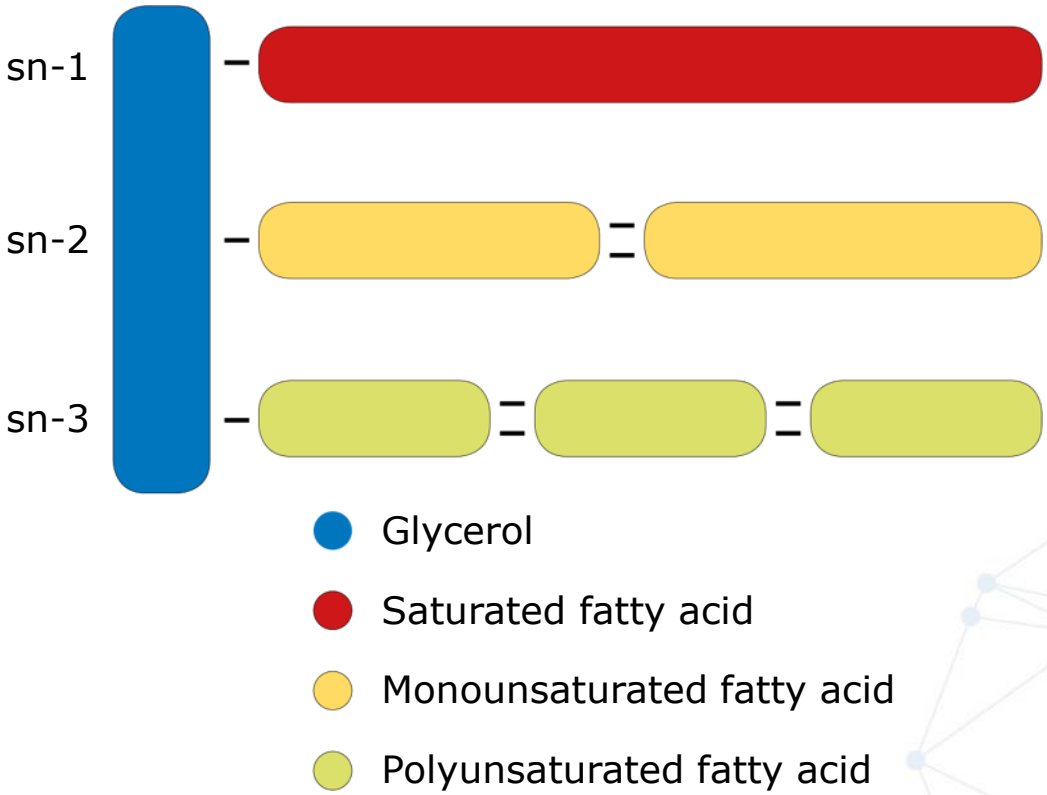


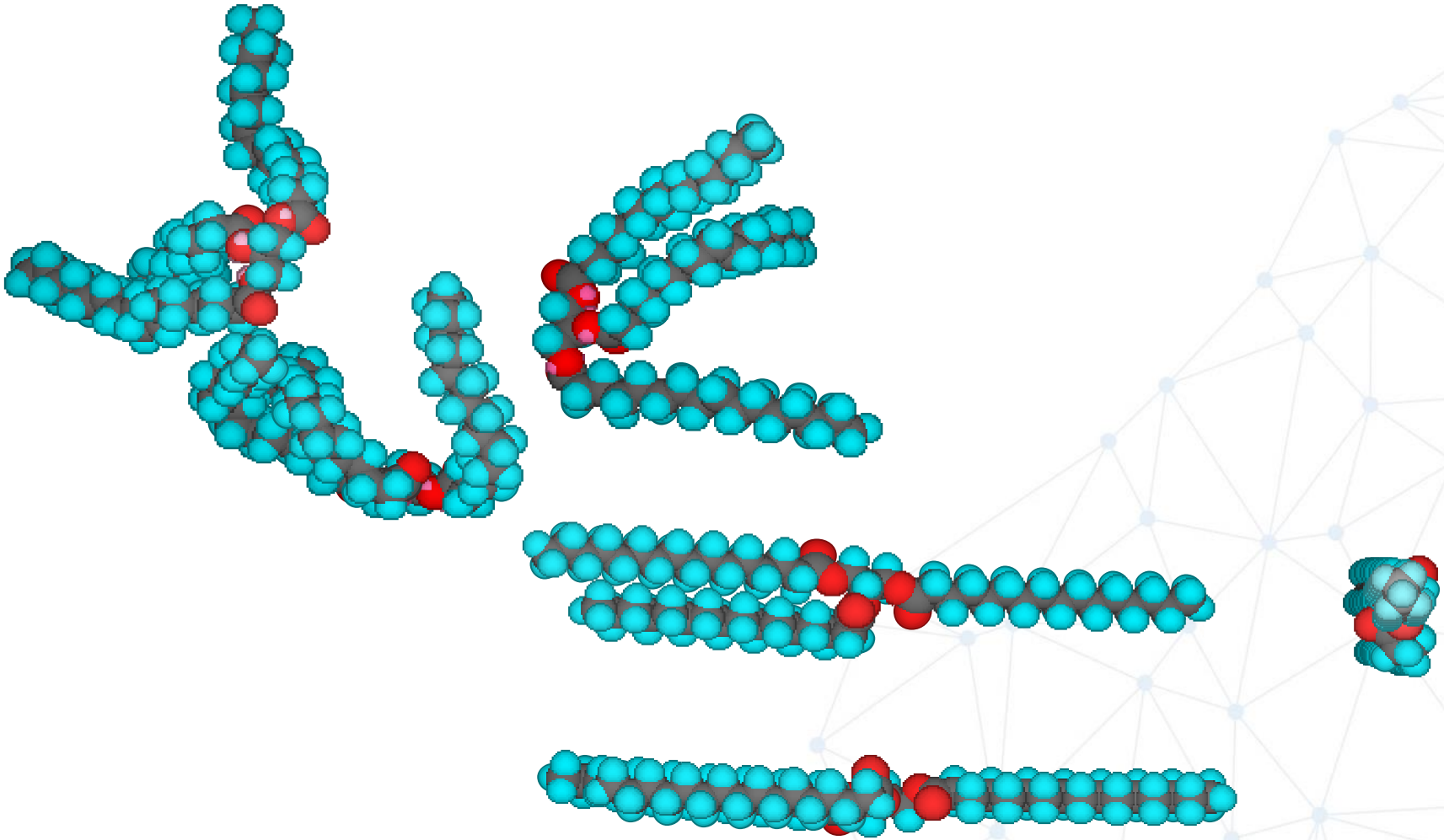
Triglycerides are complex esters of fatty acids with glycerol



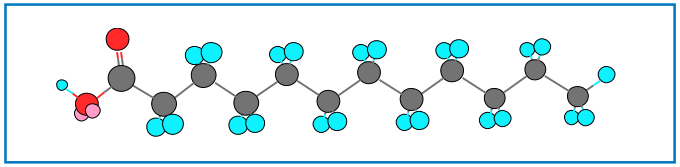
Natural FA's ~ 20
Possible TG's = n^3

$\Rightarrow$ 8000 possible TG's

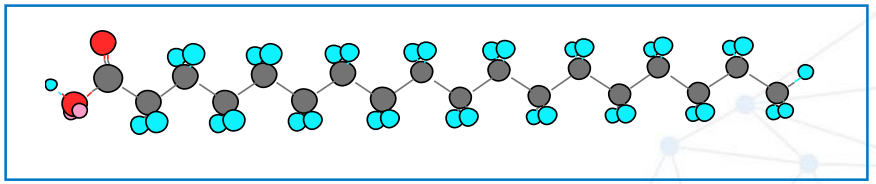
Oils are liquid, fats are solid (kind of)



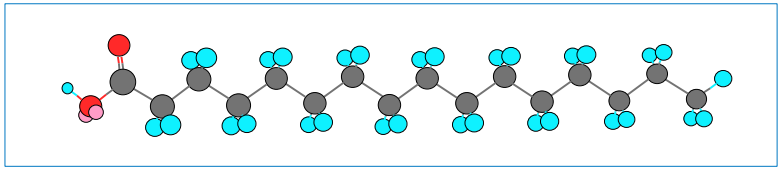
Most common natural fatty acids



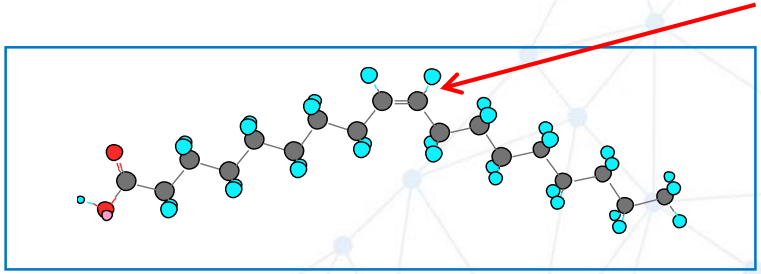
Lauric acid, 12 carbons



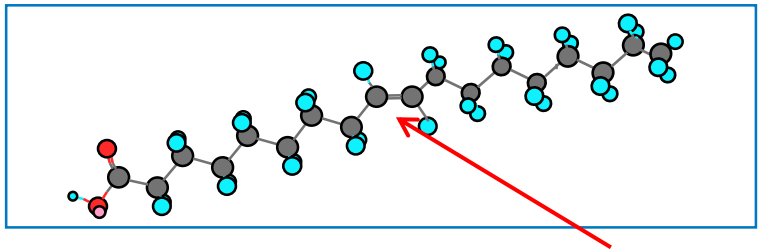
Stearic acid, 18 carbons



Palmitic acid, 16 carbons



Oleic acid, 18 carbons, 1 double bond



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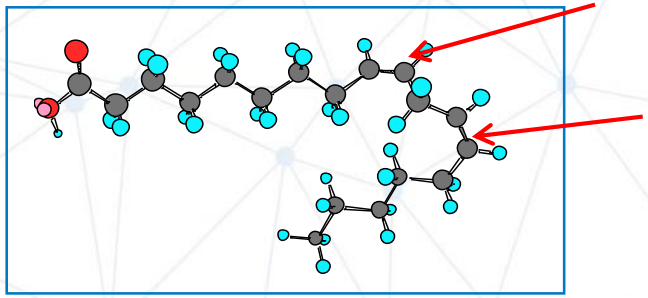
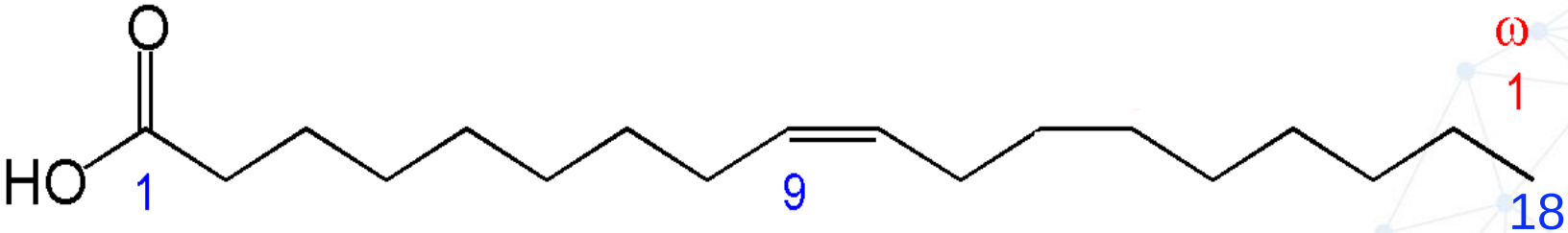
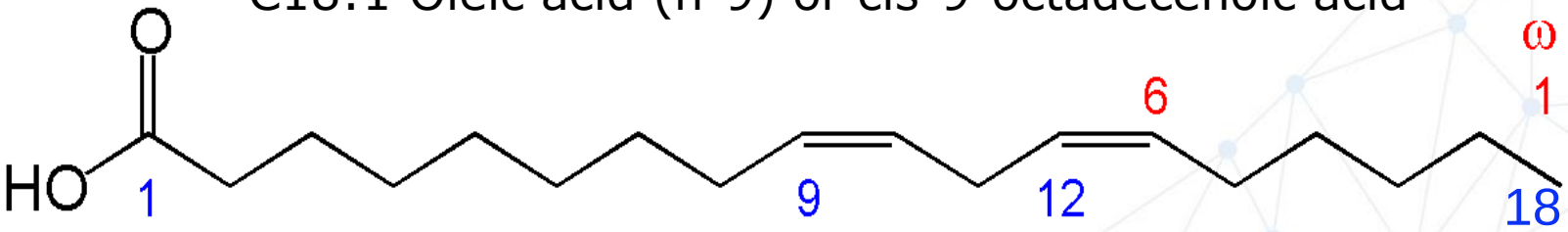


Linoleic acid, 18 carbons, 2 double bonds

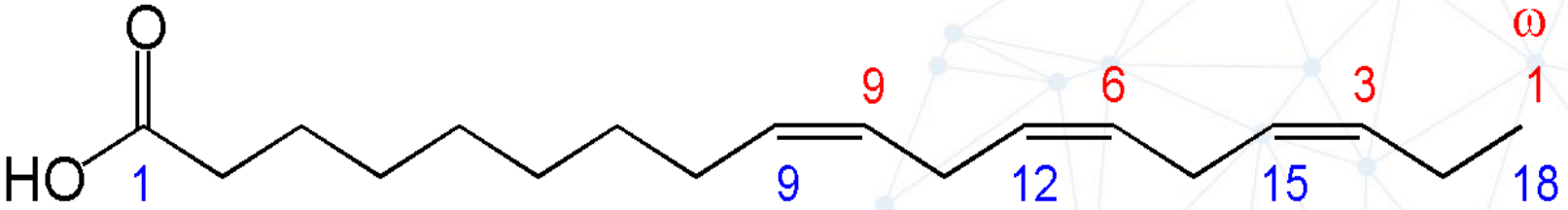
Alpha – omega versus 1–18: the naming of unsaturated fatty acids



C18:1 Oleic acid (n-9) or cis-9-octadecenoic acid



C18:2 Linoleic acid (n-6) or 9,12-octadecadienoic acid



C18:3 α-Linolenic acid (n-3) or 9,12,15-octadecatrienoic acid

Vegetable oils are characterised by their fatty acid composition

	C_{12}	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
Liquid						
Soybean		10	4	23	53	8
Rapeseed (Canola)		4	2	59	21	11
Corn		11	2	27	58	
Cotton		24	3	17	53	
Sunflower		6	4	20	67	
High oleic Sunflower		4	4	85	8	
Groundnut (Peanut)		10	3	42	38	
Olive		13	2	71	11	
Solid						
Palm		44	4	40	10	
Palm kernel	48	8	2	15	2	
Coconut	47	9	3	7	2	
Tropical						
Shea butter		4	43	45	6	
Illipé butter		17	44	35	1	
Mango butter		7	42	43	4	

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Drastic difference in oxidative stability

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Often shows separation of distinct liquid and solid triglycerides

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"Lauric Oils"
Low melt point solids

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"Stearics"
Higher melt point solids

Properties are determined by fatty acid and triglyceride composition

This fat

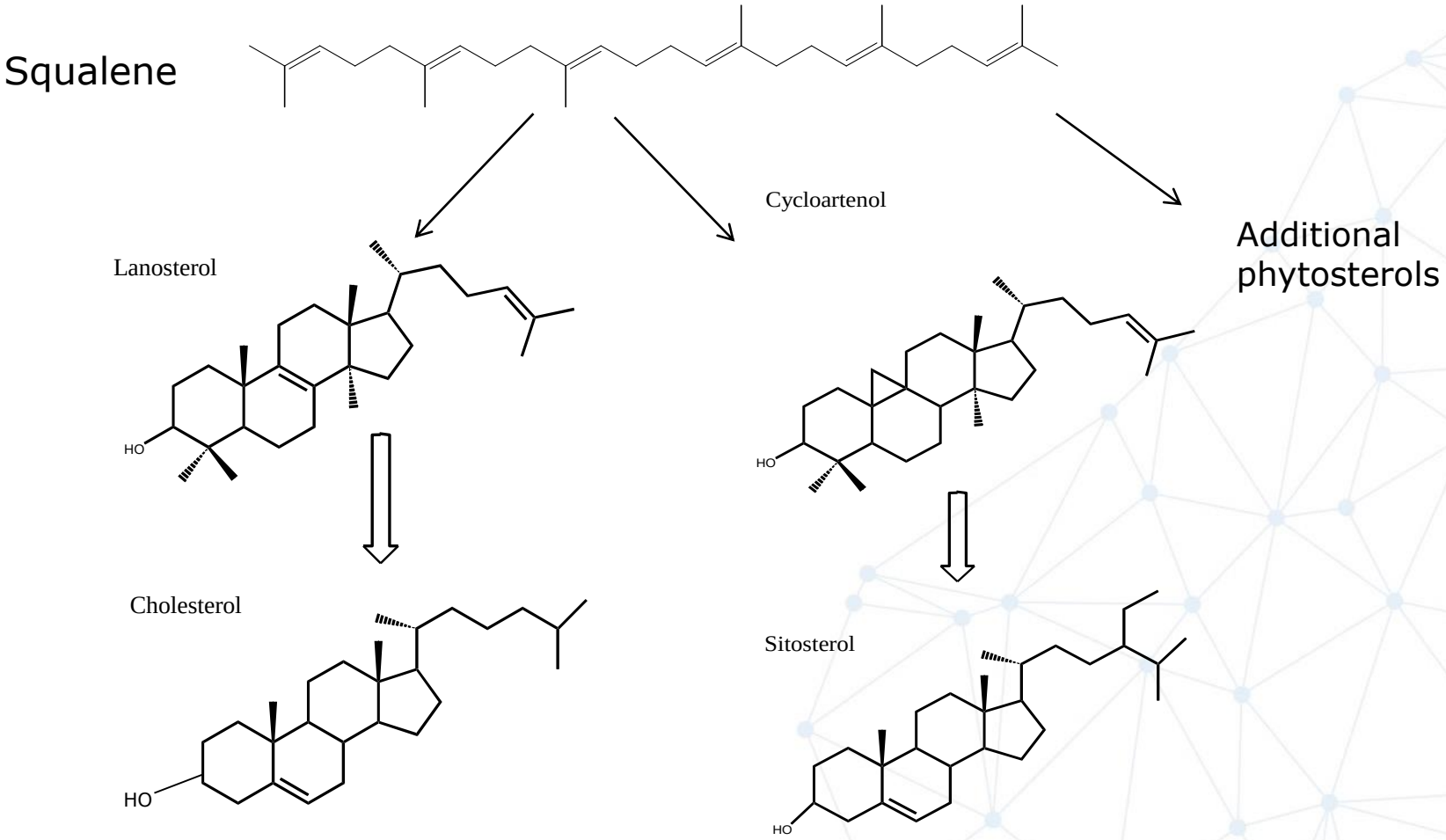
has completely different physical properties compared to this fat

Yet fatty acid compositions are identical

Vegetable oils – minor components

- Most vegetable oils also contain non-triglyceride oil-soluble lipids originating in the seeds
- Not removed by processing:
  - Phytosterols & triterpene alcohols
  - Tocopherols (Vitamin E)
  - Wax esters
- Typically removed by processing:
  - Carotenoids
  - Phospholipids
  - Glycolipids
  - Free fatty acids

Cholesterol has the same origin as phytosterols



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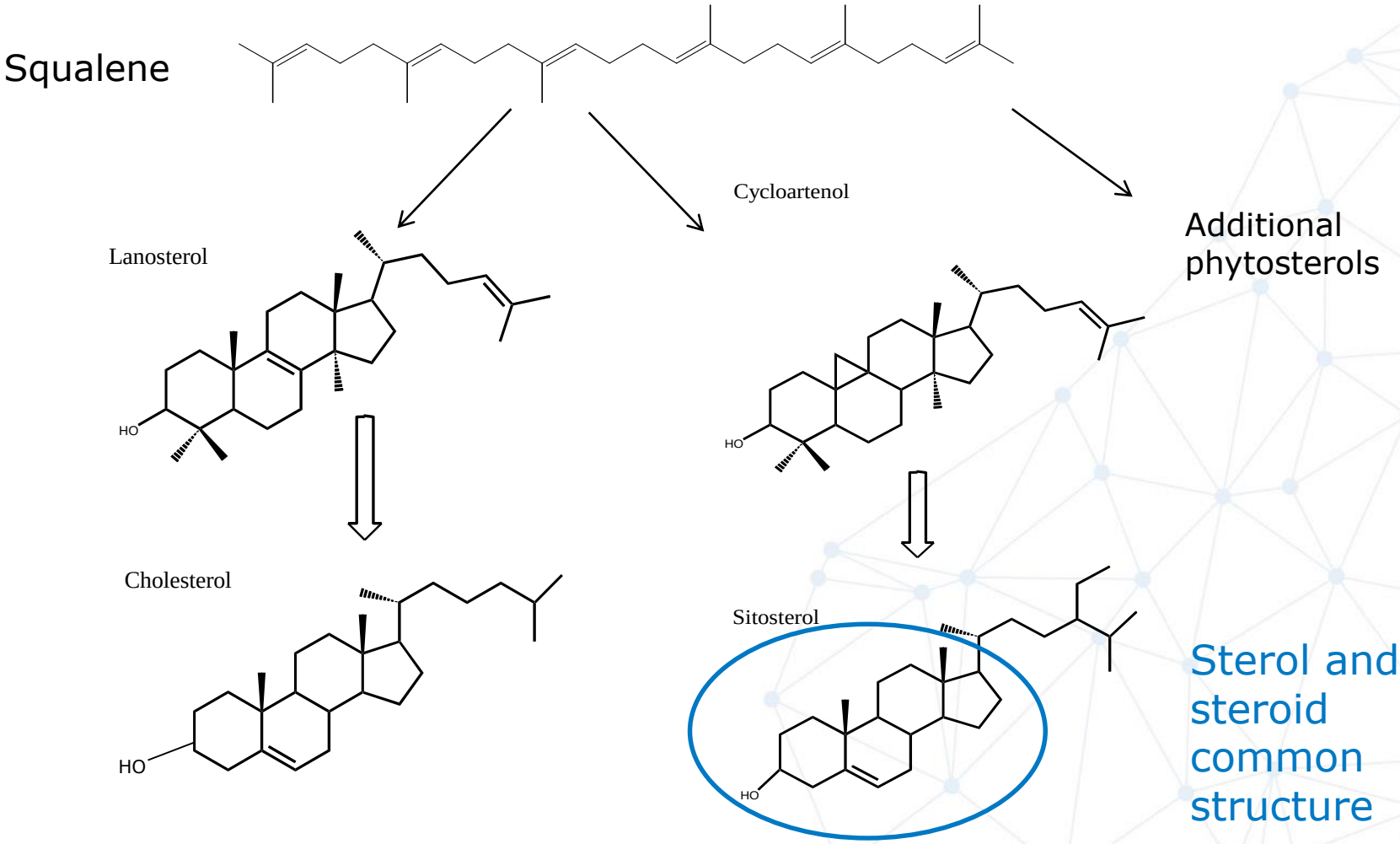

Sterol and steroid common structure

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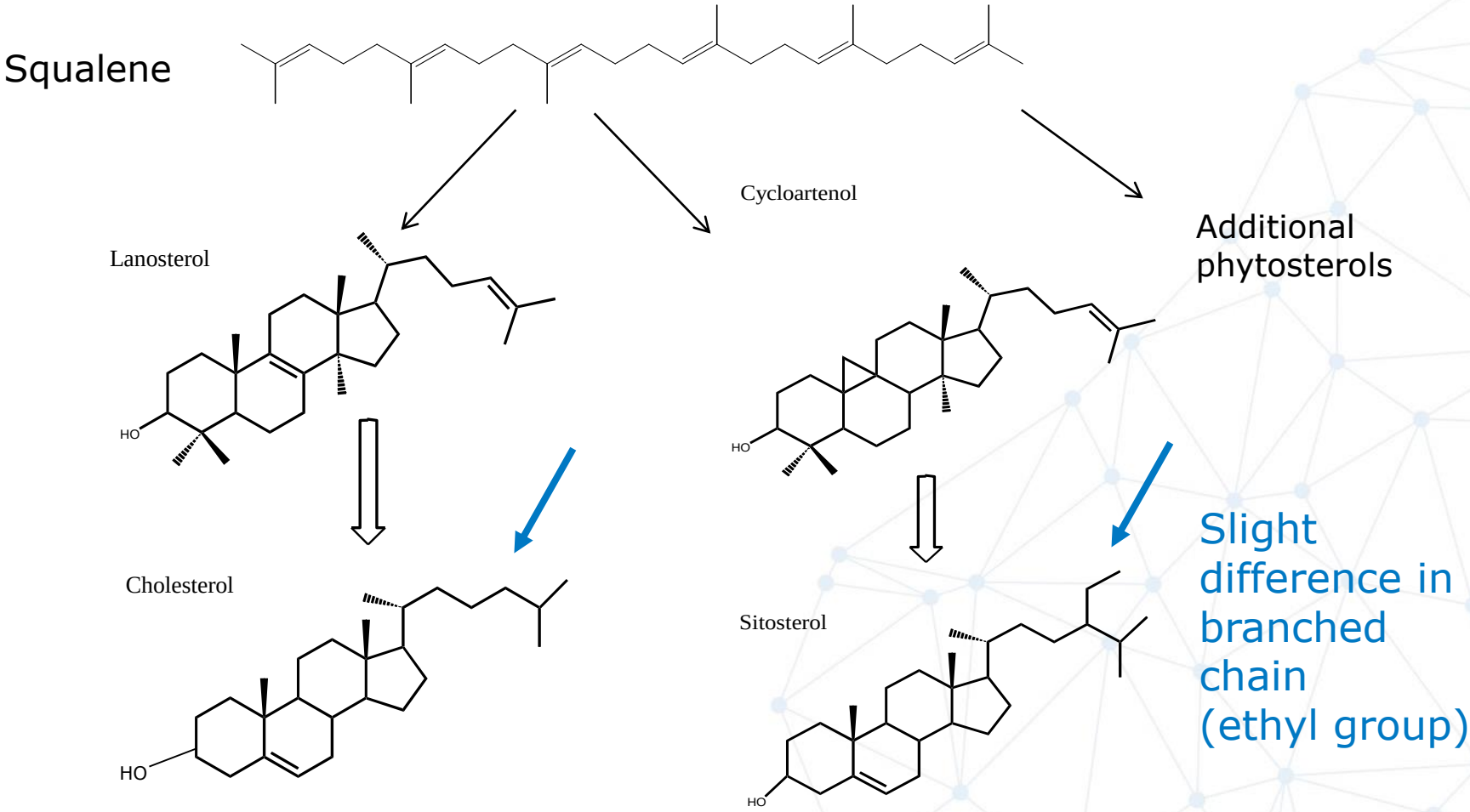


Sterol content of some vegetable oils

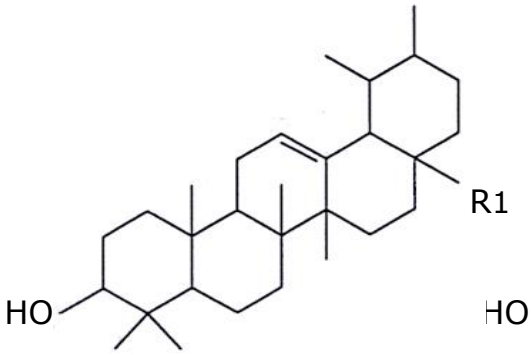
Vegetable oil	Typical sterol content (%)	Dominating sterols
Soybean oil	0.4	β-sitosterol, Campesterol
Rapeseed oil	0.7	β-sitosterol, Campesterol
Palm oil	0.3	β-sitosterol, Campesterol
Olive oil	0.3	β-sitosterol
Sunflower oil	0.4	β-sitosterol, Δ7 Avenasterol
Avocado oil	0.8 - 2%	β-sitosterol

Pentacyclic triterpene alcohols & esters

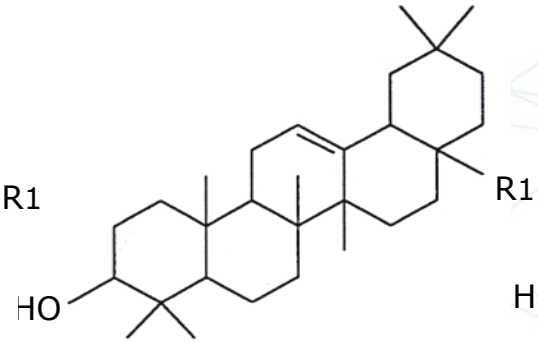
Triterpene family	Triterpene	R1
Lupane	**Lupeol** Betulin Betulinic acid	CH3 CH2OH COOH
Oleanane	**β-Amyrin** Erythrodiol Oleanolic acid	CH3 CH2OH COOH
Ursane	**α-Amyrin** Uvaol Ursolic acid	CH3 CH2OH COOH

Influence of chemical structure:

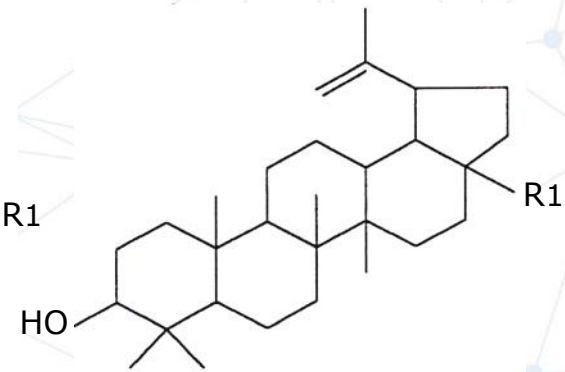
- Bioactivity
- Polarity
- Melting point



Ursane



Oleanane



Lupane

Oils and fats with triterpene esters

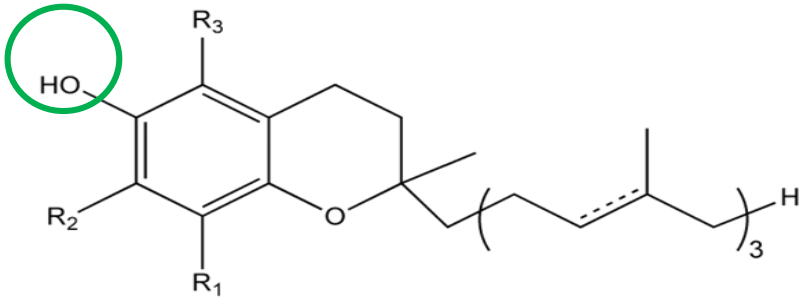
- All vegetable oils contain low levels of triterpenes and their esters
  - Typically 0.1–0.5 %
- Lanolin contains lanosterol and cholesterol at high levels
- Rice bran oil, corn fibre oil and other cereal based oils can contain up to 2% triterpene esters
- The richest source of triterpene esters is shea butter
  - 3–10 % in shea butters and liquid shea butter oil
  - Up to 65% in concentrates

Tocopherols

Oil soluble antioxidants

Free radical scavenger

Tocopherol structures



Tocopheryl esters

- Needs hydrolysis to be efficient as antioxidants
- Low skin penetration

	R1	R2	R3	Vit E activity (%)
α-tocopherol	CH3	CH3	CH3	100
β-tocopherol	CH3	H	CH3	50
γ-tocopherol	CH3	CH3	H	10
δ-tocopherol	H	H	H	3

Tocopherol content of vegetable oils

- The tocopherol content of oil and fats depends on several factors
  - Origin of oil
    - Polyunsaturated >monounsaturated>>saturated
    - Example: soybean oil >1000 ppm versus shea butter <100 ppm
    - Cold climate > warm climate
  - Processing
    - Lower temperature in deodorization preserves tocopherol content
  - Quality of raw material and ingredient
    - Old seeds and long storage time depletes tocopherol content of finished ingredient

Conclusions

- Vegetable oils and fats are lipids
  - Lipid composition varies with regard to fatty acid, triglyceride and minor lipid composition. Influenced by plant origin, growth and climate conditions as well as processing.
- Among the minor lipids their are valuable bioactive components
  - but just a few of them at a functional content.
- The choice of oil phase influence final product attractivenes
  - Considering quality, physical properties, skin feel, stability, shelf life, safety and sustainability profiles.