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N-3 Pufa Enriched Emulsified Foods And Strategies For Their Stabilization

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n-3 PUFA Enriched Emulsified Foods and Strategies for Their Stabilization

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Outline

- Introduction
- Lipid oxidation
- Factors affecting oxidation in complex emulsified foods
- Effect of oil quality
- Effect of ingredients
- Optimization of production process
- Use of delivery systems
- Antioxidants in emulsified foods
- Conclusions
- Acknowledgements

Lipid Oxidation

Initiation:	RH	$\longrightarrow$	$R\bullet$
Propagation:	$R\bullet + O_2$	$\longrightarrow$	$ROO\bullet$
	$ROO\bullet + RH$	$\longrightarrow$	$ROOH + R\bullet$
	$ROOH$	$\longrightarrow$	$RO\bullet + OH^-$
	$RO\bullet + ROOH$	$\longrightarrow$	$ROO\bullet + ROH$
	$RO\bullet + RH$	$\longrightarrow$	$ROH + R\bullet$
	$\bullet OH + RH$	$\longrightarrow$	$H_2O + R\bullet$
Termination:			
High O_2	$2\ ROO\bullet$	$\longrightarrow$	NRP (non radical products)
Low O_2	$ROO\bullet + R\bullet$	$\longrightarrow$	NRP
	$2\ R\bullet$	$\longrightarrow$	NRP

Initiation

Oxidizability depends on number of abstractable hydrogen atoms, i.e. allylic hydrogen atoms

Oxidizability "index": H indicates doubly allylic hydrogens

PUFA	Symbol	H	Oxidizability
Linoleate	18:2	2	20
Linolenate	18:3	4	41
Arachidonate	20:4	6	55
DHA	22:6	10	102

Pryor 1994

Primary and secondary initiation:

Metals play important role

Radicals via electron transfer

$M^{n+1} + RH \longrightarrow M^{n} + R\bullet + H^{+}$ direct H abstraction

Radicals via peroxide decomposition

$M^{n+} + ROOH \longrightarrow M^{(n+1)+} + RO\bullet + OH^{-}$ reaction 1

$M^{(n+1)+} + ROOH \longrightarrow M^{n+} + ROO\bullet + H^{+}$ reaction 2

Reaction 1: typically $Fe^{2+} \rightarrow Fe^{3+}$ or $Cu^{+} \rightarrow Cu^{2+}$

Rate of reaction 1 >> Rate of reaction 2

Peroxides always present

→ Homolytic ROOH scission important initiation mechanism

Further peroxide decomposition

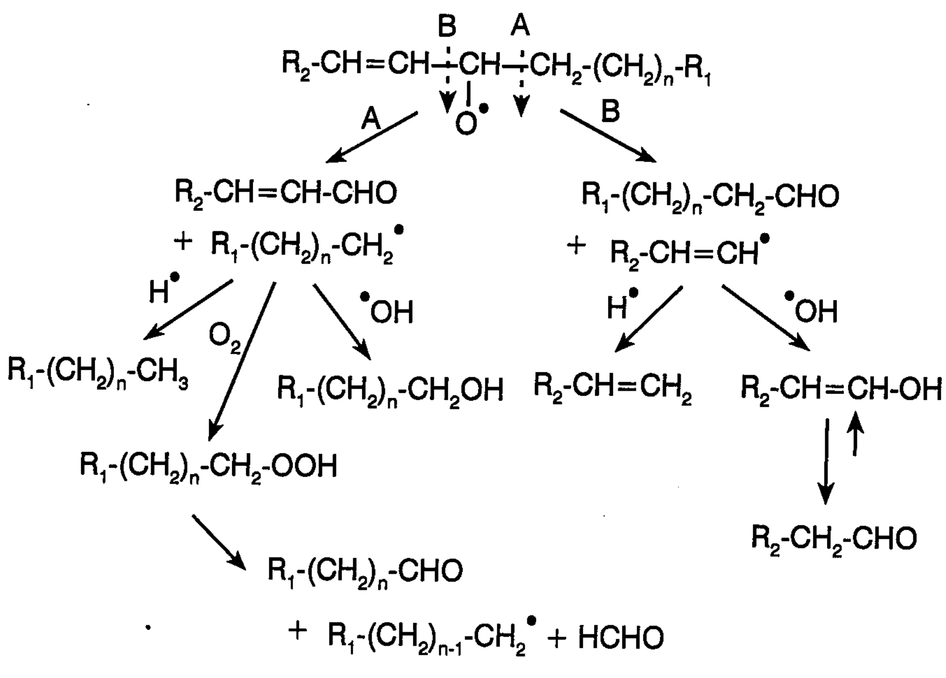
Metal ions catalyzes this reaction

β-cleavage of alkoxyl radicals after homolytic scission:

R_2 -↓- CH(O•) -↓- R_1 → Aldehydes + other volatiles

↘ ↙

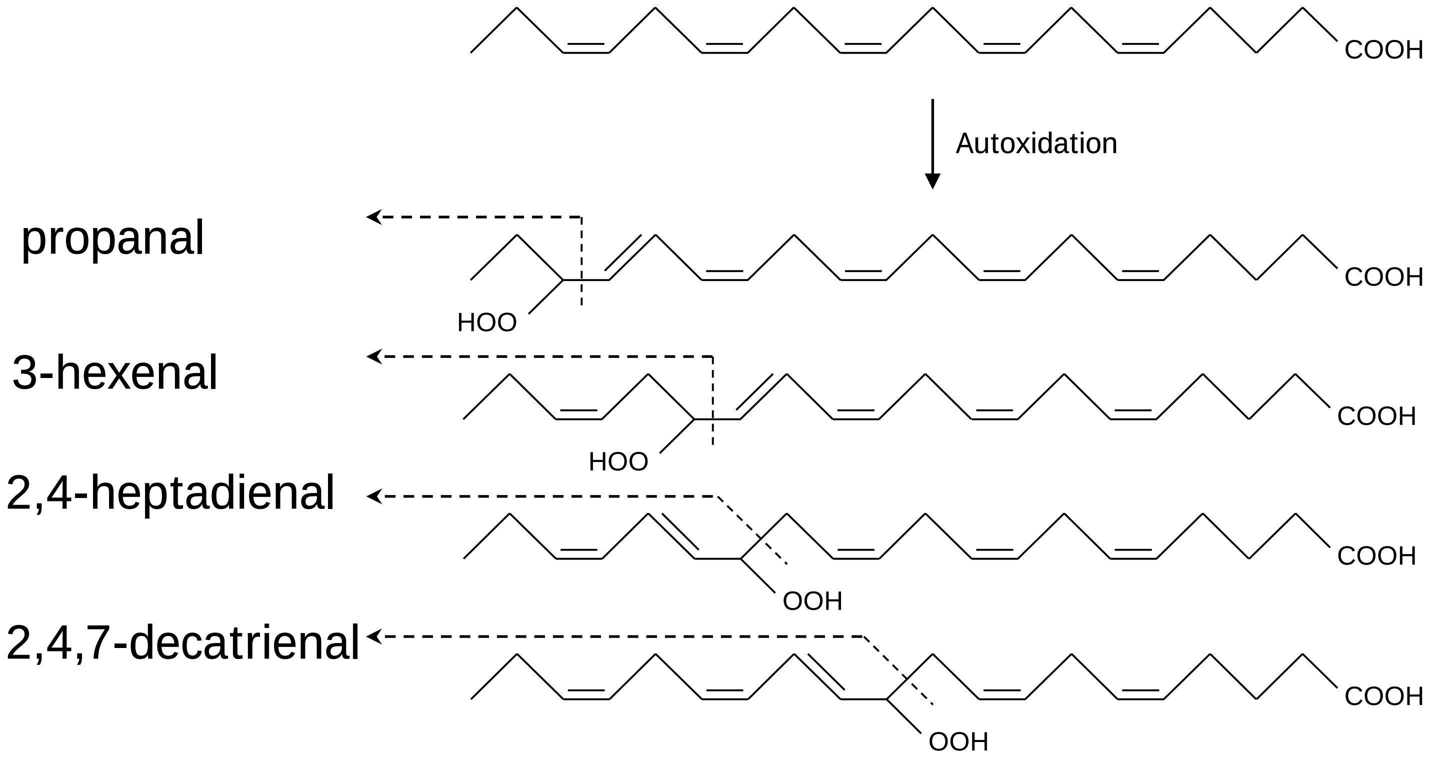
Off flavors



Aldehydes
Alkyl radicals
Olefin radicals

Frankel 1998

Oxidative decomposition of EPA



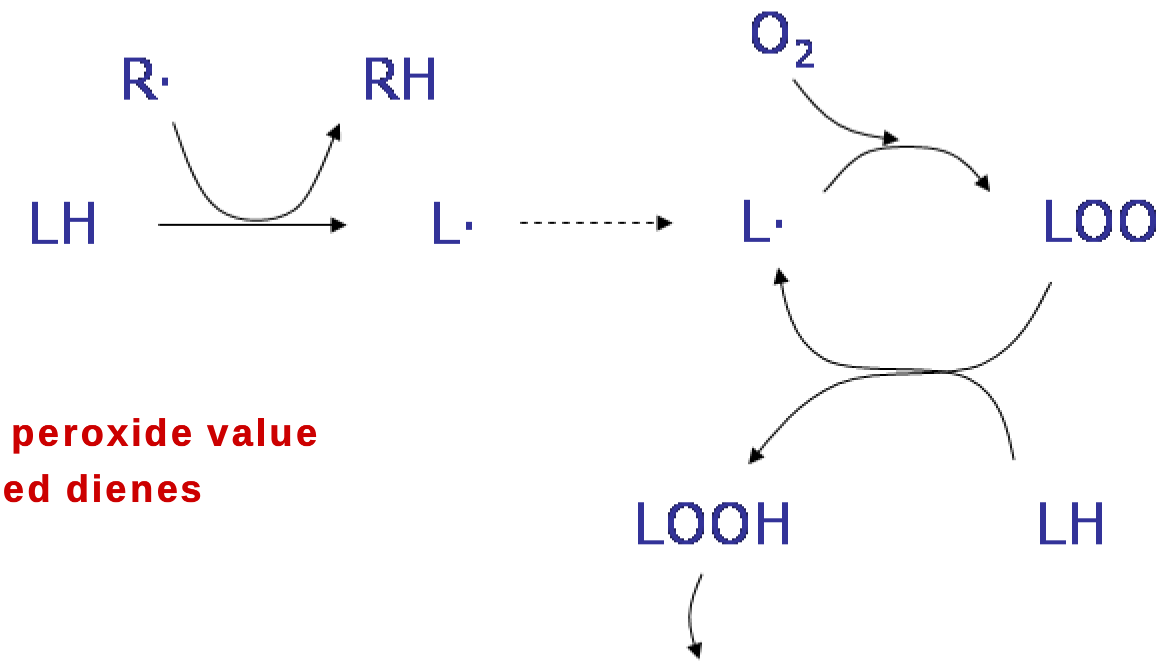
Flavour thresholds

TABLE 3 Threshold Values of Compounds Formed from Oxidized Oils

Compounds	Threshold (ppm)
Hydrocarbons	90–2150
Substituted furans	2–27
Vinyl alcohols	0.5–3
1-Alkenes	0.02–9
2-Alkenals	0.04–2.5
Alkanals	0.04–1.0
trans,*trans*-2,4-Alkadienals	0.04–0.3
Isolated alkadienals	0.002–0.3
Isolated *cis*-alkenals	0.0003–0.1
trans,*cis*-Alkadienals	0.002–0.006
Vinyl ketones	0.00002–0.007

Source: Akoh and Min, Food Lipids, Marcel Dekker, 1998

Oxidation and analysis of oxidation



Hydroperoxides: peroxide value (PV) or conjugated dienes

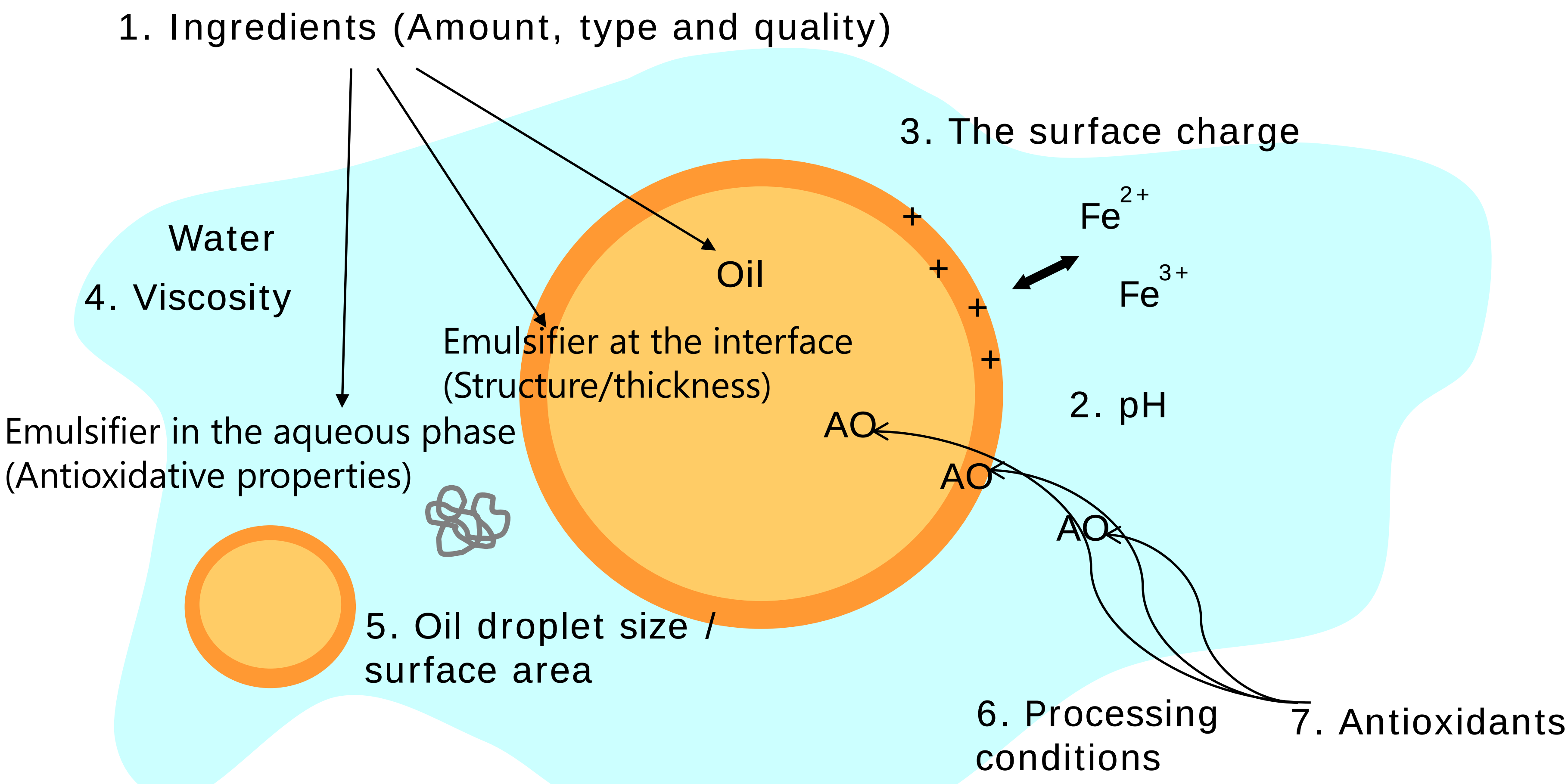
Volatiles: Anisidine value, TBARS, GC / MS (HS, DHS, SPME)

Volatile oxidation products

Sensory evaluation

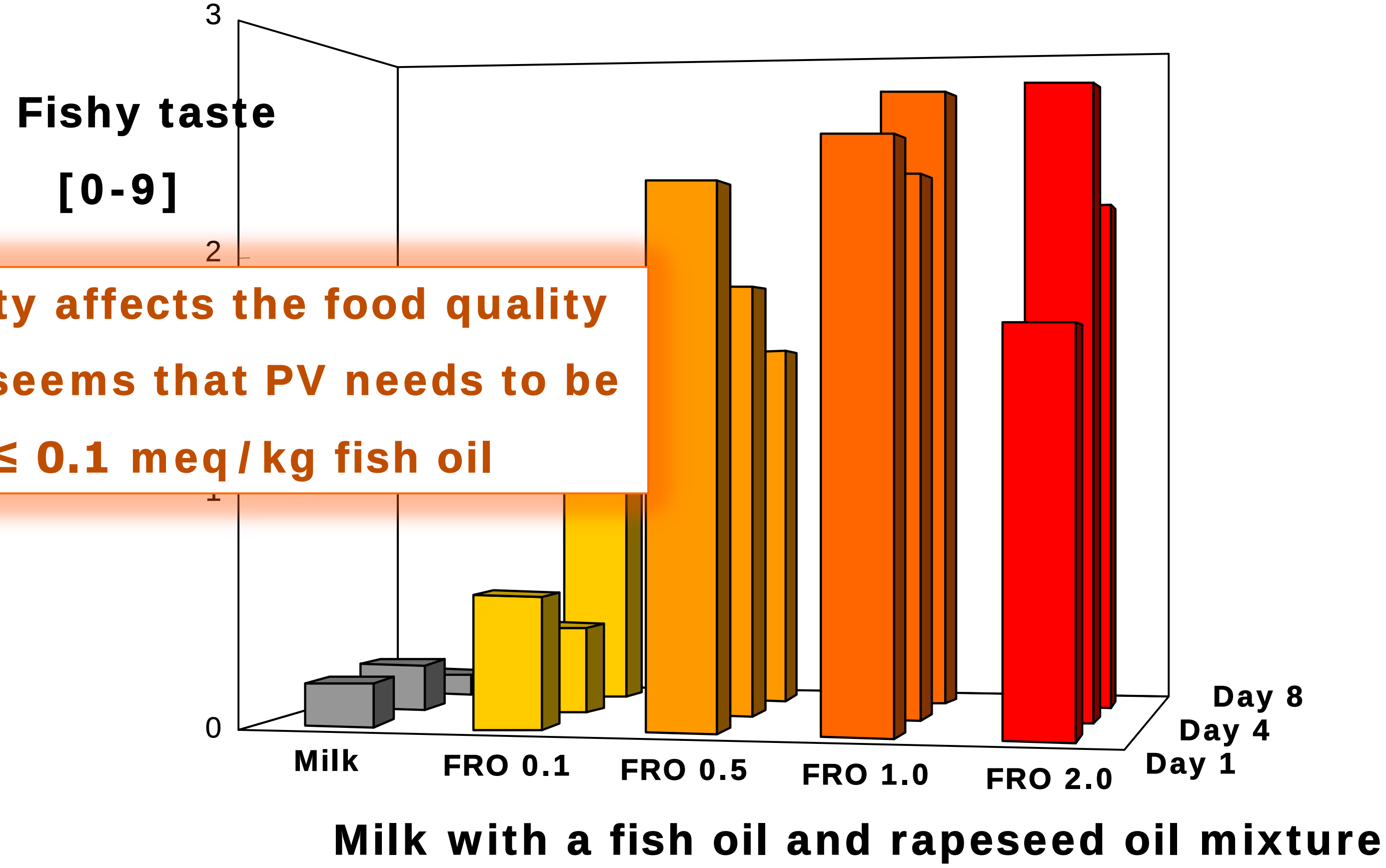
Rancid off-flavour

Factors that can affect lipid oxidation in emulsified foods:



Effect of oil quality

Fish oil enriched milk



Oil quality affects the food quality
→ seems that PV needs to be
≤ 0.1 meq / kg fish oil

Let et al., 2005. Int. Dairy J. 15:173-182

Effect of food composition

Comparing Milk and Drinking yoghurt:
Effect of Ingredients in Yoghurt

Intensity of fishy off-flavour (0-9):

	Week 0	Week 1	Week 3
Milk	5.4 ± 1.5	6.0 ± 2.4	7.4 ± 1.0
Yoghurt (CA+P+FS)	0.0 ± 0.1	0.5 ± 1.0	0.4 ± 0.7
Yoghurt (CA+P)	0.4 ± 0.5	0.9 ± 1.4	1.0 ± 1.3
Yoghurt (CA)	0.4 ± 0.5	0.7 ± 1.0	1.3 ± 0.9
Yoghurt	0.5 ± 0.4	0.8 ± 1.0	1.6 ± 1.2

CA: Citric acid; P: Pectin; FS: Fruit preparation and sugar

- Fish oil enriched milk oxidised much faster than fish oil enriched yoghurt
- Ingredients added to yoghurt did not affect oxidation

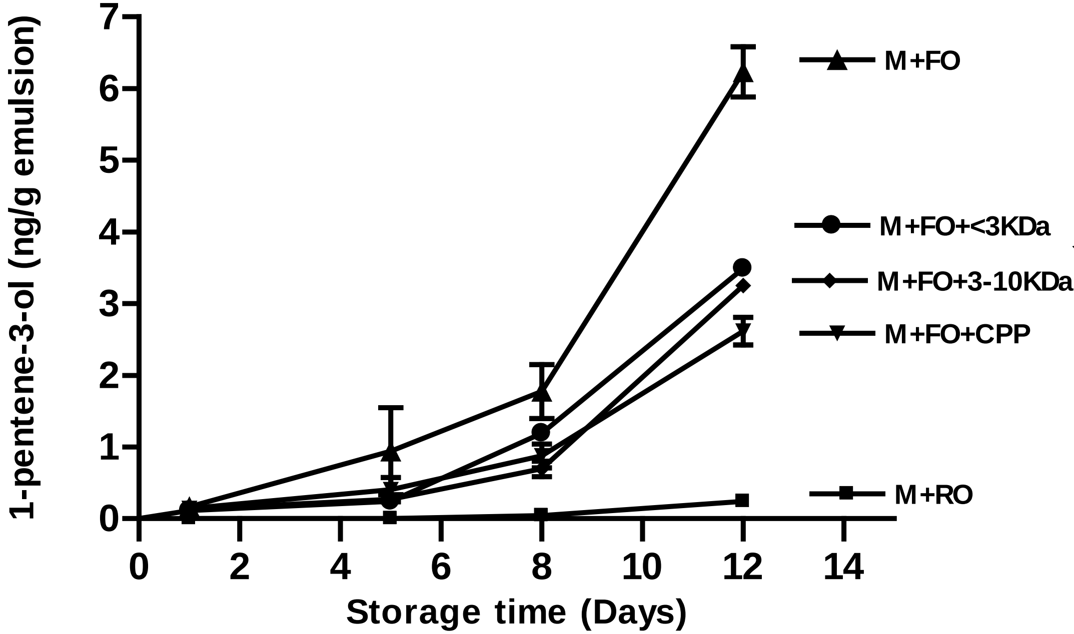
***Nielsen, Klein & Jacobsen, 2009, Eur. J. Lipid Sci. Technol*. 111, 337-345**

Comparing Milk and Yoghurt:
Antioxidant Assays on Peptide Fractions in Yoghurt

	Crude protein	Peptide fractions (KDa) >30	10-30	3-10	<3
Radical scavenging (DPPH)	+++	+++	+++	++	++
Metal chelation	+	+	+	+++	+++
Reducing power	+	+	+	++	+++

Farvin, Nielsen, Baron & Jacobsen, 2010 Food Chem. 123, 1081-1089.

Comparing Milk and Yoghurt:
Oxidative Stability of Milk with Peptide Fractions from Yoghurt



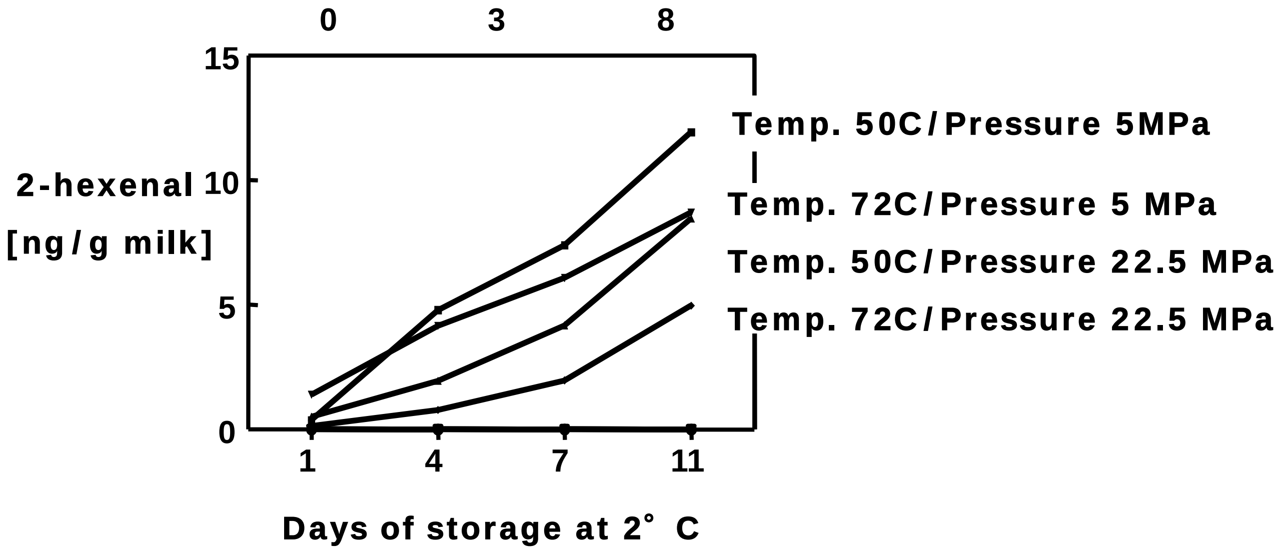
Low molecular weight peptides reduce oxidation

Farvin, Nielsen, Baron & Jacobsen, **2010** ***Food Chem.*** ***123, 1081-1089***.

Optimising homogenization conditions

- Temperature and pressure

Effect of Emulsification Conditions:
Milk Affected by Temperature and Pressure



- Homogenization with a low temperature and a low pressure leads to more oxidation than a high temperature and a high pressure!

Let, Jacobsen, Sørensen & Meyer (2007), J. Agric. Food Chem. 55:1773-1780

Homogenisation Conditions Affect Protein Composition at the Interface

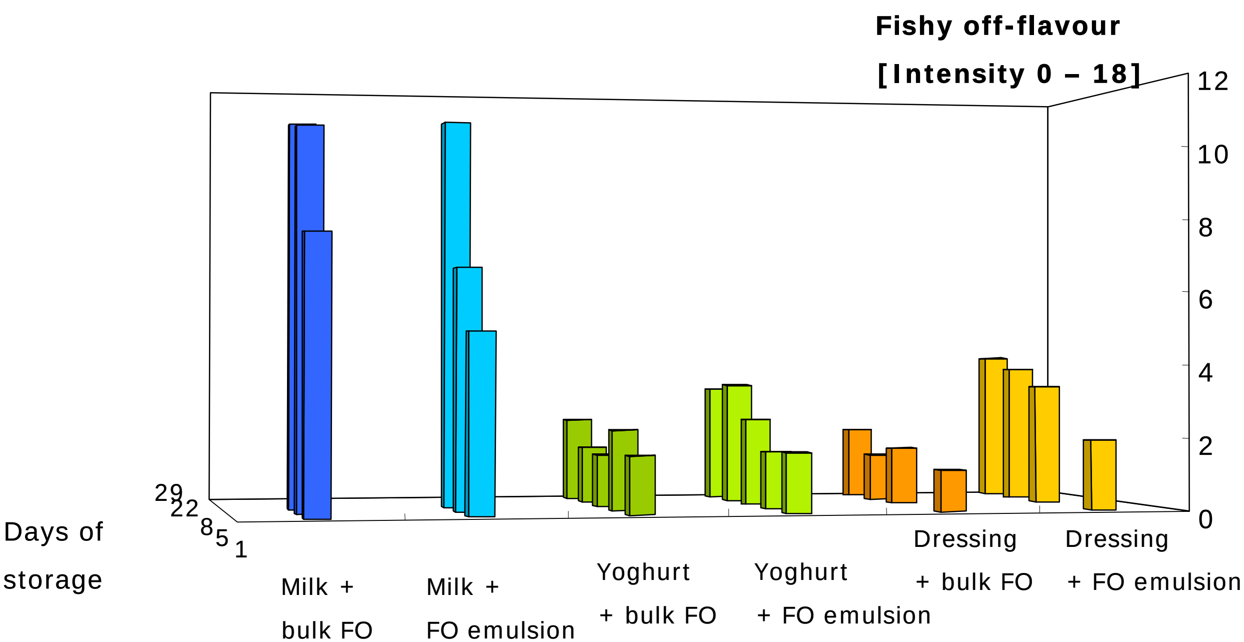
Pressure [MPa]	Temperature [°C]	β-lactoglobulin	α_{s1}-casein	α_{s2}-casein
Reference, no treatment		4.92	5.18	4.19
5	50	8.01	5.94	5.14
	72	10.17	4.28	4.09
15	50	9.36	5.21	5.08
	72	14.56	4.55	4.59
22.5	50	9.45	4.56	4.23
	72	13.72	3.68	3.74
		+	-	-

Sørensen, Baron, Brüggemann, Pedersen & Jacobsen (2007) J. Agric. Food Chem. 55:1781-1789

Effect of using an omega-3 PUFA delivery system

The Effect of Delivery Systems:
Bulk oil vs. Fish Oil Emulsion

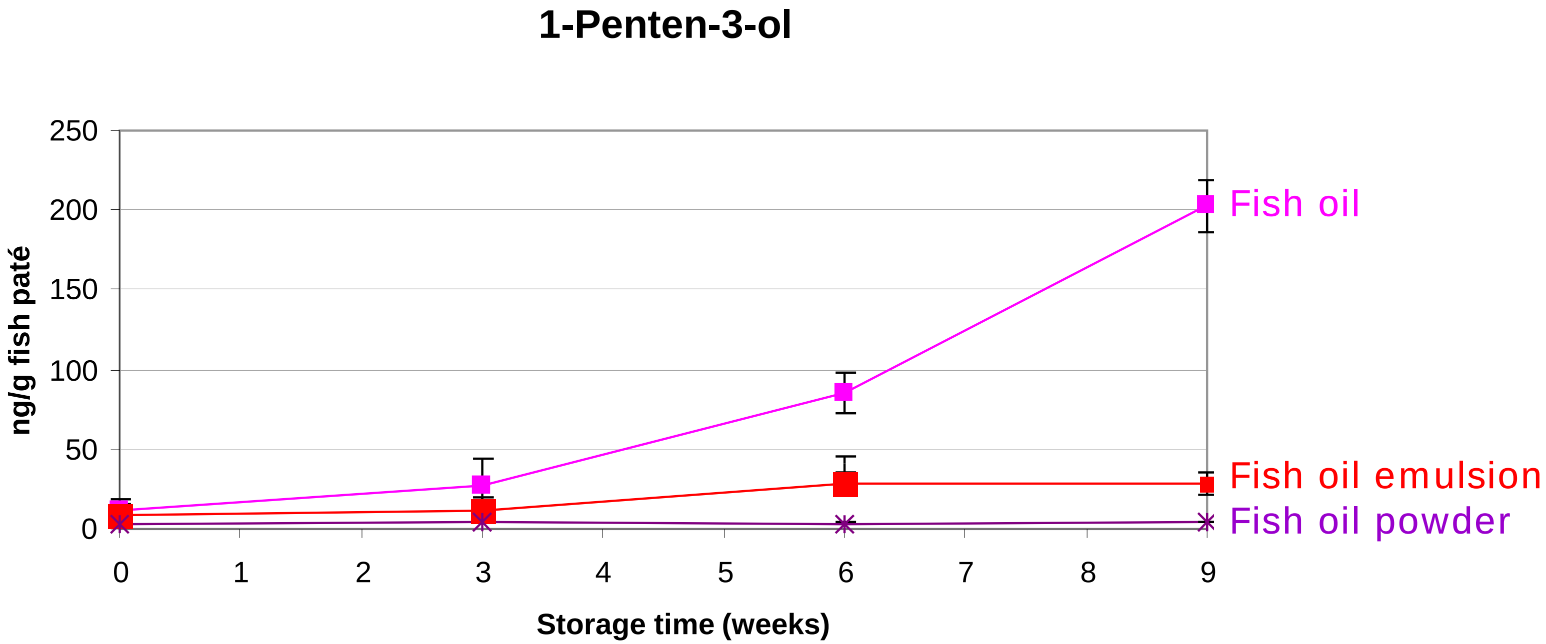
Milk oxidized much more than both yoghurt and dressing



Yoghurt and dressing with fish oil-in-water emulsion tend to be more fishy than those with neat fish oil

Let, Jacobsen & Meyer (2007) J. Agric. Food Chem. 55:7802-7809

Omega-3 enriched fish paté:
Bulk oil vs. Emulsion or Powder



- Oxidation rate: FO powder < FO emulsion < FO
- Similar results in fitness bars

Nielsen & Jacobsen, J. Food Biochemistry (2013), 37, 88-97

Effect of antioxidants in omega-3 enriched foods

Antioxidants

Antioxidants = Compounds that prevent or delay lipid oxidation

1) Primary antioxidants / Radical scavenging

→ Inactivate reactive radicals

2) Secondary antioxidants

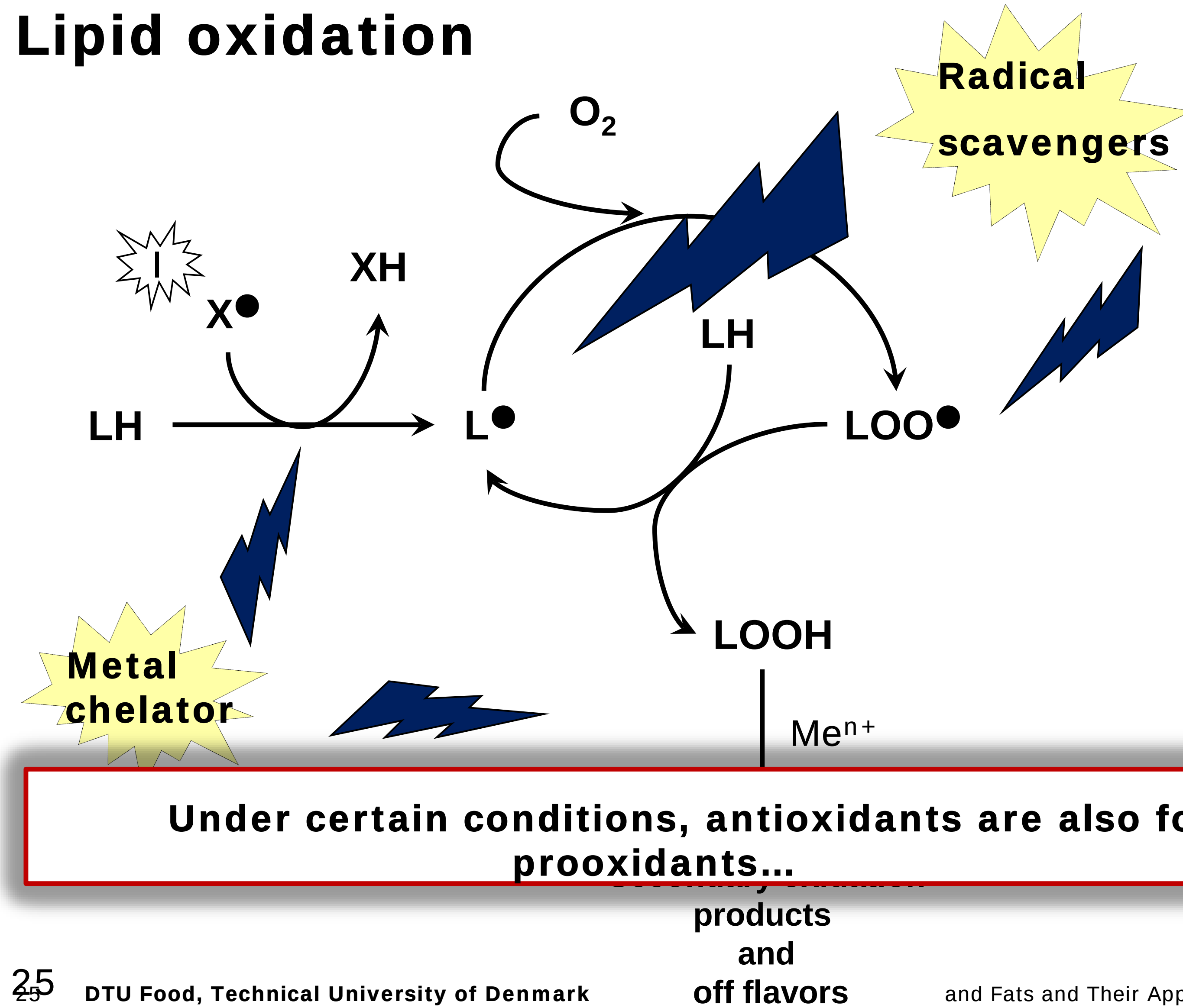
→ Bind oxygen

Chelate metal ions

Quench singlet oxygen

Regenerate other antioxidants

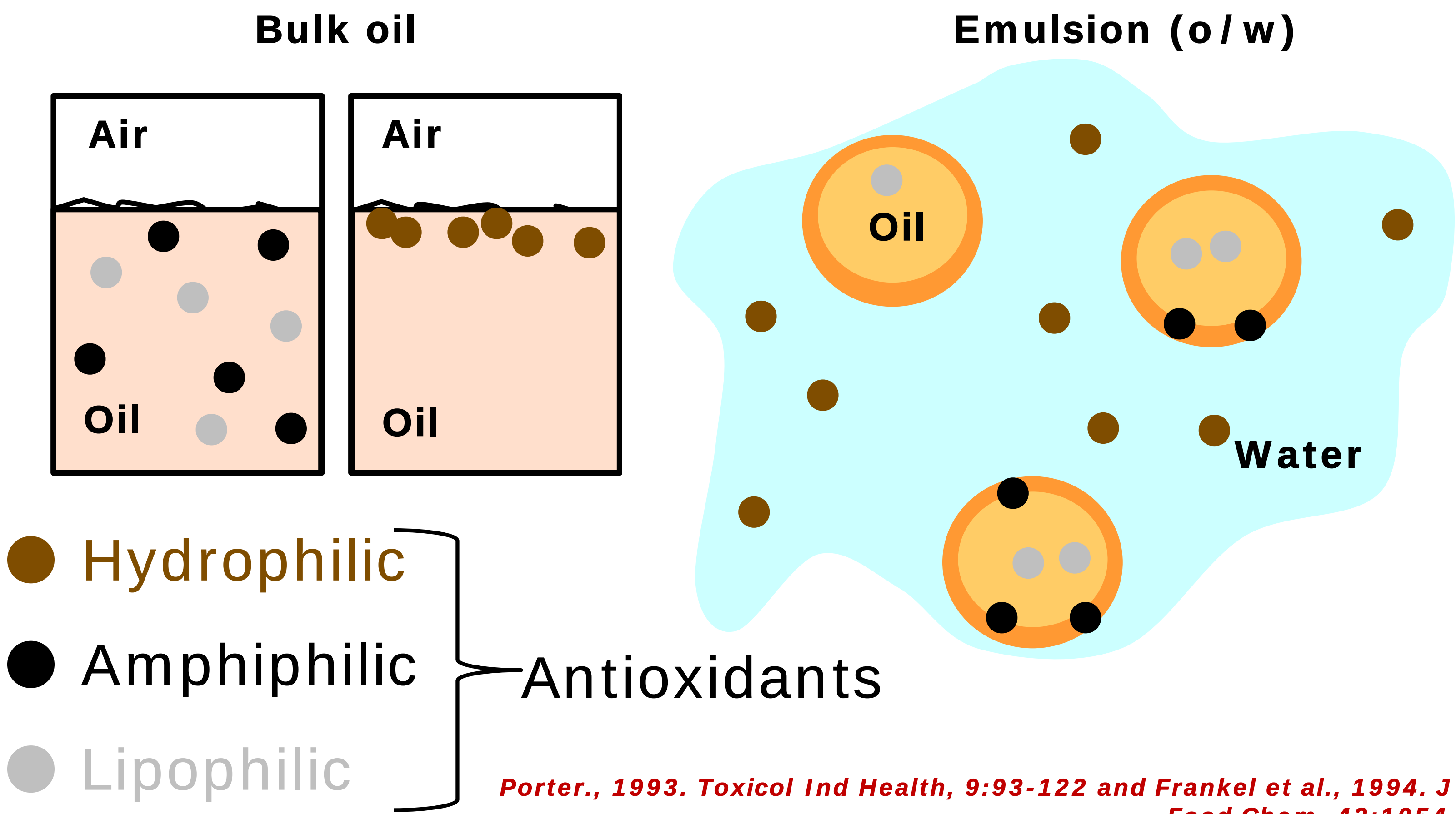
Lipid oxidation



Under certain conditions, antioxidants are also found to be prooxidants…

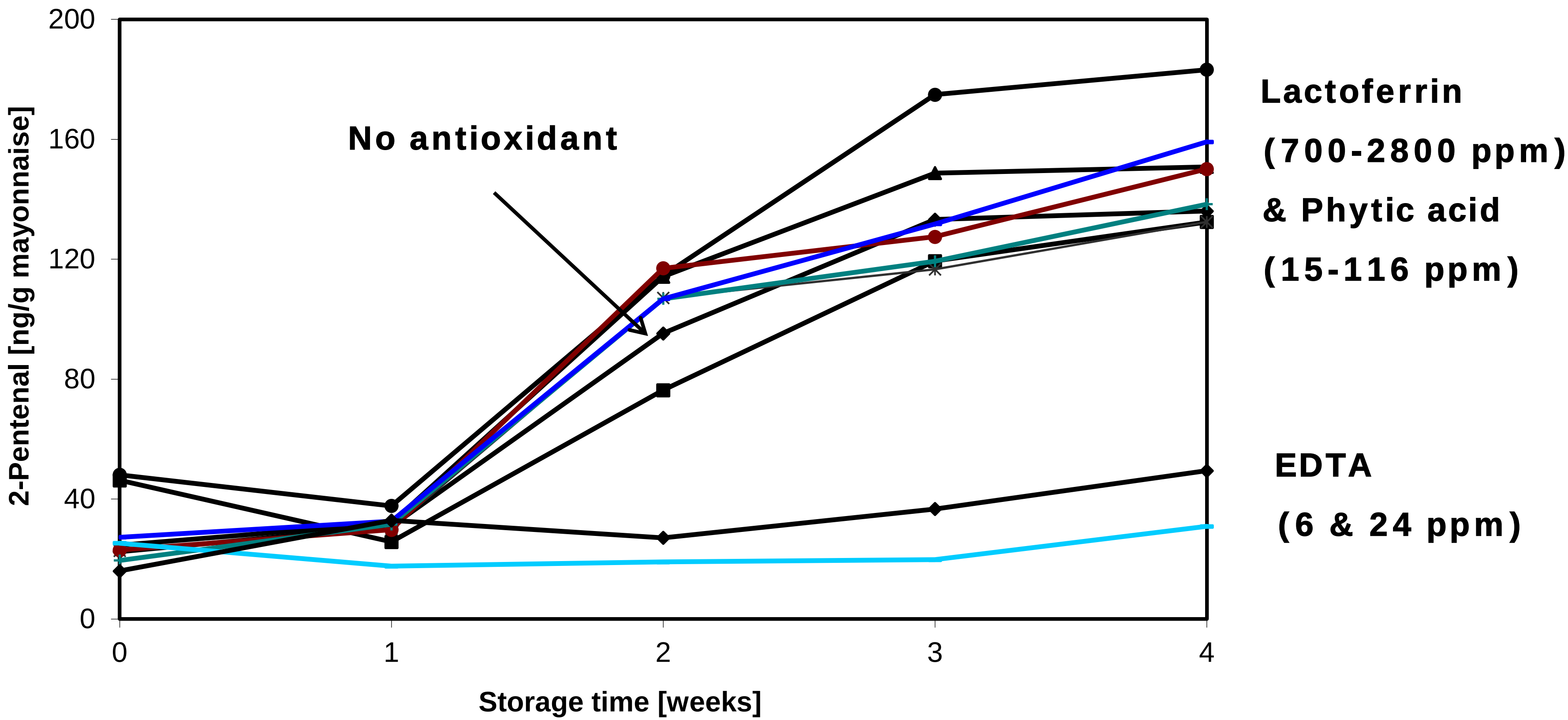
Polar paradox hypothesis

Interfacial phenomena in antioxidant activity



Porter., 1993. Toxicol Ind Health, 9:93-122 and Frankel et al., 1994. J Agric Food Chem, 42:1054-1059

AO in fish oil enriched mayonnaise



Nielsen et al., 2004. J. Agric. Food Chem. 52:7690-7699

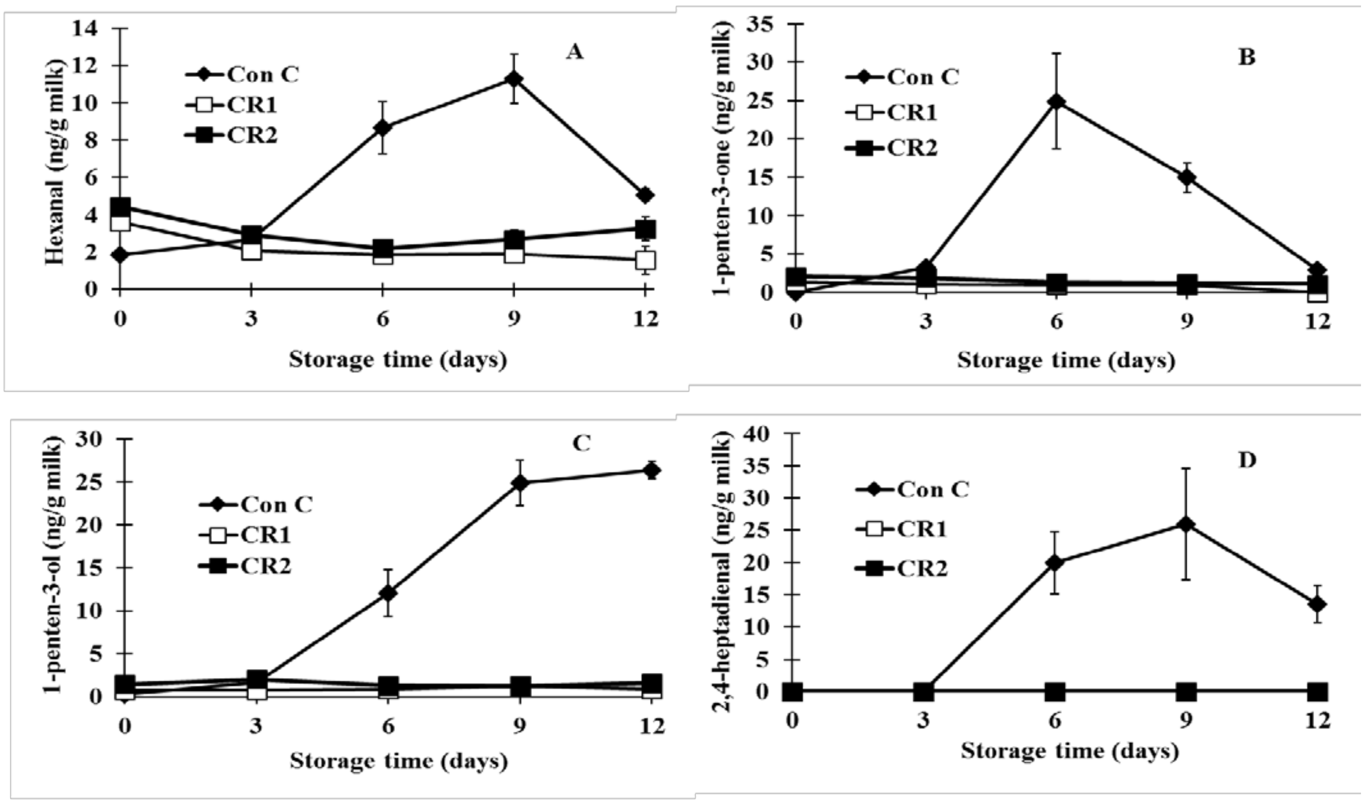
Antioxidant effects in fish oil enriched foods

- Different antioxidants have very different effects in different foods
- Possibly due to different mechanisms of action and localizations

	Tocopherol	Ascorbyl palmitate	Ascorbic acid	EDTA	Propyl gallate/ Gallic acid	Lactoferrin	Caffeic acid
Milk 1.5% fat	Weak anti	Anti		Anti to no			
Milk drink 1.5% fat		Pro		Anti		Weak anti to pro	
Drinking yoghurt 1.5% fat				Anti			
Dressing 25% fat	Weak anti	Pro		Anti			
Mayonnaise 80% fat	Weak anti to pro	Pro	Pro	Anti	Pro	Weak anti to pro	
Energy bars 6.2% fat	Anti to weak pro	Pro		Pro			Pro

Pro: Prooxidative; Anti: Antioxidative

Effect of rosemary extracts on fish oil enriched milk



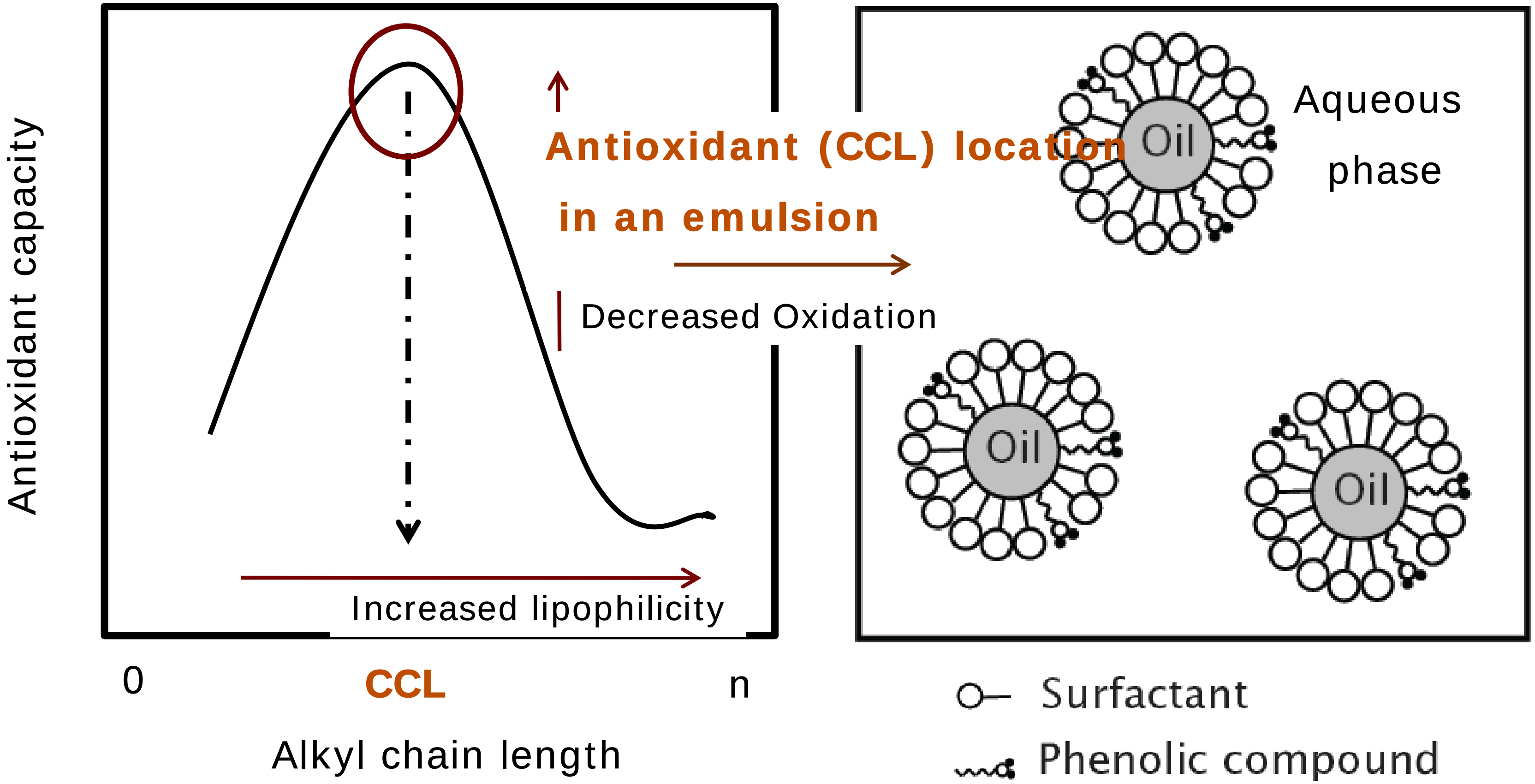
Rosemary extracts (0.03 % or 0.06 %) efficiently prevented lipid oxidation

Tocopherol levels were stable in milk with rosemary extracts

Qui, Jacobsen and Sørensen, Food Chem (2018)

Lipophilised antioxidants

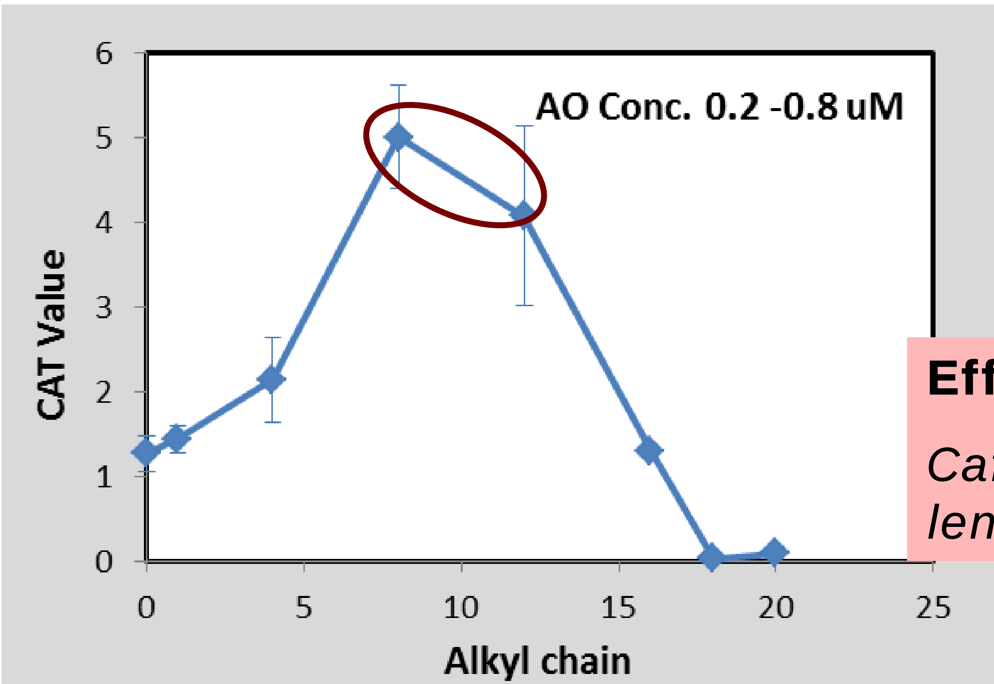
Cut-off effect (Model emulsions, o/w)

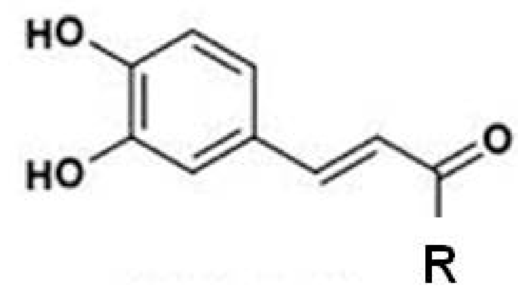


CCL = Critical chain length

Modified from Laguerre et al., 2013. In: Lipid Oxidation: Challenges in Food systems, 261-295

Caffeates as antioxidants





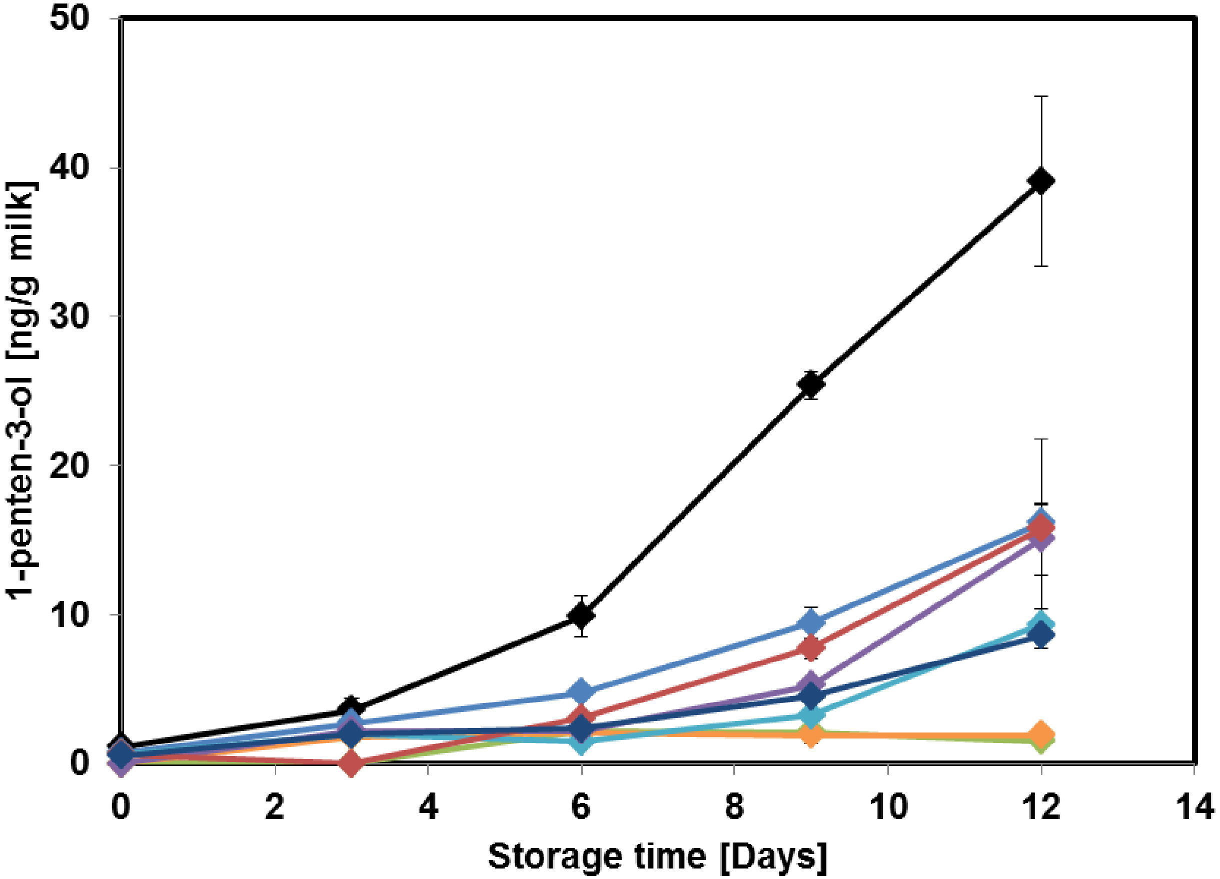
Efficacy of Caffeates

Caffeates with medium chain length

Conjugated Autoxidizable Triene (CAT) Assay

Emulsion (o/w): Phosphate buffer, Brij, Tung Oil. AAPH as initiator

Sørensen et al. 2014. J. Agric. Food Chem. 62, 12553–12562



Day 12

Con
CA C_0
CA C_{16}

CA C_{12}

CA C_8
CA C_{20}

CA C_4
CA C_1

General trend of volatile development

Lowest concentration: CA C_4 and CA C_1

The "cut-off" effect is influenced by the food system → different results in mayonnaise

Conclusions

- Ingredients can affect lipid oxidation
- Oil quality is more important in some systems than in others
- The emulsifiers used and the composition of the interface in emulsions affect lipid oxidation
- Emulsification processes must be optimised to minimise oxidation
- Delivery emulsions can reduce lipid oxidation, but delivery emulsion must be optimized for each food system

Conclusions

- The same antioxidant can have very different effects in different food systems
- Antioxidant efficacy cannot be predicted from polar paradox or from simple emulsion systems
- Rosemary extracts are efficient in some omega-3 enriched food systems
- Antioxidants are most efficient when located at the oil-water interface

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