

# **Natural Antioxidants: Great Potential for Use in Seafood**

**Isabel Medina and José Manuel Gallardo**  
**Instituto de Investigaciones Marinas del CSIC**  
**Vigo SPAIN**



# Oxidation in Fish Lipids

- Fish or seafood containing bioactive lipids are a main goal for food companies claiming for products with stable omega-3 oils
- However, it is a very susceptible material: HIGH PUFA content and HIGH HEME-Proteins content
- Generation of off-flavours associated to Rancidity
- Fatty and semi-fatty species  
Horse mackerel, mackerel, herring

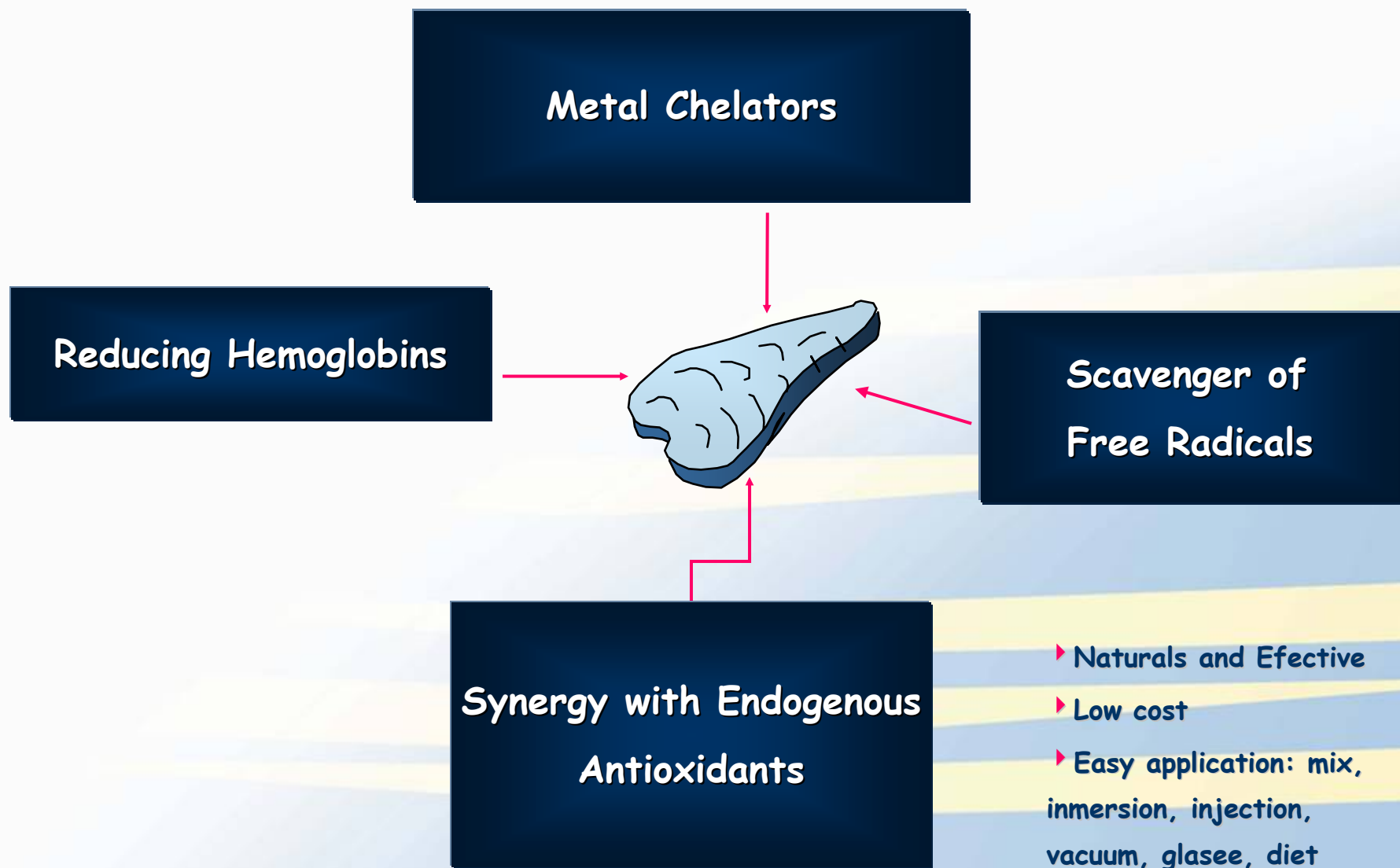


# Antioxidants



- The use of antioxidants is emerging as an effective methodology for controlling rancidity in oils and food
- Their role is to inhibit or retard the progress of lipid oxidation
- They can inhibit the formation of free radicals
- They can interrupt the free radical chain
- Consumers and food industry request natural antioxidants substituting those synthetics

# Natural Antioxidants in Fish Products



# Natural Antioxidants in SEAFOODplus



- Cinnamic acids present in vegetable extracts:

Coumaric, Chlorogenic, Ferulic and Caffeic acids

- Catechins present in tea extracts:

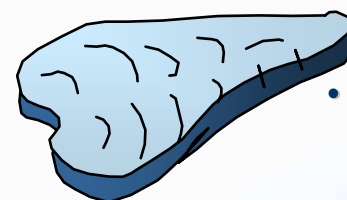
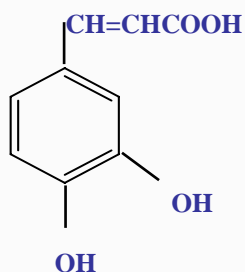
Catechin, gallocatechin, catechin gallate, gallocatechin gallate

Naturals and Effective in other matrices

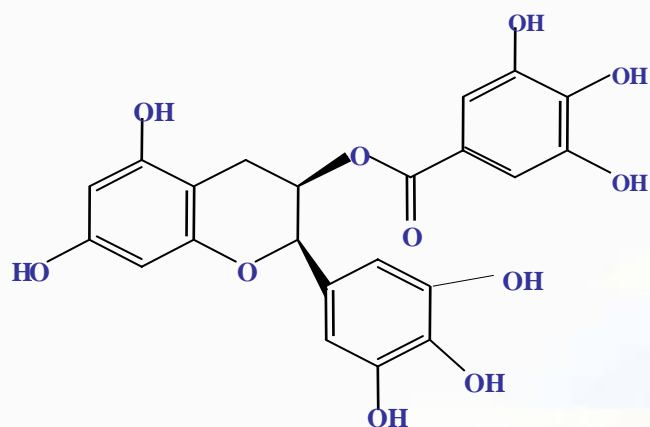
Cost

Application

# Natural Antioxidants in SEAFOODplus

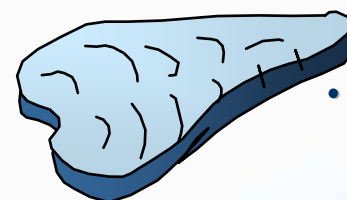
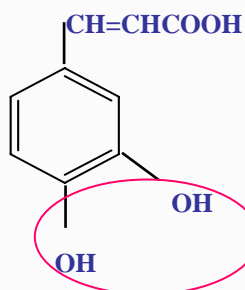


- Fish minced muscle
- Fish fillets

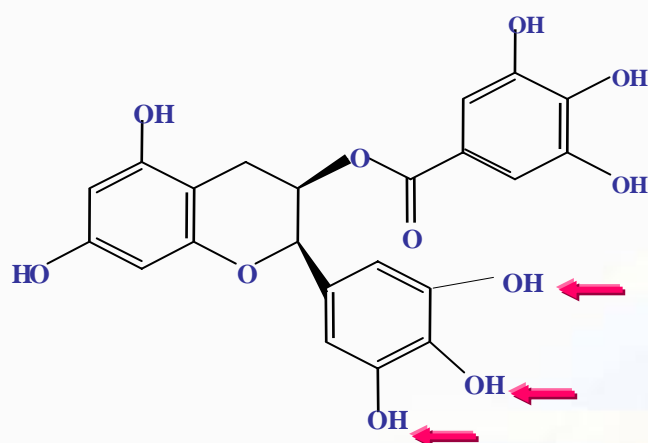


Inhibition of PUFA Oxidation  
Extension of Shelf-Life of the Seafood Product  
Protection of Biactive Lipids

# Natural Antioxidants in SEAFOODplus



- Fish minced muscle
- Fish fillets



Different molecular features  
Different in vitro properties  
Different location  
**DIFFERENT EFFICIENCY**



# In vitro Efficiency of Natural Antioxidants



N° donated electrons: Reducing power

- Caffeic > Ferulic > Chlorogenic >> Coumaric
- Propyl gallate >>> BHT





## Chelating Capacity (AEDT reference)

- Caffeic = Chlorogenic >>> Ferulic = Coumaric
- BHT > Propyl gallate

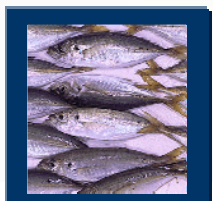
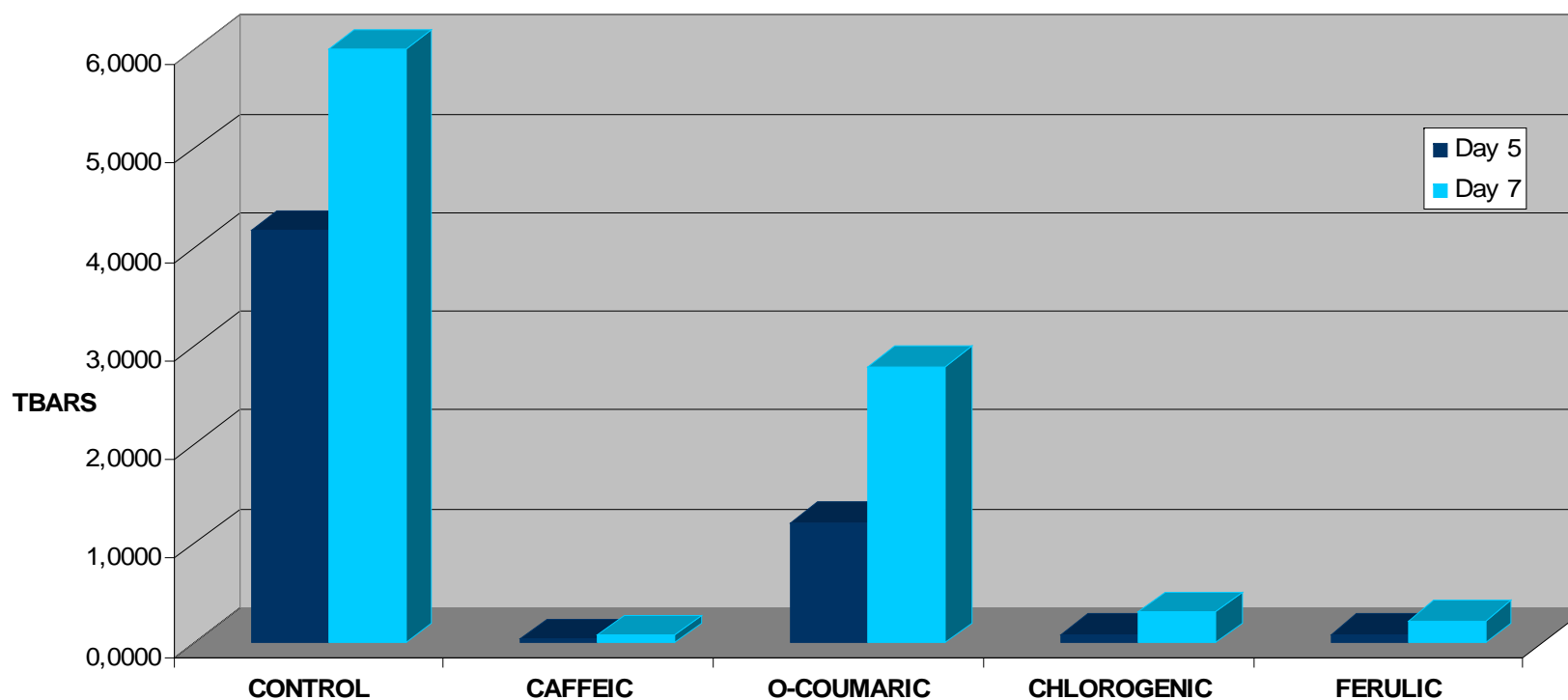


## Partitioning Coefficients: Polarity

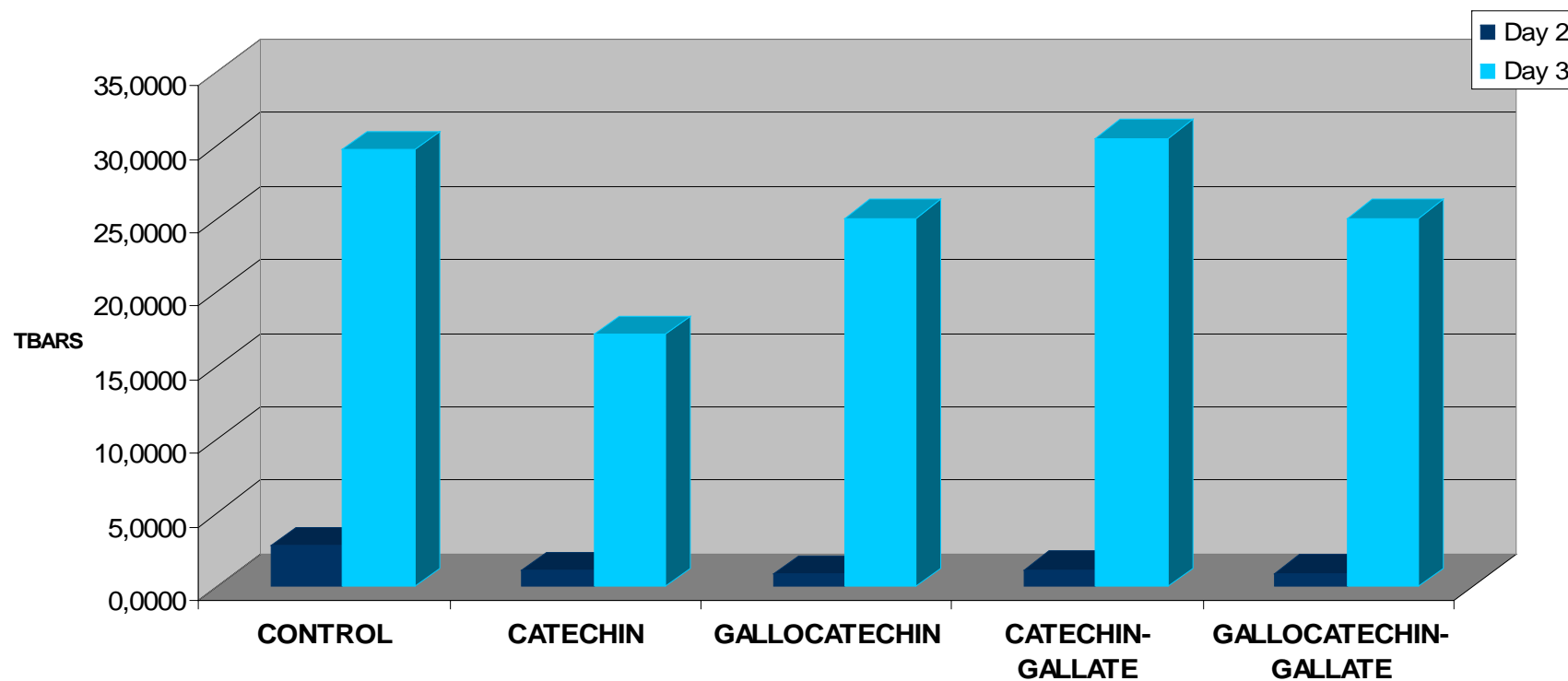
- Caffeic = Chlorogenic >> Coumaric >> Ferulic
- Propyl gallate > BHT



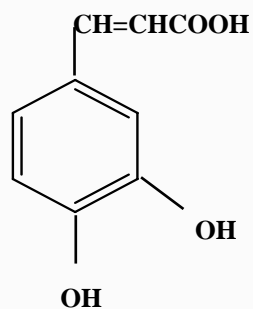
# Efficiency of Antioxidants on Fish Muscle



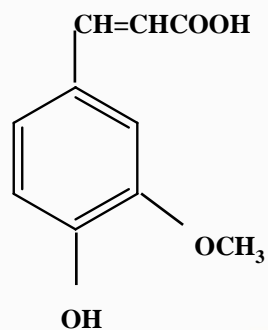
# Efficiency of Antioxidants on Fish Muscle



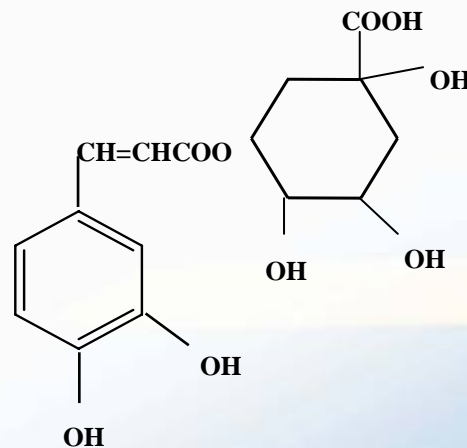
# Efficiency of Antioxidants on Fish Muscle



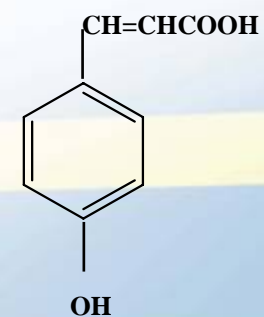
Caffeic acid



Ferulic acid



Chlorogenic acid



Coumaric acid

*Decreasing effectiveness*

# Efficiency of Antioxidants on Fish Muscle



- Effectiveness is confirmed in frozen horse mackerel and salmon at  $-10^{\circ}\text{C}$
- Confirming data in frozen horse mackerel and salmon at  $-18^{\circ}\text{C}$

In collaboration with Nick Hedges, Unilever

# *In vitro* and *In muscle* Efficiency of Antioxidants



Rate of formation of oxidation products/mol antioxidant against  
In vitro activity

	Cinnamic Acids
Reducing power	- 0.97*
Chelating activity	- 0.57
Polarity	0.13

Nº donated electrons: is  
significantly correlated

Chelating ability and polarity: are  
not correlated



# Synergy with Endogenous Antioxidants



- In vivo, fish contains an antioxidant system that stabilizes its high content of unsaturated lipids.  $\alpha$ -Tocopherol, ubiquinone, carotenoids, glutathione and ascorbate.
- In post mortem conditions, those endogenous antioxidants are consumed sequentially.

**Can our antioxidants reinforce the action of the Endogenous System?**

# Cinnamic Acids and Tocopherol

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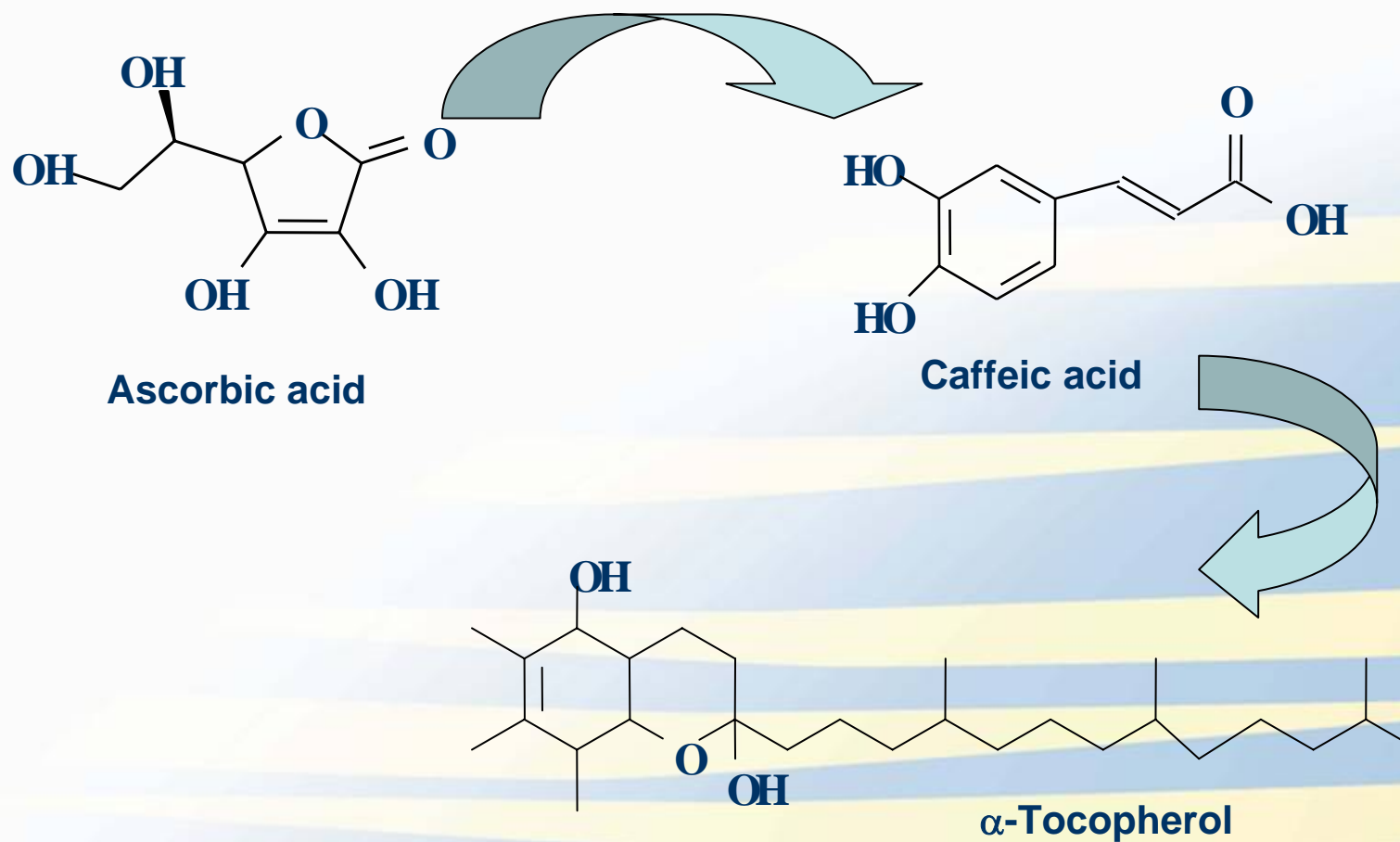
- Tocopherol is being preserved in presence of caffeic acid
- Ascorbic Acid is being consumed in presence of caffeic acid

# Synergy with endogenous antioxidants



- Consumption of Ascorbic acid does not influence the rate of oxidation
- $\alpha$ -Tocopherol seems to be the most important factor for stabilising lipid oxidation
- What is happening in the Endogenous balance in presence of Caffeic Acid?

# Possible Mechanism



# Concentration ratio

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- Experiments with different horse mackerel fishes
- Preliminary data shows there is not a single correlation between the percent of fat/ppm antioxidant and the rate of oxidation. Other parameters must be considered

- Chlorogenic Acid and Caffeic Acid Are Absorbed in Humans. Olthof et al, J Nutr 2001, 131: 66-71.
- Absorption of phenolic acids in humans after coffee consumption. Nardini et al, J Agric Food Chem 2002, Sep 25; 50(20): 5735-41.
- Anti-apoptotic activity of caffeic acid, ellagic acid and ferulic acid in normal human peripheral. blood mononuclear cells: A Bcl-2 independent mechanism. Khanduja et al, Biochim Biophys Acta-Gen Subj 2006, 1760 (2): 283-289.
- Inhibition of DNA methylation by caffeic acid and chlorogenic acid, two common catechol-containing coffee polyphenols. Lee et al, Carcinogenesis 2006, 27 (2): 269-277.

# CONCLUSIONS



- It is possible to design Natural Antioxidants for Fish Products
- Molecular features plays a significant role on efficiency: The ability for donating electrons seems to be a significant parameter for selecting the highest efficient antioxidant
- The mechanisms involved in the action of Antioxidants in muscle must be understood: Effect of the endogenous reductor system
- An increase on the functional properties of the fish product can be achieved by the employment of bioactive compounds such as phenolics or flavanoids.



# Acknowledgements

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THANKS



## Institute of Marine Research-CSIC SPAIN



# A better life with seafood...



[www.seafoodplus.org](http://www.seafoodplus.org)