

Effect of the mode of incorporation of antioxidants on the oxidative stability of oil-in-water emulsions

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17th Euro Fed Lipid Congress
20–23 October 2019 · Sevilla · Spain

European Federation for the Science and Technology of Lipids

Effect of the mode of incorporation of antioxidants on the oxidative stability of oil-in-water emulsions

Tayse da Silveira[ab]*, Claire Bourlieu-Lacanal[a], Jérôme Lecomte[a], Erwann Durand[a], Maria Figueroa[a], Mickael Laguerre[c], Inar Castro[b], Pierre Villeneuve[a]

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[c] Naturex, Avignon, France

**Food Engineer*

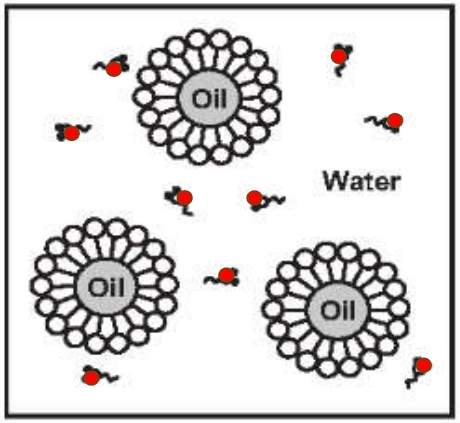
PhD in Food Science

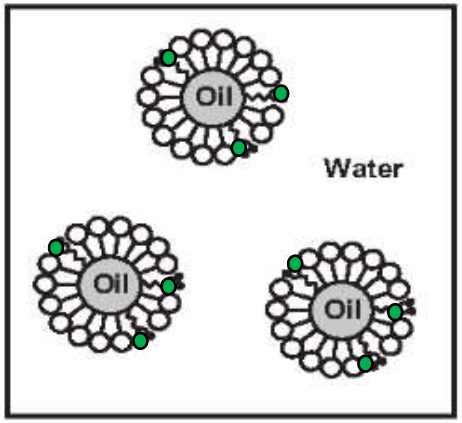
Postdoctoral Researcher

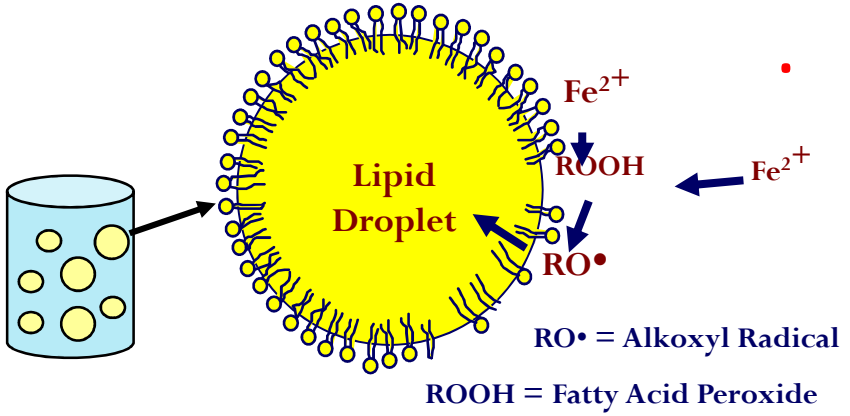
Background

Polar Paradox
Porter et al., 1989

● Polar antioxidants ● Non polar antioxidants

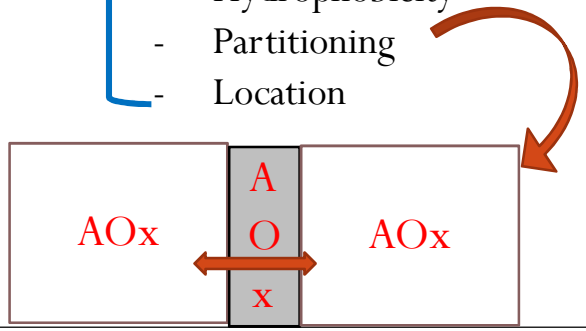




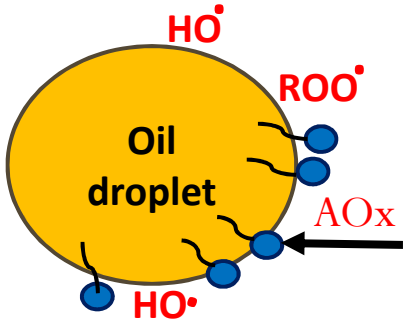


Antioxidants (Aox)

- *Chemical:*
  - Reactivity
  - Number and OH position
  - OH Dissociation energy
- *Physico-chemical:*
  - Hydrophobicity
  - Partitioning
  - Location

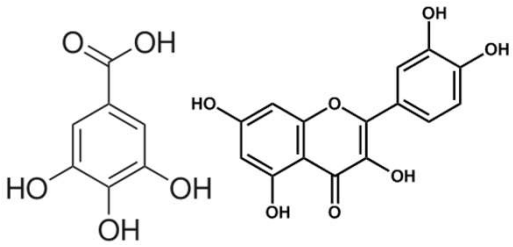


BE STRONG AND BE AT THE RIGHT PLACE



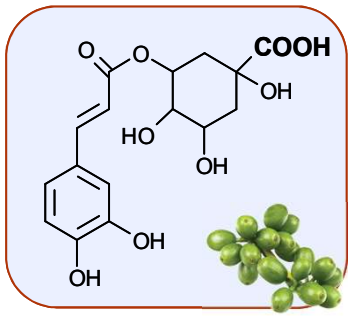
Which antioxidant?

Phenolic compounds and Phenolipids



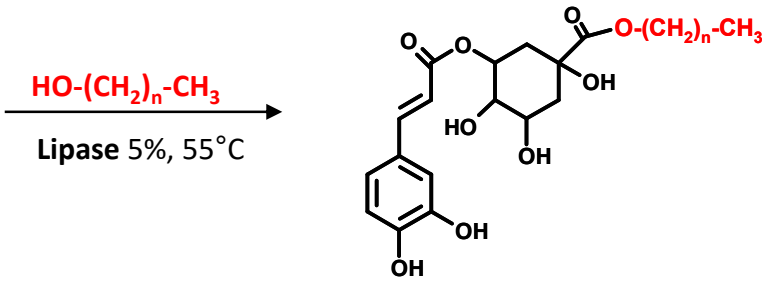
PHENOLIPIDS: ADJUSTING AND OPTIMIZING AOX EFFICIENCY OF PHENOLIC COMPOUNDS

CHLOROGENIC ACID



Lopez Giraldo *et al.*, Enz. Microb. Tech., 2009

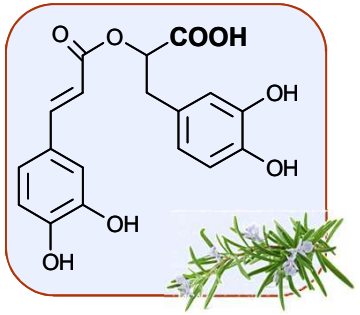
(A) ENZYMATIC ESTERIFICATION



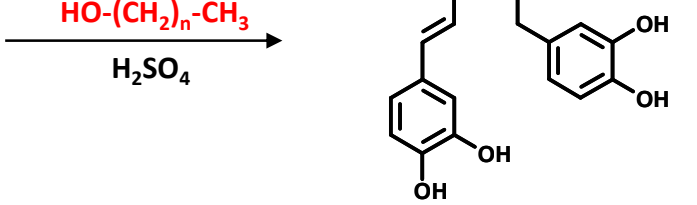
Lipophilic group

n = 0	(methyl)
n = 3	(butyl)
n = 7	(octyl)
n = 11	(dodecyl)
n = 15	(hexadecyl)
n = 17	(octadecyl)
n = 19	(eicosyl)

ROSMARINIC ACID



(B) CHEMICAL ESTERIFICATION



Lecomte *et al.*, *J. Am. Oil Chem. Soc.*, 2010

n = 0	(methyl)
n = 3	(butyl)
n = 7	(octyl)
n = 11	(dodecyl)
n = 15	(hexadecyl)
n = 17	(octadecyl)
n = 19	(eicosyl)

AOxs with varying polarities can be synthesized

LIPOPHILIZATION: chemical or enzymatic linkage of phenolic compounds with lipophilic groups(e.g. alkyl alcohols or fatty acids)

ROLE OF THE EMULSIFIER: interactions

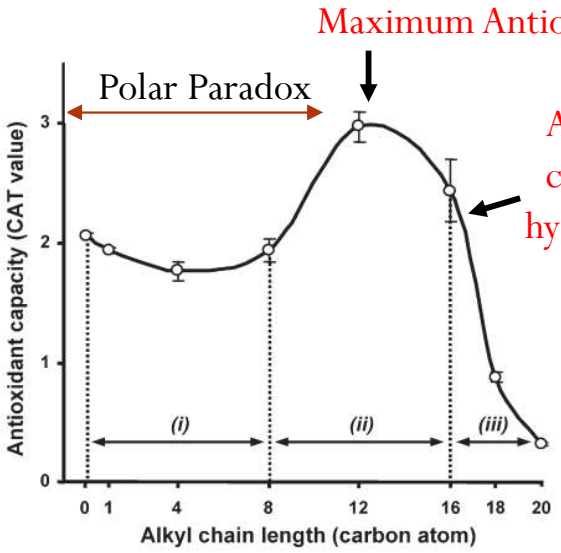
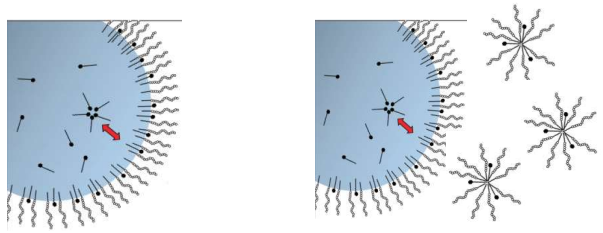


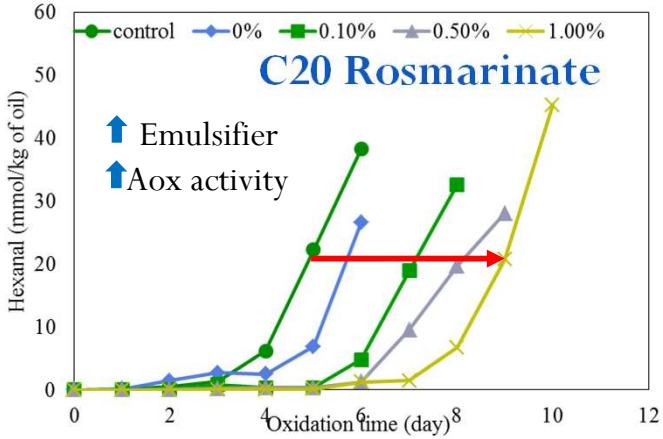
Figure 3. CAT value (mol of Trolox per mol of tested compound) of chlorogenic acid and its esters vs the alkyl chain length.

Contradiction of the Polar Paradox
The cut-off effect (COE)
(Laguerre et al., 2009)

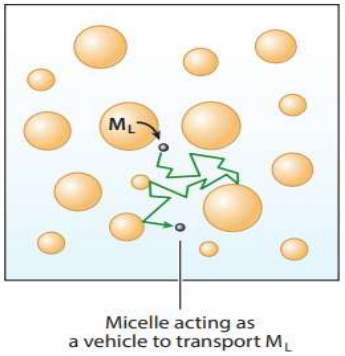


Below CMC Above CMC

Critical micellar concentration



Panya et al., JAFC, 2012



- Modify AOx location by solubilization in micelles, modulating AOx efficiency
- Micelles could act as carriers of highly hydrophobic AOxs

M_L = lipophilic molecule

From Laguerre et al., Annual R.F.S.Tech, 2017

Rosmarinates (160 µM) in low moisture foods (crackers)

EFFECT OF MODE OF INCORPORATION

➡ **Mode of incorporation modified C12 efficiency**

RC20> RC12 >> RC0

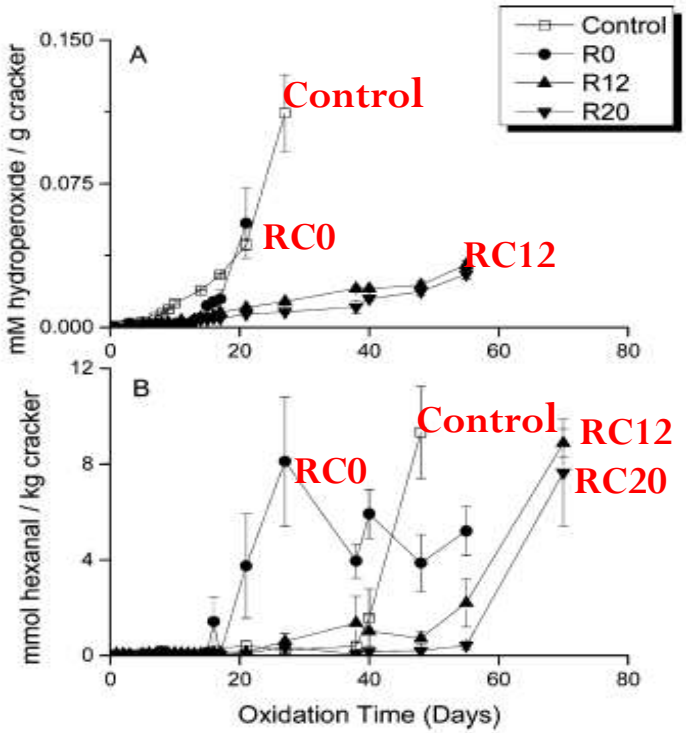


Figure 2. (A) Lipid hydroperoxides and (B) headspace hexanal in crackers with rosmarinic and its esters (chain lengths = 0, 12, or 20 carbons) incorporated into the lipid prior to dough formation. Crackers were stored in the dark at 55 °C. Standard error bars are smaller than data points in some instances.

Incorporation of phenolipids **in the lipid phase** prior to dough formation

Barden et al., JAFC, 2015

RC20 >> RC12 > RC0

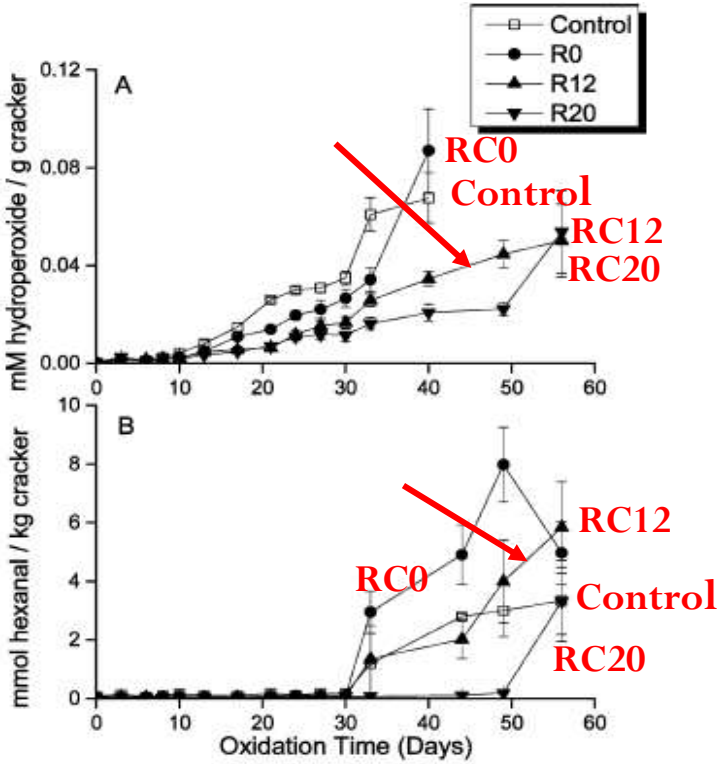


Figure 3. (A) Lipid hydroperoxide and (B) headspace hexanal formation in crackers made by incorporating rosmarinic ester antioxidants (chain lengths = 0, 12, or 20 carbons) into the aqueous phase prior to dough formation. Crackers were stored in the dark at 55 °C. Standard error bars are smaller than data points in some instances.

Incorporation of phenolipids by **mixing in the aqueous phase** prior to dough formation

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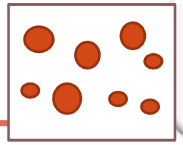


HYPOTHESIS AND OBJECTIVES

Emulsion System I - one type of oil

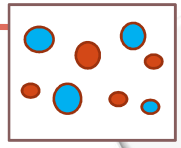
➢ **Effect of mode of incorporation on the AOx**

The mode of incorporation of antioxidants in o/w emulsions affects their dynamic equilibrium in the emulsion system and reshape their efficiency.



Emulsions constituted of a single droplet of unsaturated oil

Emulsion System II – two types of oil



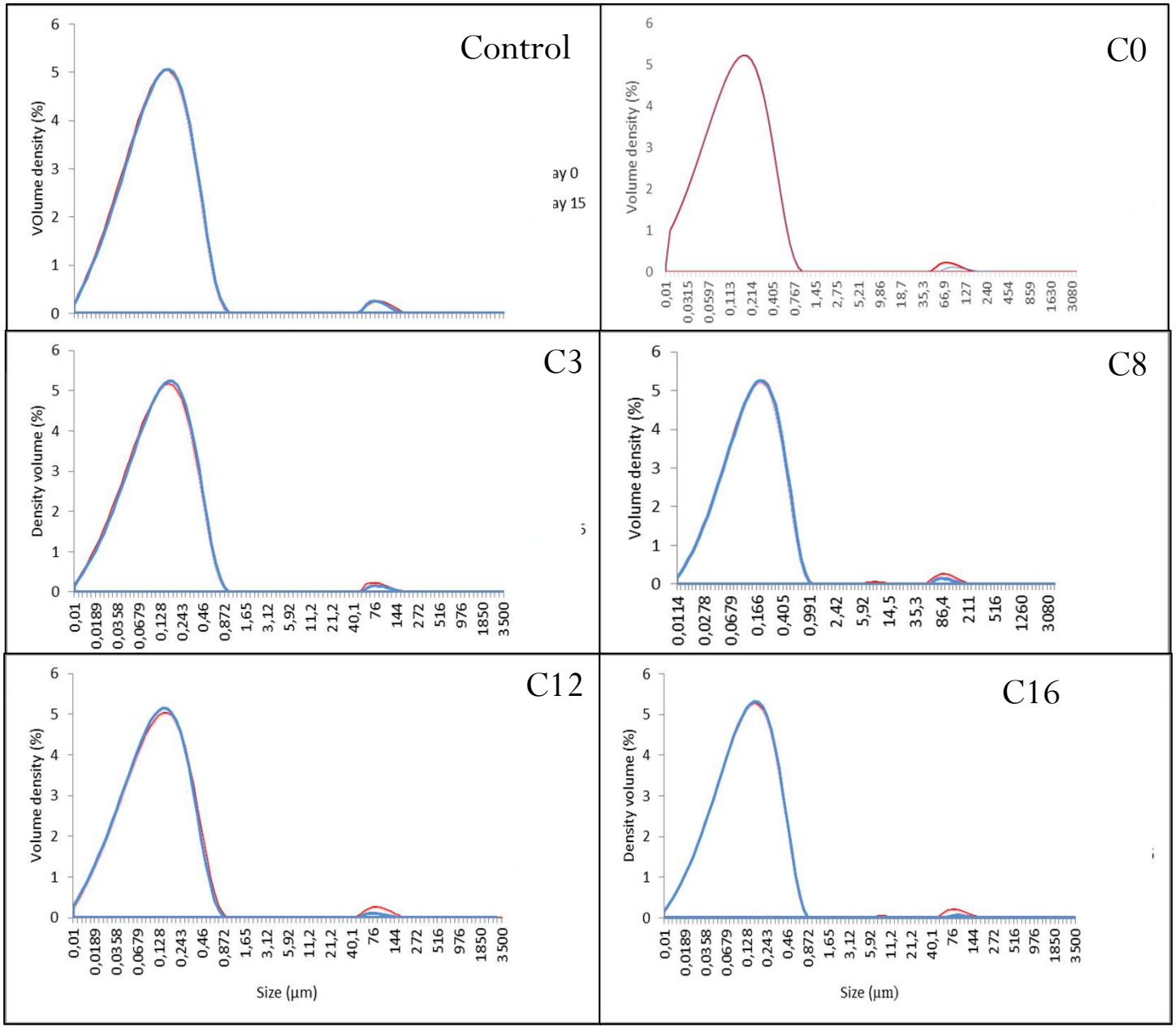
Emulsions constituted of two populatins of unsaturated oil

➢ **Effect of micelles on these systems above**

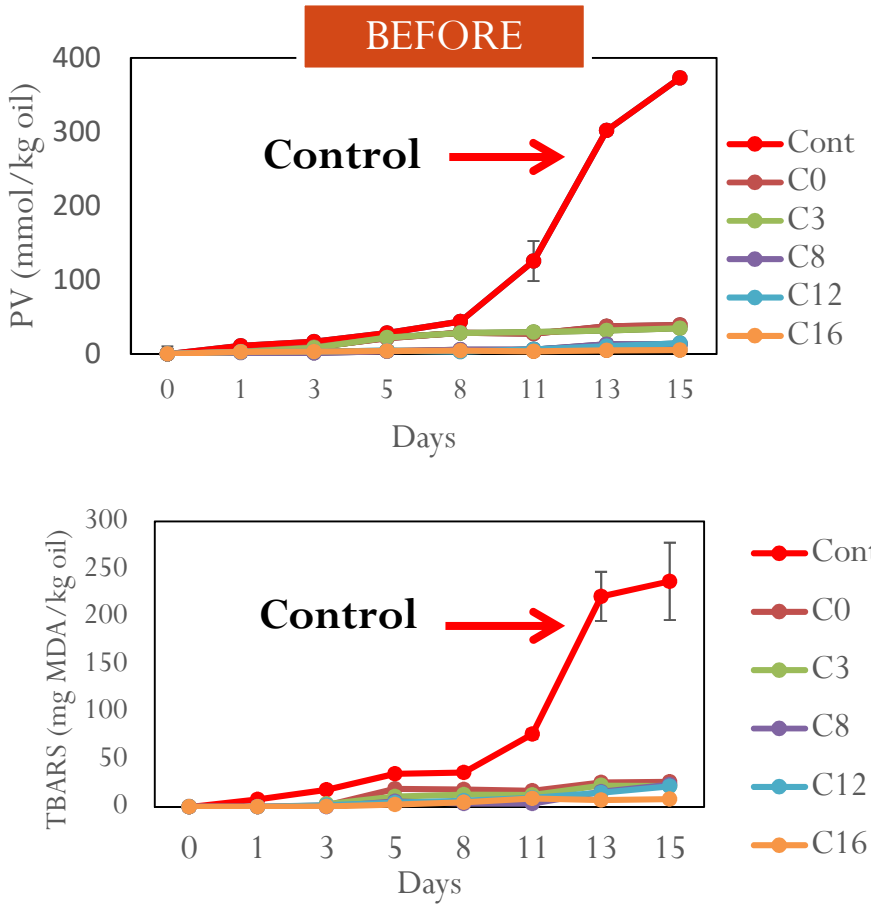
An excess of emulsifier in the aqueous phase could interefere in the AOx behavior, by, for example, favoring its transfer from one droplet to another.

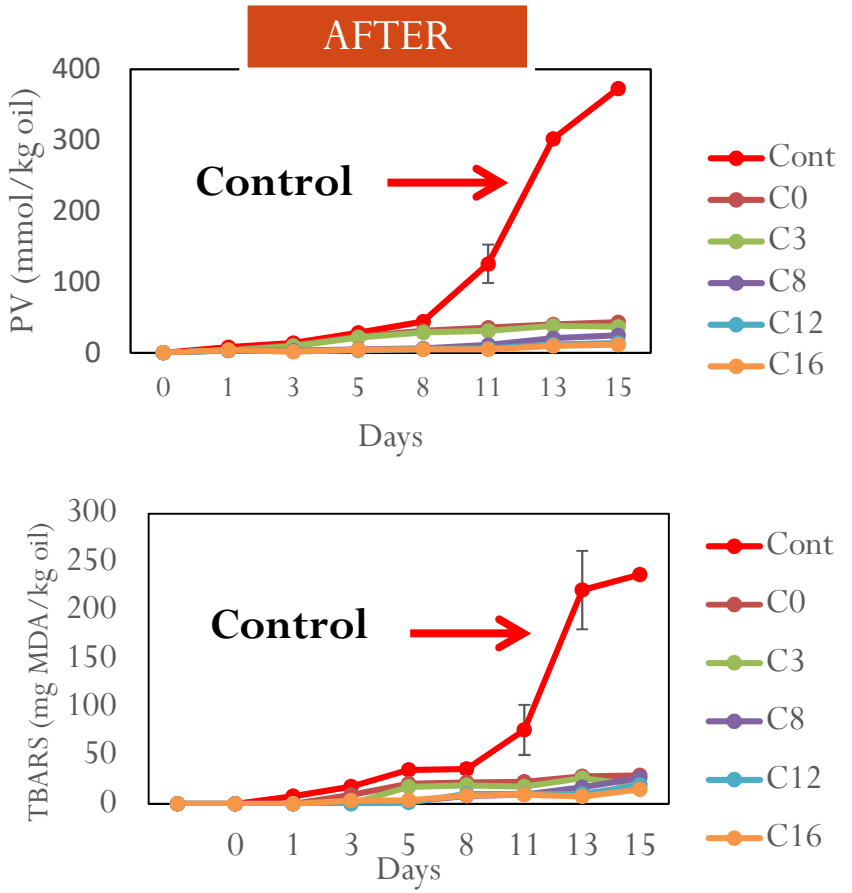
Investigate the effect of the presence of micelles in these systems

All studied emulsions were physically stable over oxidation time



Oxidative stability





✓ All the applied AOxs exhibited an antioxidant effect compared to the control, regardless of the emulsifier concentration and mode of incorporation

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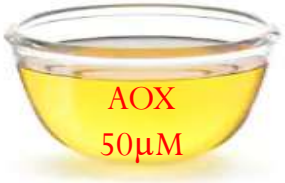
Emulsion system I : single lipid droplets emulsion system

1% Rapeseed, non stripped

AOxs added in the oil phase **BEFORE** emulsification

x

AOxs added in the aqueous phase **AFTER** emulsification





⇩

Aqueous phase pH 7.0

Emulsifier:
Sodium dodecyl sulfate (SDS)

- Below CMC
- Above CMC

CMC: presence of micelles

⇩

Pre-emulsion/Homogenization



⇨

Oxidation 40°C/15 days
Peroxide value (PV), TBARS

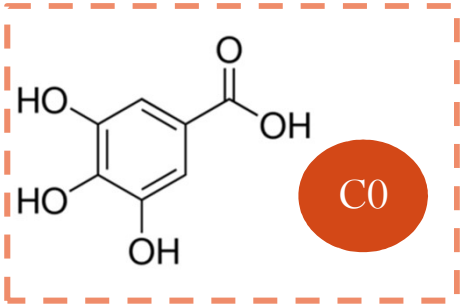


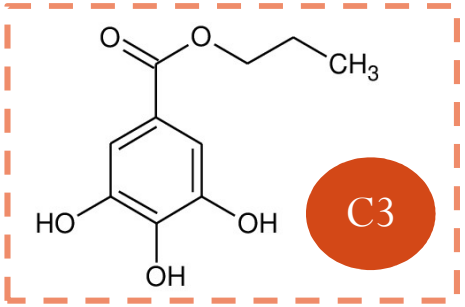
Control:
No antioxidant

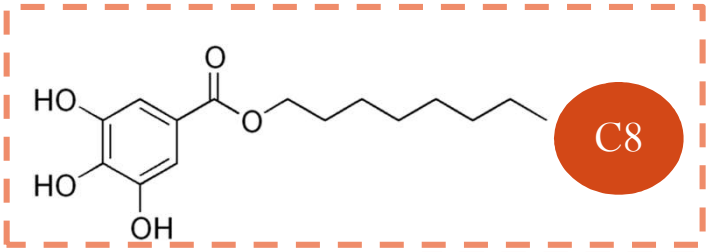
Emulsion system I: single lipid droplets emulsion system

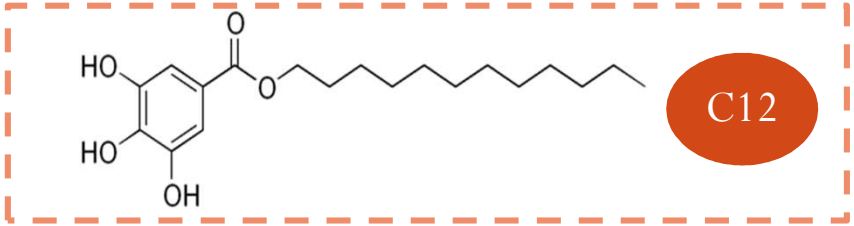
➢ Experimental design

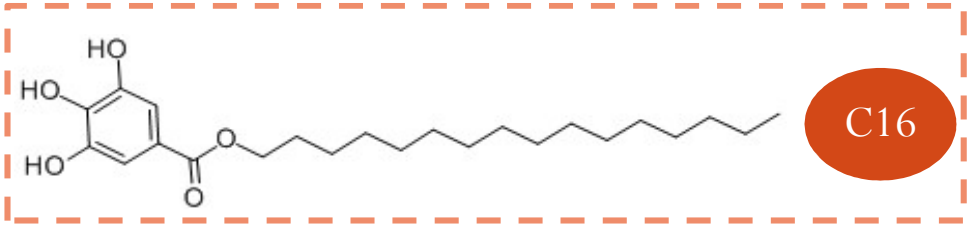
Gallic acid and Gallate esters C3-C16



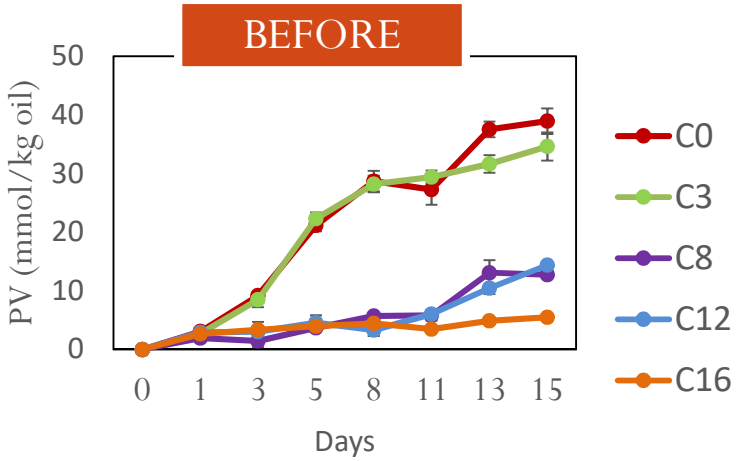


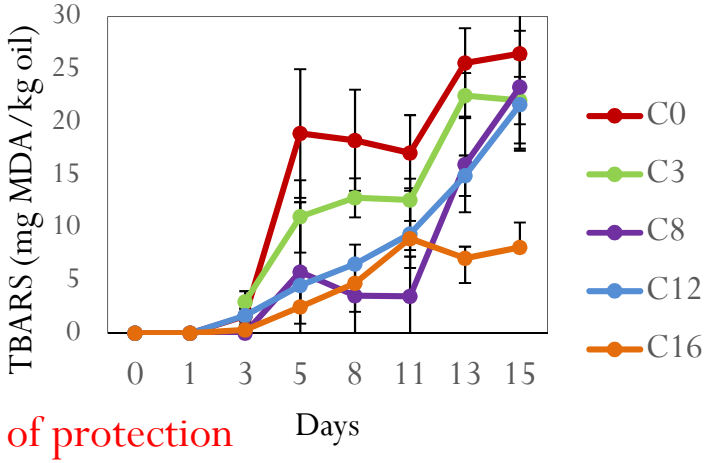






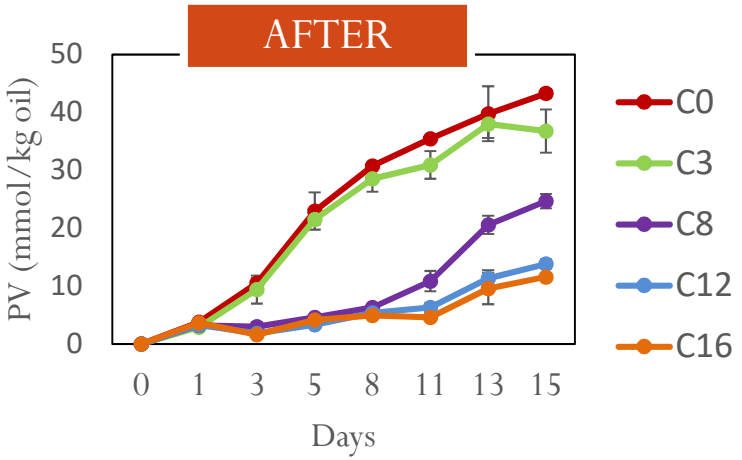
RESULTS: Oxidative stability below CMC

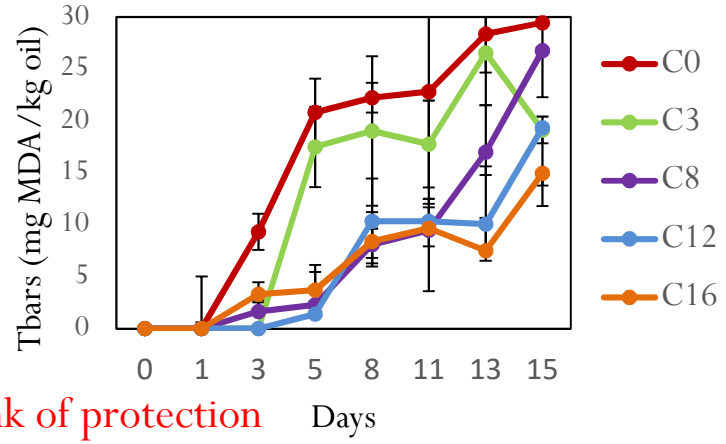




Rank of protection

C16>C12~C8>C3~C0





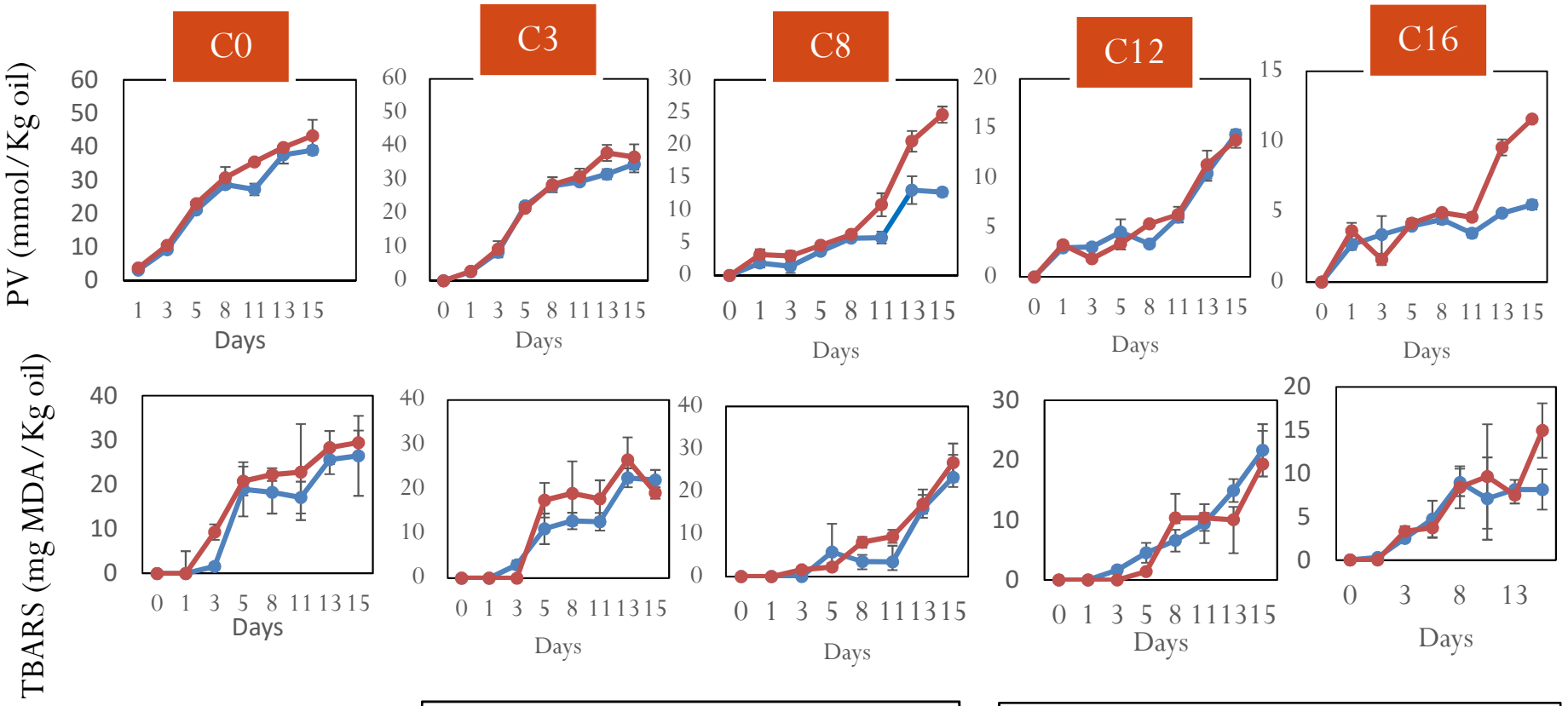
Rank of protection

C16~C12>C8>C3~C0

✓ No cut-off effect (both modes of incorporation) – agreement with the Polar Paradox

✓ Rank of AOxs: best C16 and C12, with slight effect of the mode of incorporation

RESULTS: Oxidative stability below CMC

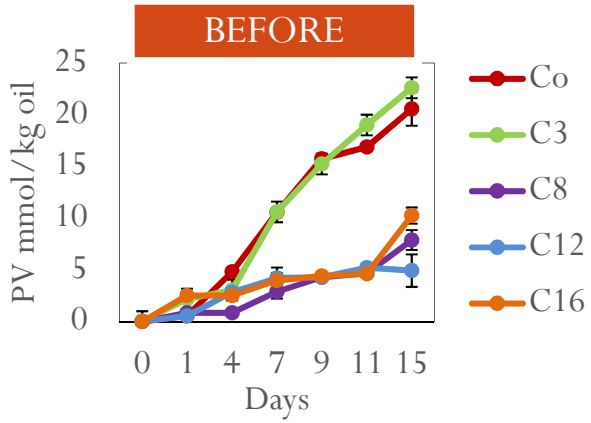


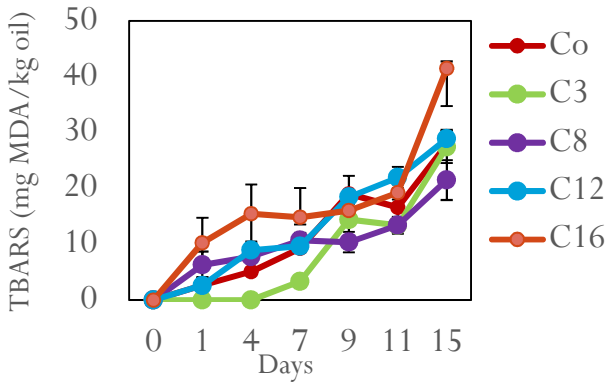
AOx incorporation BEFORE emulsification

AOx incorporation AFTER emulsification

- ✓ Individual effect of mode of incorporation: affected mainly C8 and C16, with lower oxidation when AOx was incorporated before
- ✓ In general, mode of incorporation slightly affected the others AOxs

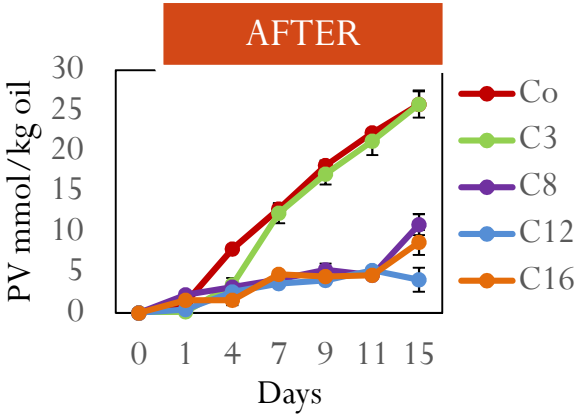
RESULTS: Oxidative stability Above CMC

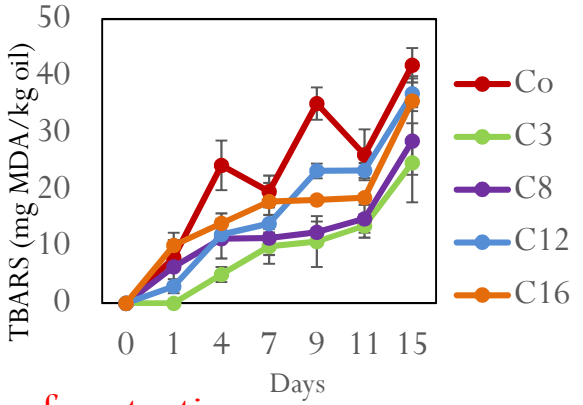




Rank of protection

C16~C12 ~C8 >C0~C3



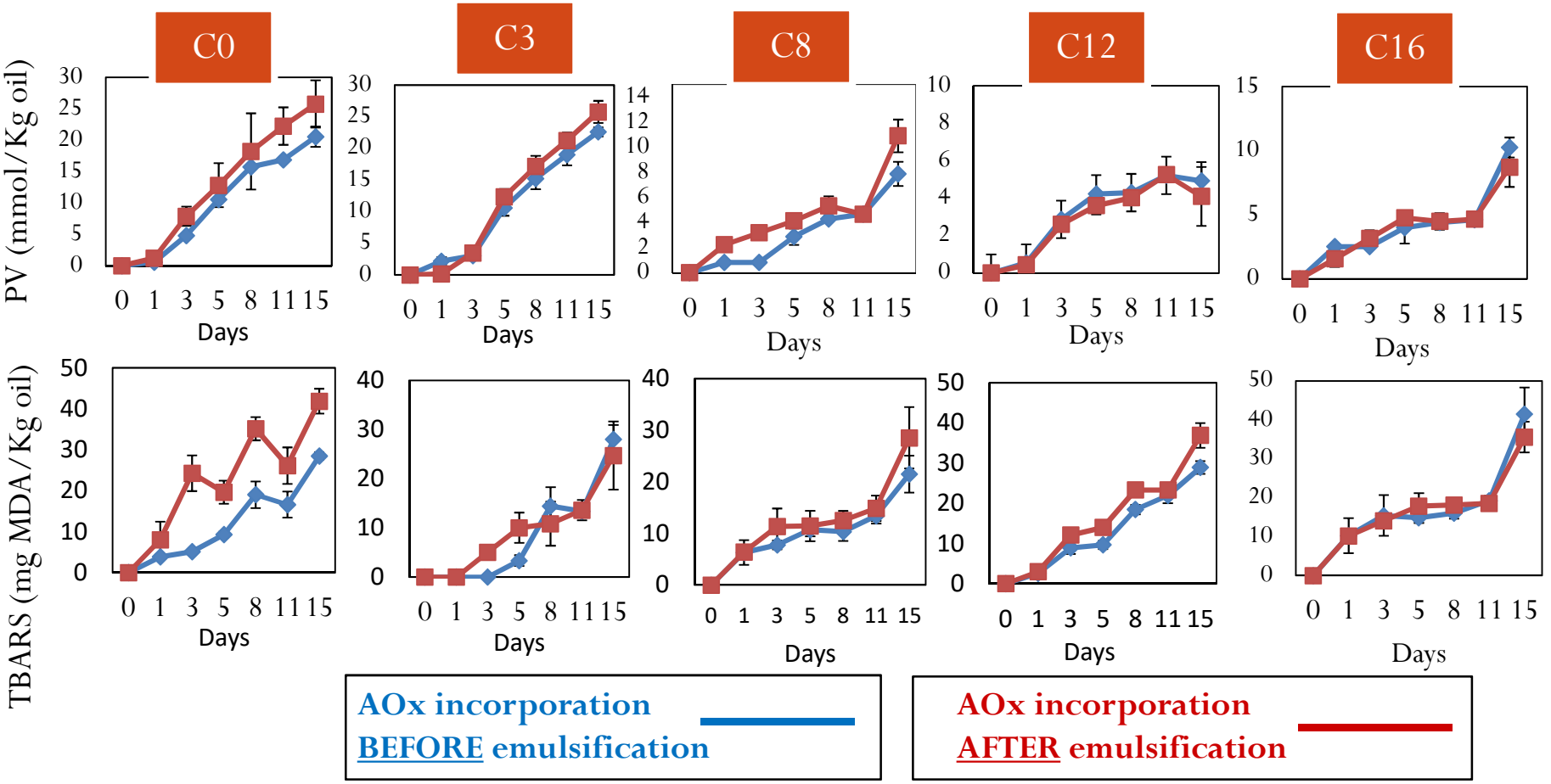


Rank of protection

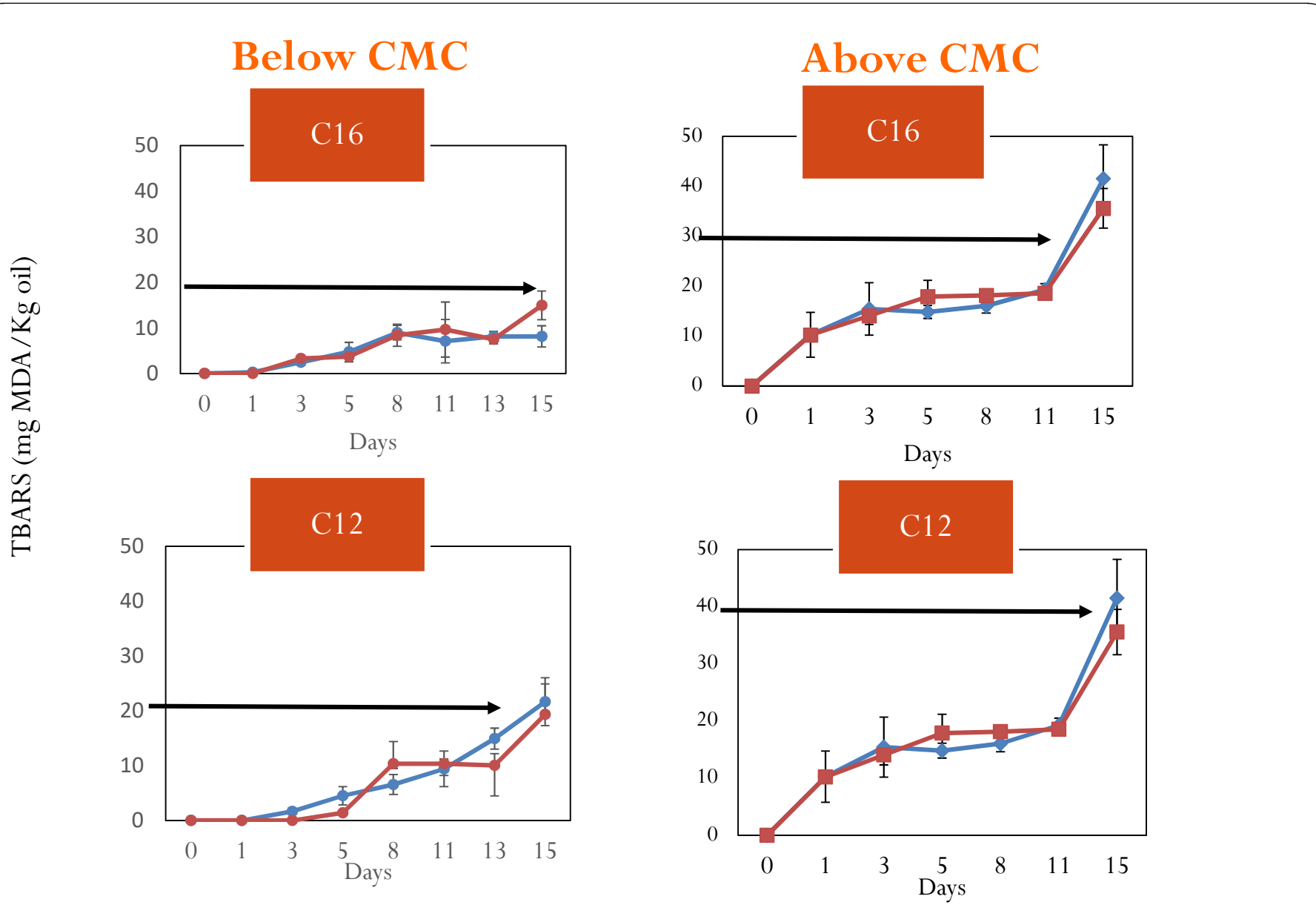
C16~ C12~C8>C0~C3

- ✓ Rank of AOxs: Same as bellow CMC
- ✓ In presence of micelles, Rank of Aoxs was not affected by mode of incorporation
- ✓ Higher formation of TBARS for long chain compounds (C12 and C16)

RESULTS: Oxidative stability Above CMC



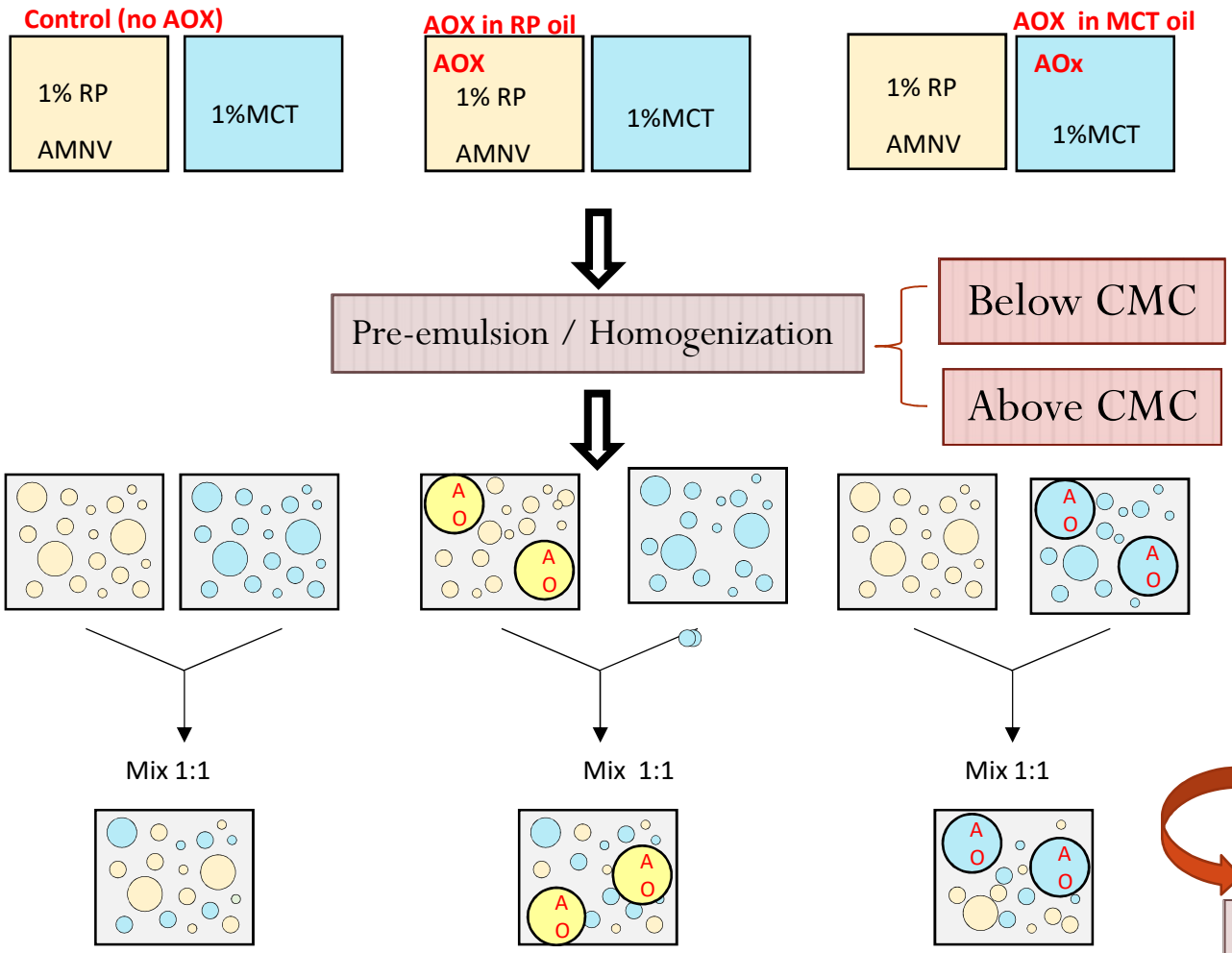
- ✓ Individual effect of mode of incorporation: C16 and C8 were less affected by the mode of incorporation
- ✓ In general, effect of mode of incorporation slightly or no affected the others AOxs



✓ Possible effect of micelles on long chain compounds for formation of secondary compounds

Emulsion system II: mixed lipid droplets emulsion system

Experimental design



RP: Unsaturated Rapeseed, non stripped

MCT: satuarated medium chain triglycerides

AMVN: lipophilic radical initiator 2,2'-azobis (2,4-dimethylvaleronitrile)



Oxidation 40°C/16 hours
Peroxide value (PV), TBARS

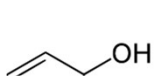
Aox present in only one of the lipids population

Emulsion system I I: mixed lipid droplets emulsion system

Experimental design

Enzymatic synthesis and purification of rutin ester C16

Lue et al., J Am Oil Chem Soc, 2010

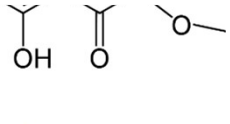


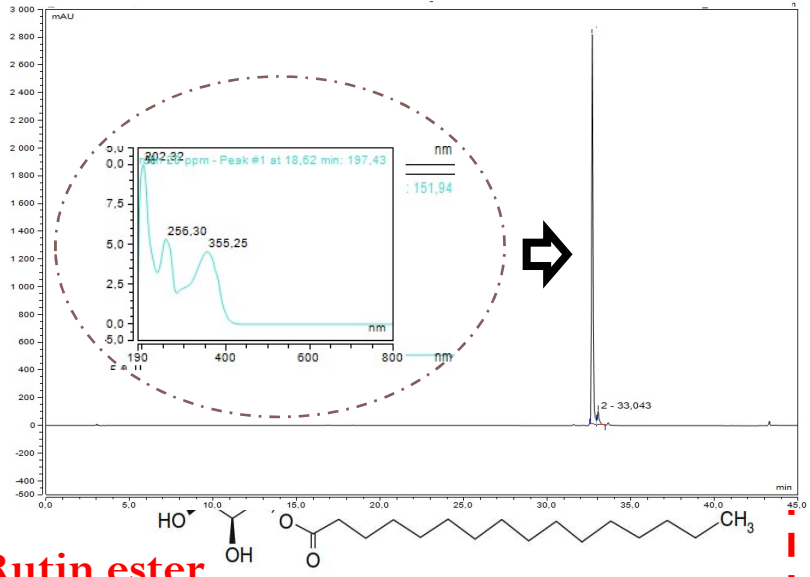
RC0

Rutin + Palmitic acid (C16:0) ➡ Rutin ester C16 + H_2O

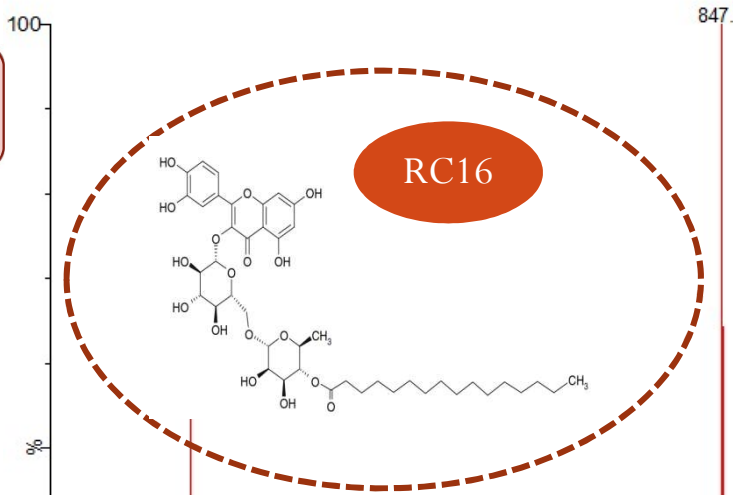
Lipase

55°C / 4 days





Rutin ester



HO

HC

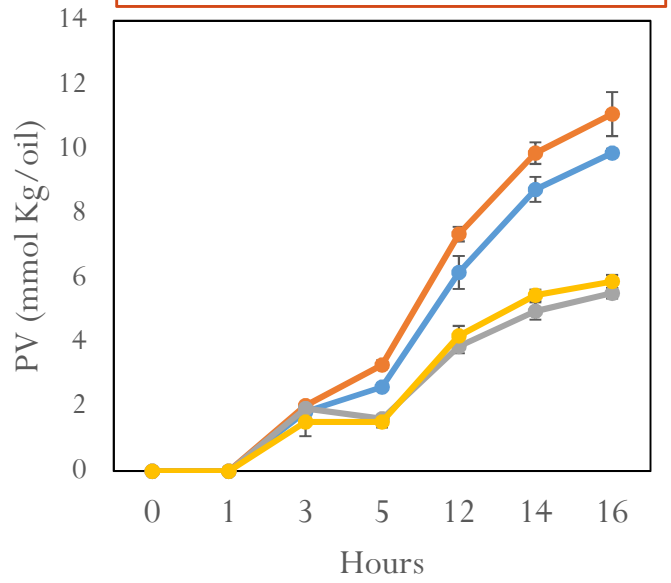
G

17th Euro Fed Lipid Congress
20–23 October 2019 · Seville · Spain

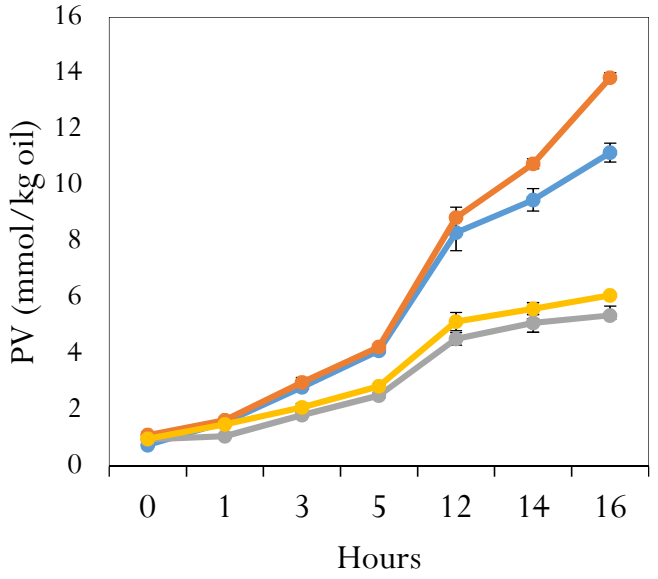
RESULTS: Oxidative stability

Gallic acid (GC0) *vs.* Gallate ester C16 (GC16)

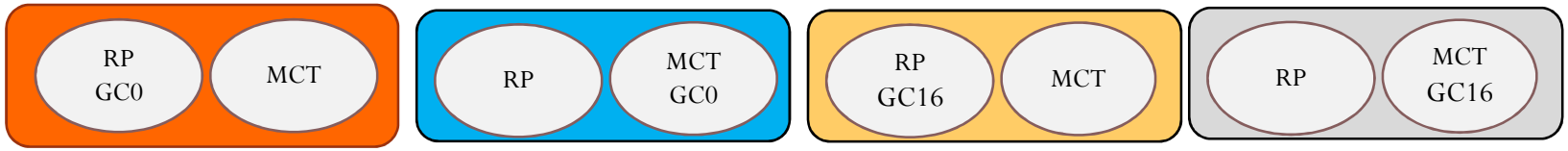
Below CMC



Above CMC



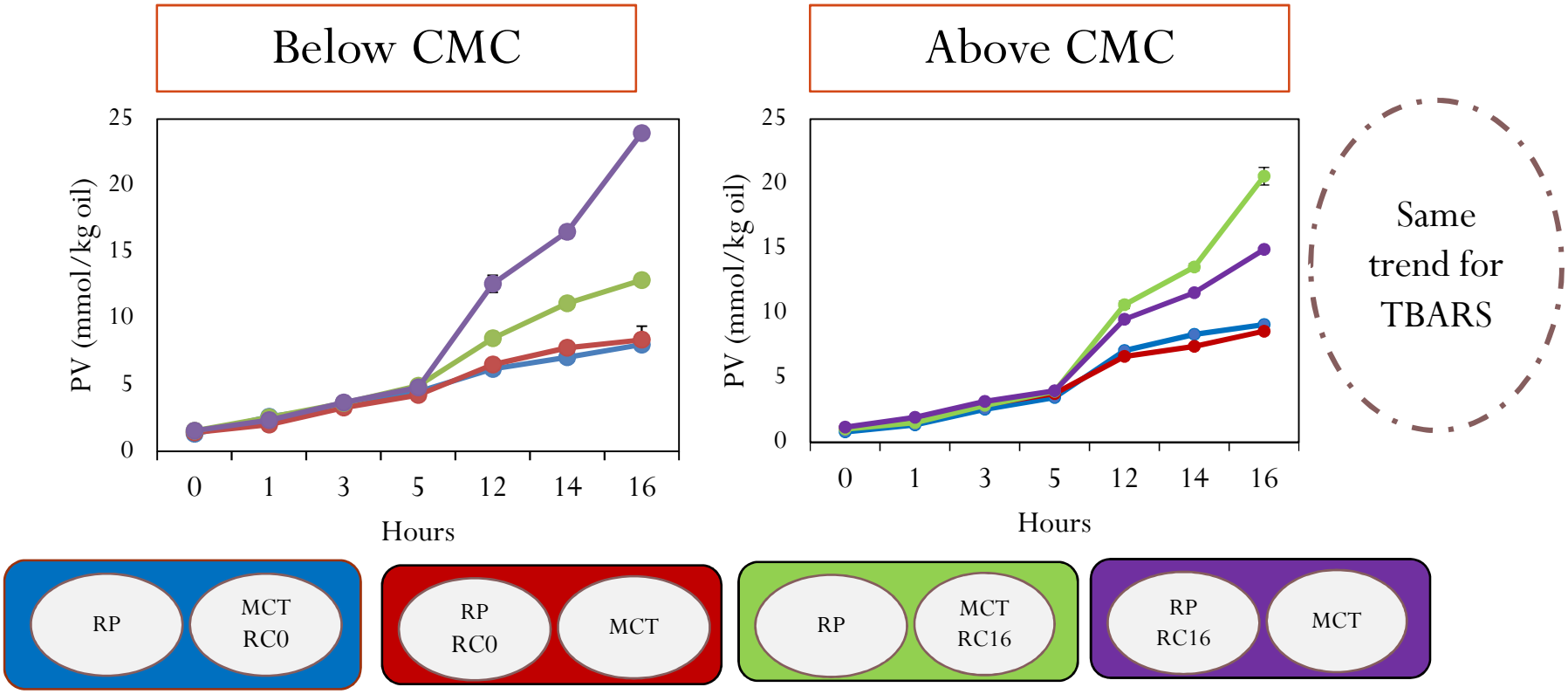
Same trend for TBARS



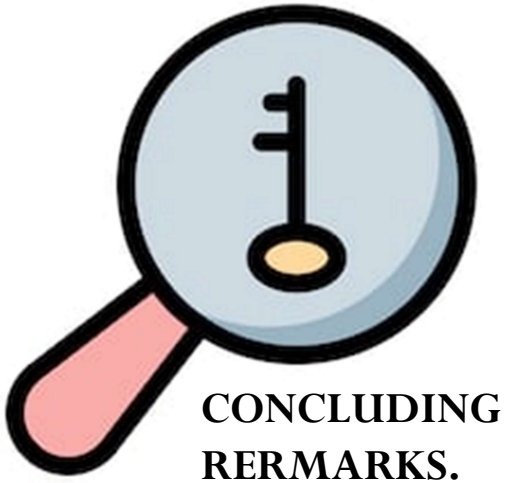
- ✓ GC16 was more effective than GC0
- ✓ For GC0, modes of incorporation slightly affect results whereas micelles did not
- ✓ For GC16, no difference between the modes of incorporation and micelles

RESULTS: Oxidative stability

Rutin (RC0) *vs.* Rutin ester C16 (RC16)



- ✓ RC0 was more effective than RC16
- ✓ For RC0, no difference between modes of incorporation and micelles
- ✓ For RC16, mode of incorporation and micelles did affect



CONCLUDING RERMARKS.

1 Hypothesis 1

✓ Mode of incorporation

- In single lipid droplet emulsions (System I), mode of incorporation affected mainly C8 and C16.
- The effect of incorporating AOXs in different lipid droplet populations (System II) showed to be molecule-dependent, with significant effect only for very bulky compounds (RC16).

2 Hypothesis 2

✓ Presence of micelles

- In single lipid droplets emulsions (System I), the presence of micelles affected mainly long chain compounds (TBARS value).
- In emulsions with different lipid droplet populations (System II), the effect of the presence of micelles also seems to be related with the molecule bulkiness

THANK YOU FOR YOUR ATTENTION!

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Agropolymer engineering & emerging technologies

UNIVERSITE MONTPELLIER

Concluding remarks and future studies



- The mode of incorporation affected the efficiency of the antioxidants in a single lipid emulsion system.
- In mixed lipid systems, the effect of the mode of incorporation depended on the compounds and on the chain chain length. No effect was observed for Gallate ester C16, while for Gallic acid (C0), it was more effective when added to MCT droplets.
- Rutin and Rutin ester C16 showed an opposite behavior to that of Gallic acid and Gallates.
- An [illegible] of emulsifier reshaped the antioxidant activity of phenolipids in a single lipid em[illegible]tem.
- For [illegible]ed lipid emulsion system, an excess of emulsifier only affected Rutin ester C16 behavior.
- W[illegible]

3

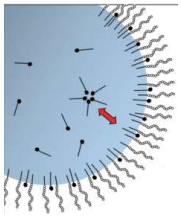
✓ Future studies

- Investigate the behavior of Emulsion System II using a hydrophlici radical initiator
- Investigate the mechanisms underlying our observations

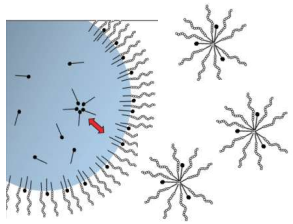
[illegible]lved in the observed systems

ROLE OF THE EMULSIFIER: Interactions

Panya et al., JAFC, 2012



Below CMC

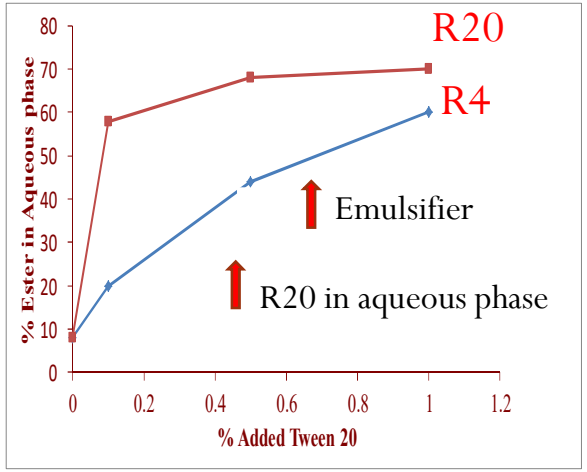


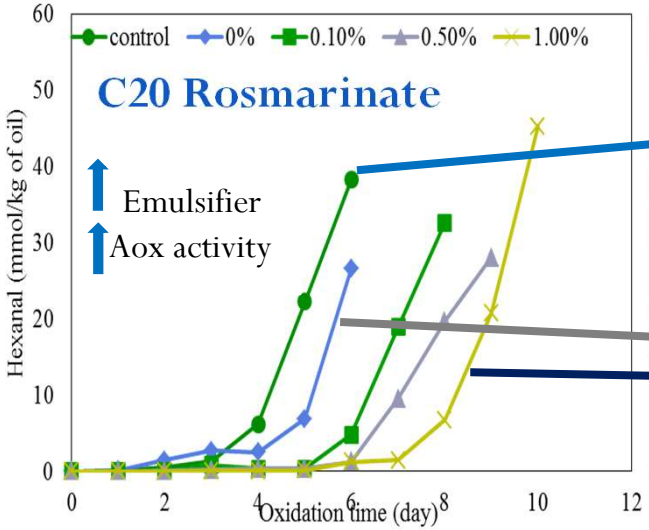
Above CMC

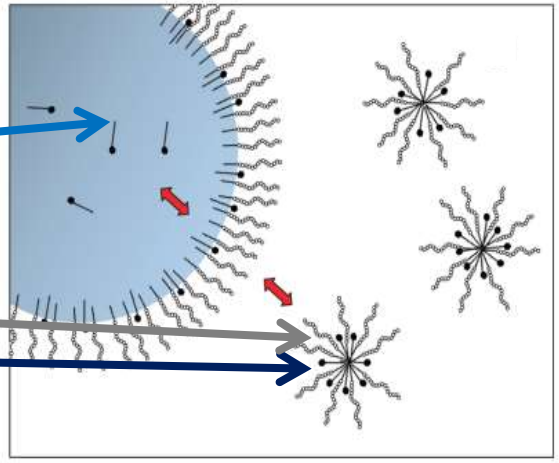
Critical micellar concentration

AOx location, distribution

Modulation of AOx efficiency by solubilization in micelles

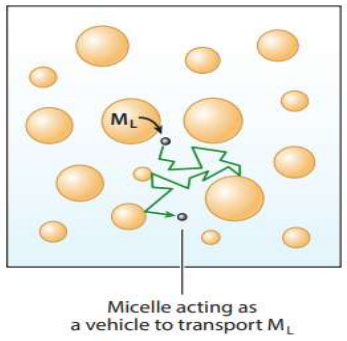






ROLE OF THE EMULSIFIER

- Could emulsifier micelles act as carriers of highly hydrophobic AOxs?

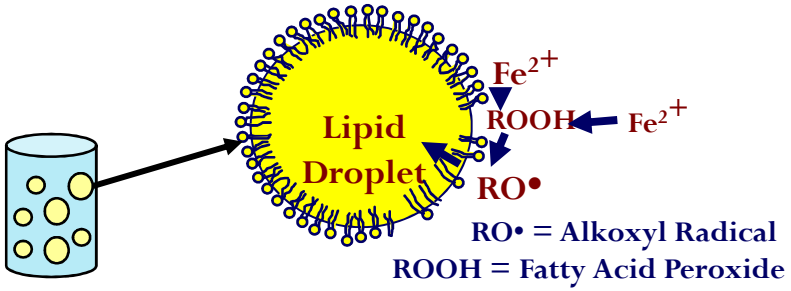


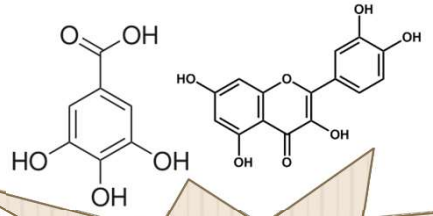
M_L = lipophilic molecule

Laguerre, Annu. Rev. Food Sci. Technol, 2017

Background

➢ Lipid oxidation in oil-in-water emulsions (o/w)





Which antioxidant (AOx)?

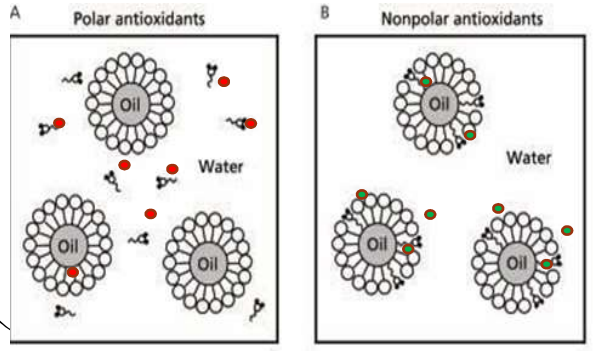
Interfacial phenomena in emulsion oxidation (Frankel et al., 1994)

What makes good an antioxidant in o/w emulsions?

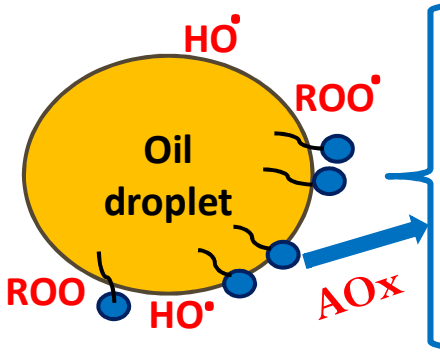
Phenolic compounds and Phenolipids

Polar Paradox
Porter et al., 1989

BE STRONG AND BE AT THE RIGHT PLACE



- Polar antioxidants
- Non polar antioxidants



➢ *Chemical:*
- Reactivity
- Number and OH position
- OH Dissociation energy

➢ *Physico-chemical:*
- Partitioning
- Location
- Hydrophobicity