Lipids and Lipid Oxidation

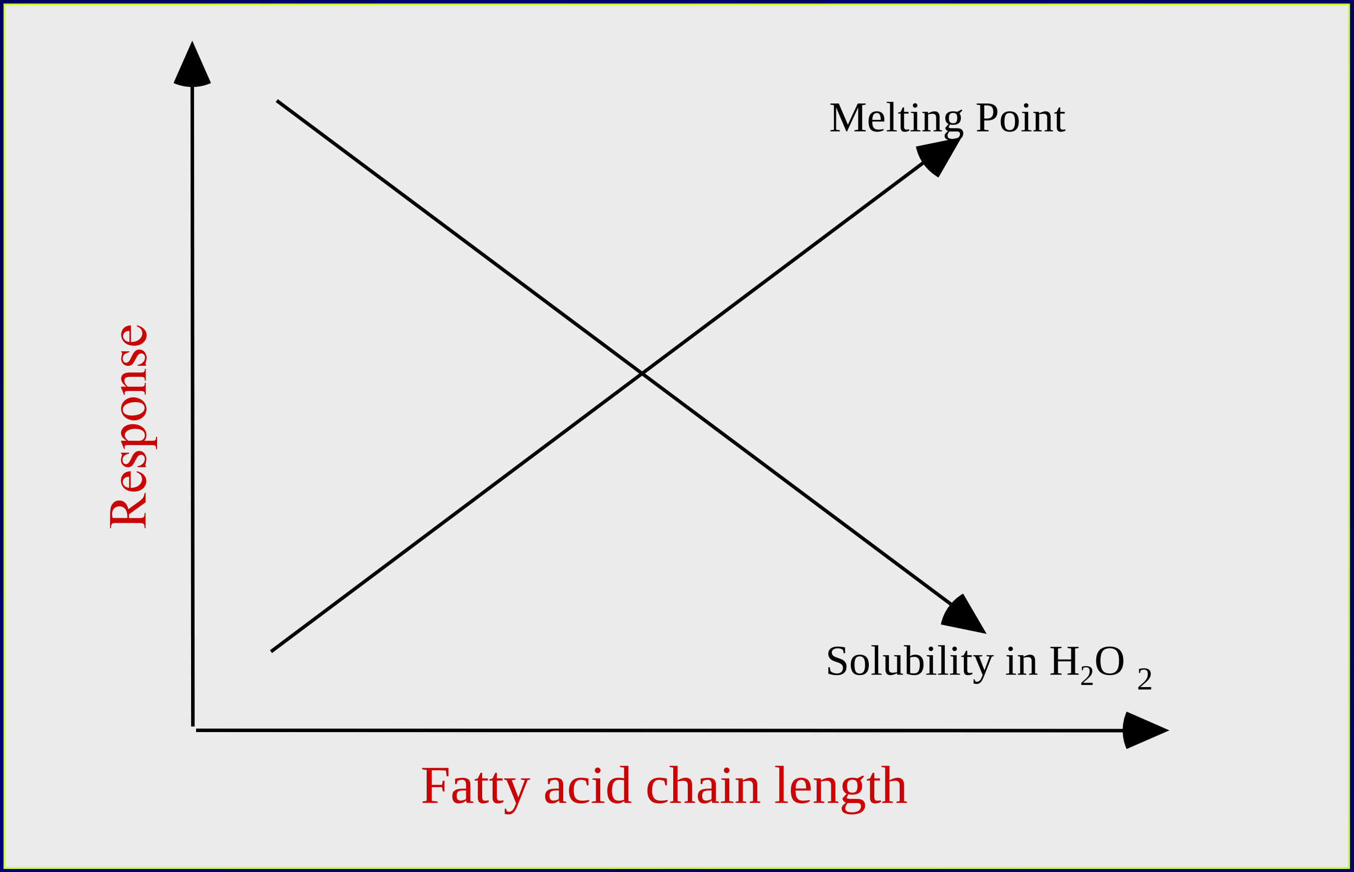
Lipids

Properties depend on structure

- Length of fatty acids (# of carbons)
- Position of fatty acids (1^{st}, 2^{nd}, 3^{rd})
- Degree of <u>un</u>saturation
- Unsaturated fats oxidize *faster*
- Preventing lipid oxidation is a constant battle in the food industry

Fatty Acids

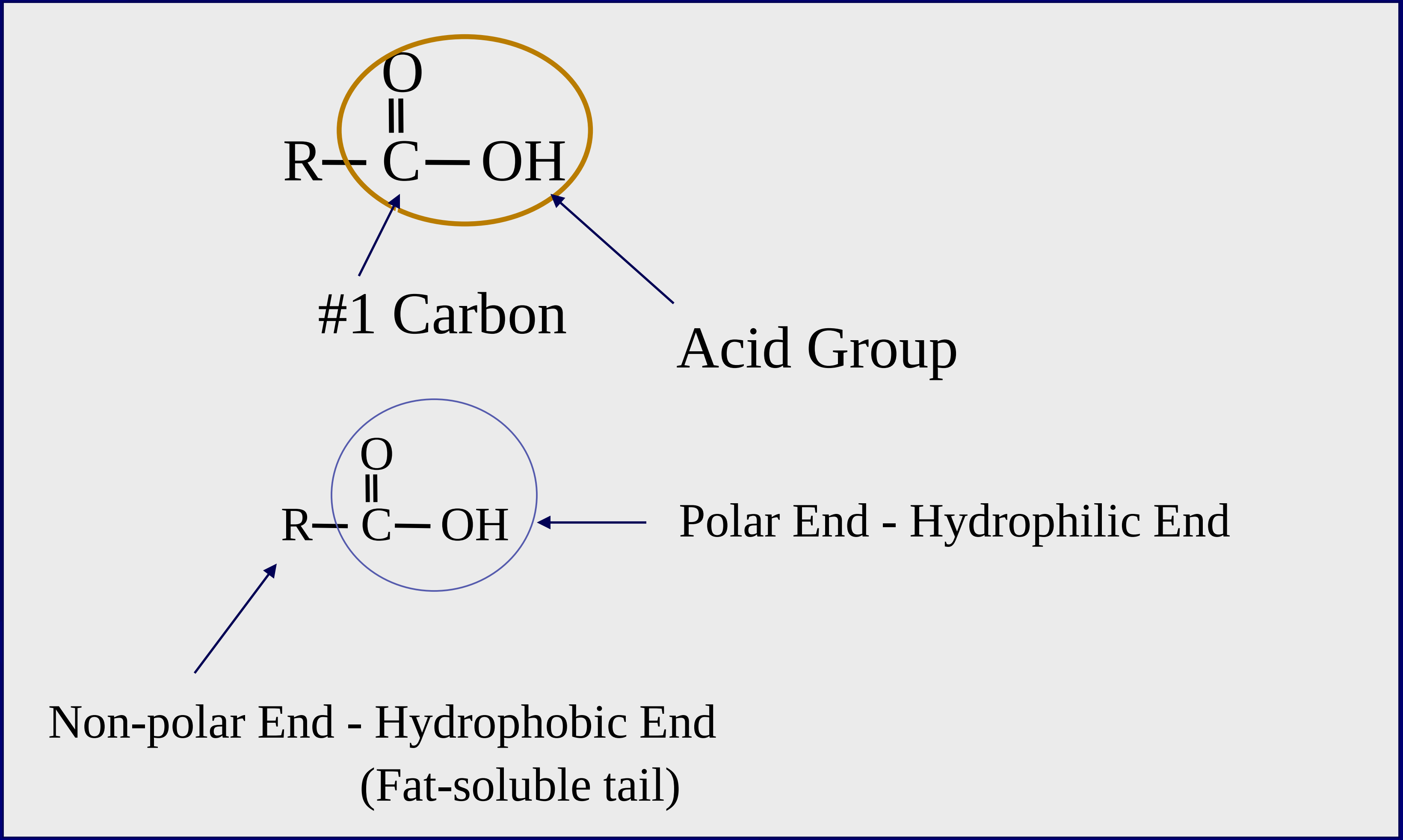
Melting Points and Solubility in Water



Characteristics of Fatty Acids

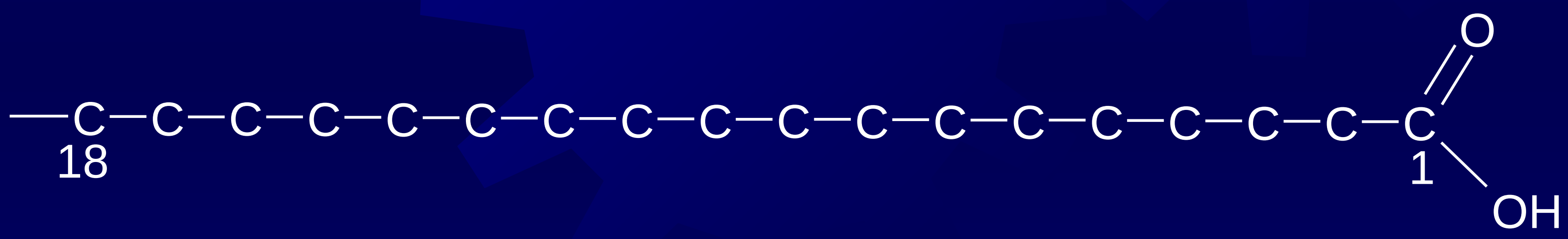
Fatty Acids	M.P.(C)	mg/100 ml in H_2O
C4	- 8	
C6	- 4	970
C8	16	75
C10	31	6
C12	44	0.55
C14	54	0.18
C16	63	0.08
C18	70	0.04

Fatty Acids


O
R— C— OH
#1 Carbon
Acid Group
O
R— C— OH
Polar End - Hydrophilic End
Non-polar End - Hydrophobic End
(Fat-soluble tail)

Quantification and Numeration

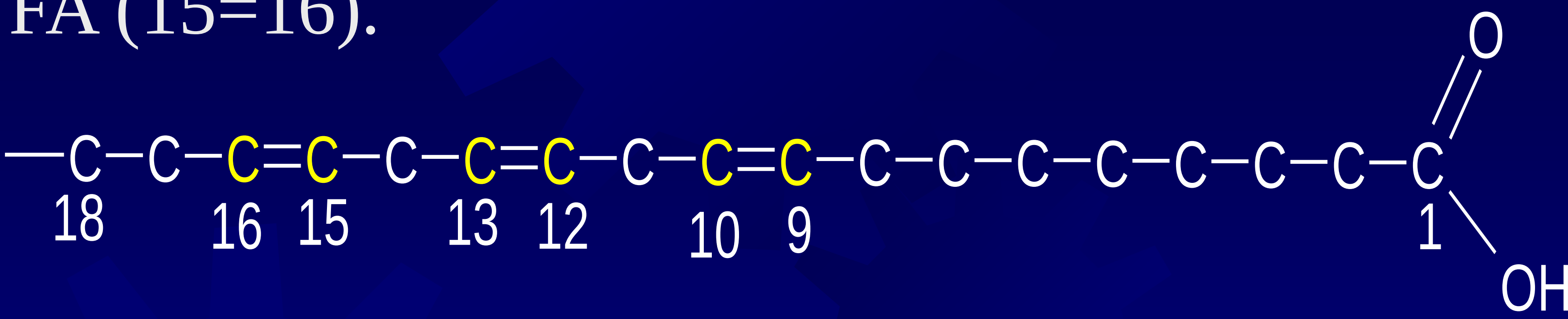
- For ID, we start counting the number of carbons starting with “1” at the carboxylic acid end.



9,12,15-octadecatrienoic	α-linolenic	18:3(n-3)	278.4
6,9,12,15-octadecatetraenoic	stearidonic	18:4(n-3)	276.4

Lipids 101

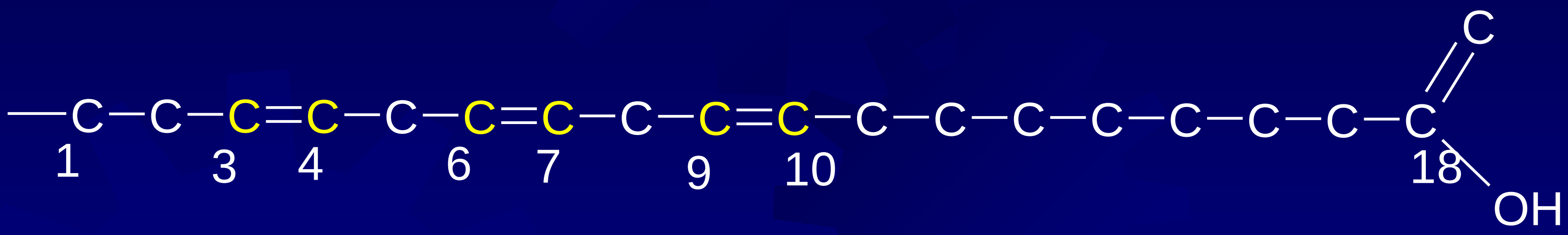
- For the “18-series” (18:0, 18:1, 18:2, 18:3) the double bonds are usually located between carbons 6=7, 9=10, and 12=13.
- Some plants synthesize differently, to create an n-3 FA (15=16).



9,12,15-octadecatrienoic	α-linolenic	18:3(n-3)	278.4
6,9,12,15-octadecatetraenoic	stearidonic	18:4(n-3)	276.4

Lipids 101

- In the biomedical field uses the OMEGA (*w*) system (or “n” fatty acids).
- Counts carbons in the opposite direction, starting with the <u>methyl end</u>
- Now the 15=16 double bond is a 3=4 double bond or an *w*-3 fatty acid



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6,9,12,15-octadecatetraenoic	stearidonic	18:4(n-3)	276.4

Where Do We Get Fats and Oils?

- "Crude" fats and oils are derived from plant and animal sources
- Most can not be used without first "refining" before they reach consumers
- During oil refining, water, carbohydrates, proteins, pigments, phospholipids, and free fatty acids are removed.
- Crude fats and oils can therefore be converted into high quality edible oils
- Oilseeds, nuts, olives, beef tallow, fish skins, etc.

Fats and Oils
Further Processing

- Degumming
  - Remove phospholipids with water
- Refining
  - Remove free fatty acids (alkali + water)
- Bleaching
  - Remove pigments (charcoal filters)
- Deodorization
  - Remove off-odors (steam, vacuum)

Fats and Oils
Further Processing

Hydrogenation

- Add hydrogen to an oil to "<u>saturate</u>" the fatty acid double bonds
  - Conducted with heated oil
  - Often under pressure
  - In the presence of a catalyst (usually nickel)
- Converts liquid oils to solid fats
- Raises melting point

The *cis*- and *trans*- forms of a fatty acid

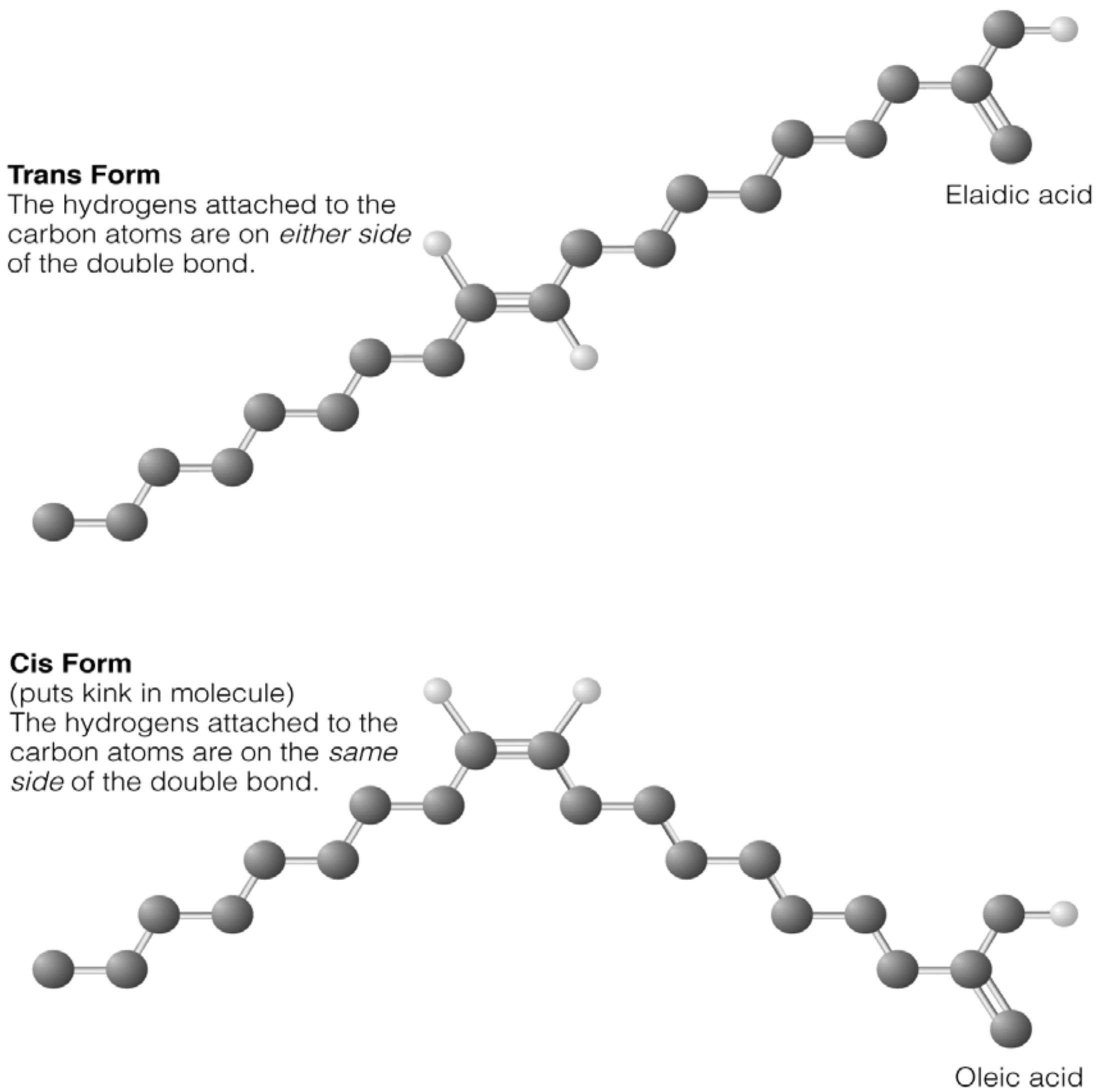


FIGURE 5.10 **The cis and trans forms of a typical unsaturated fatty acid.**

Recent advances in rapid and nondestructive determination of fat content and fatty acids composition of muscle foods

Feifei Tao & Michael Ngadi

Rapid and Non-Destructive

- Conventional methods to determine fat and fatty acids are based on the solvent extraction and GC methods
  - Time consuming, laborious, and destructive
- Impossible for large-scale detection or production lines
- Need for rapid and non-destructive techniques
- Near-infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance, and hyper-spectral imaging are promising
- Article gives an overview of the current research in application to muscle foods, pork, beef, lamb, chicken meat, fish and fish oil.
- Working principles, features, and application advantages.

Rapid and Non-Destructive

- Near-infrared spectroscopy
- 780 to 2526 nm (between red and mid-infrared regions)
- Rapid and non-destructive
- Based on the principle that chemical bonds absorb or emit different wavelengths of light when the sample is irradiated by continuous changing frequency of NIR light.
- The absorption intensity is related to the content of the chemical substances in the tested sample
- Usually responses of the C-H, O-H, N-H, and C-O bonds
- Vibrational energy changes when irradiated by NIR light

Rapid and Non-Destructive

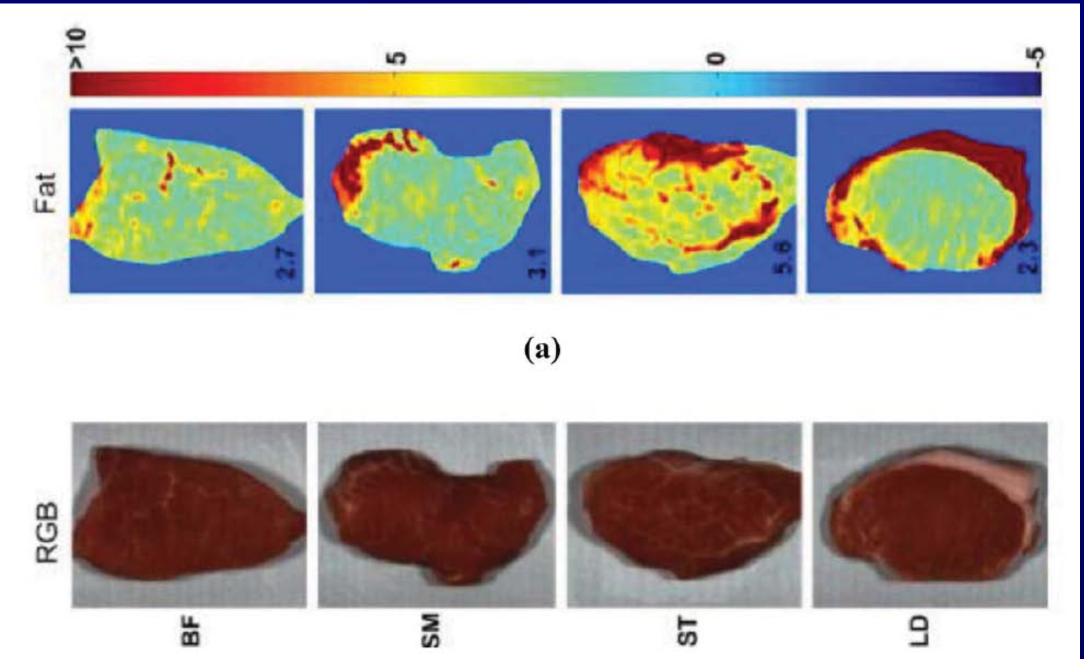
- Raman spectroscopy
- Inelastic light scattering is known as Raman radiation
- When a substance is irradiated with monochromatic light, most of the scattered energy comprises radiation of the incident frequency
- In addition, a very small quantity (0.0001%) of photons with shifted frequency is observed, and is called Raman scattering.
- Non-polar groups such as C=C, C-C, and S-S have intense Raman bands, other than the polar groups such as C=O, N-H, and O-H which have strong IR stretching vibrations.

Rapid and Non-Destructive

- Hyperspectral imaging (HIS)
- New, but rapidly growing technique that integrates spectroscopic and imaging techniques together to provide both spectral and spatial information simultaneously.
- Originally developed for remote sensing/scanning
- Carried out in reflectance, transmission, scattering, and transflectance or fluorescence modes
- Images are 3D in nature

Rapid and Non-Destructive

Hyperspectral imaging (HIS)



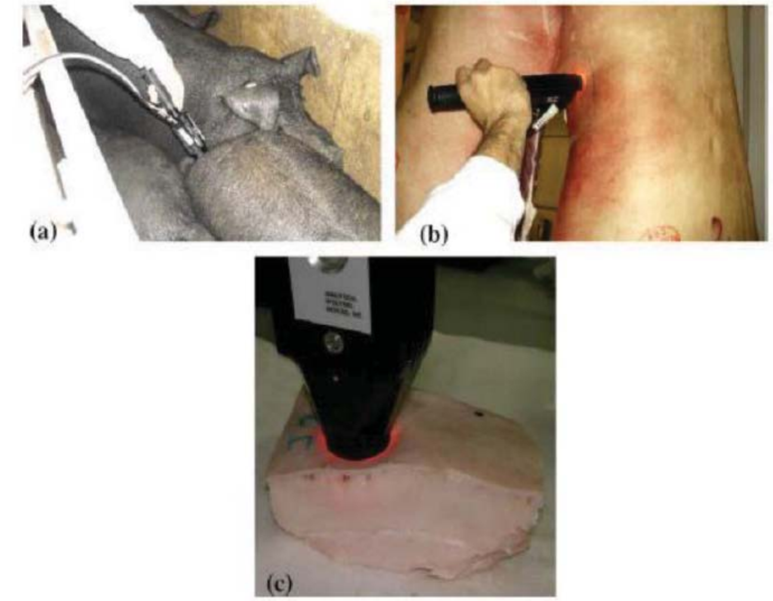


Figure 4. Collection of NIR spectra in (a) live animals, (b) carcasses, and (c) fat samples over the skin (Pérez-Marín et al., 2009).

Recent Events (2015-2018)

- **Final Determination Regarding Partially Hydrogenated Oils (Removing *Trans* Fat)**

- FDA released its’ final determination that Partially Hydrogenated Oils (PHOs) are not Generally Recognized as Safe (GRAS). The determination is based on extensive research into the effects of PHOs, as well as input from stakeholders during the public comment period.

- PHOs are the primary dietary source of artificial *trans* fat in processed foods. Removing PHOs from processed foods ***could prevent thousands of heart attacks and deaths each year***. To learn more about *trans* fat, see our *Trans* Fat page.

Recent Events

- **Implementation**
- FDA set a compliance period of three years. This will allow food companies to either reformulate products without PHOs and/or petition the FDA to permit specific uses of PHOs. Many companies have already been working to remove PHOs from processed foods and the FDA anticipates that many may eliminate them ahead of the three-year compliance date.
- It's important to note that *trans* fat will not be completely gone from foods because it occurs naturally in small amounts in meat and dairy products, and is present at very low levels in other edible oils.
- The FDA encourages consumers seeking to reduce *trans* fat intake to check a food's ingredient list to determine whether or not it contains partially hydrogenated oil.

Recent Events

- **Background**
- In January 2006, FDA required the food industry to declare the amount of *trans* fat in food on the Nutrition Facts label. FDA data indicate that many processed foods have been reformulated to reduce the amount of *trans* fat since the requirement was instituted, but a substantial number of products still contain PHOs.
- One of FDA's core regulatory functions is ensuring that food, including all substances added to food, is safe. In November 2013, FDA made a preliminary determination that PHOs are not “generally recognized as safe” (GRAS) for use in food. FDA opened a 60-day public comment period on this measure to solicit data and information on a number of issues, including:
- 1. Whether FDA should finalize its tentative determination that PHOs are no longer GRAS; and 2. How long it would take producers to reformulate food products to eliminate PHOs.
- The comment period was then extended an additional 60 days and closed March 8, 2014. The final determination was released June 16, 2015. This determination is based on extensive research into the effects of PHOs, as well as input from all stakeholders received during the public comment period.

Recent Events

- FDA to Extend Comment Period on Measure to Further Reduce *Trans* Fat in Processed Foods - UPDATED

- FDA published a notice in the Federal Register announcing its preliminary determination on November 8, 2013. FDA provided 60 days, until January 7, 2014, for interested persons to provide comments and scientific data pertaining to the notice, including specific issues that FDA sought comments on such as possible alternative approaches, time needed for reformulation, burden on small businesses, and other technical challenges to removal of PHOs from the food supply. ecember 2013

Recent Events

- **Comment from Grocery Manufacturers Association**
- The Grocery Manufacturers Association (GMA)1 is the voice of more than 300 leading food, beverage, and consumer product companies that sustain and enhance the quality of life for hundreds of millions of people in the United States and around the globe.
- The FDA improperly attributes a two-page viewpoint on the epidemiology of *trans* fat consumption to the CDC, when it was in fact a viewpoint article authored by Dietz et al. (2012) 7 , and is not a CDC study. The CDC did not estimate the alleged cardiovascular deaths due to *trans* fats that the FDA has widely promoted in numerous publications. Two authors who happened to work at the CDC published the viewpoint in the JOURNAL OF THE AMERICAN MEDICAL ASSOCIATION (JAMA). At the end of the published viewpoint, it expressly states: 'The findings and conclusions in this report are those of the authors and do not necessarily reflect the official position of the US Centers for Disease Control and Prevention."8 In its Tentative Determination, the FDA explains that the data comes from the CDC, and then cites the twopage JAMA viewpoint to support this claim- the same JAMA viewpoint that is expressly not a CDC study. The FDA clearly should have known that the report was not a CDC study, especially when it cited a JAMA viewpoint for the alleged CDC claim.

Public Comments

- ….GMA
- The CDC currently lists the estimates of cardiovascular deaths on their web site, and it specifically cites the source but does not claim that CDC authored these estimates.9 There was one instance where the CDC referenced the data, but did not cite the study properly.
- In a previously posted document called "Winnable Battles Progress Report: 201 0-2015,"10 the CDC explained, "CDC has concluded that 10,000-20,000 heart attacks and 3,000-7,000 coronary heart disease deaths each year in the U.S. could be prevented by removing artificial *trans* fat from processed foods.“
- After an IQA Request for Correction was made by GMA to the CDC on October 9, 2014, and a follow-up Request for Reconsideration was submitted on January 15, 2015, the CDC edited its "Winnable Battles" report, which now states that "CDC **researchers** have concluded that 10,000-20,000 heart attacks and 3,000-7,000 coronary heart disease deaths each year in the U.S. could be prevented by removing artificial *trans* fat from processed foods. **See Dietz, WH, Scanlon, KS. Eliminating the Use of Partially Hydrogenated Oil in Food Production and Preparation. *JAMA;* 308(2): 143-144."11** (Emphasis added).
- The CDC's correction confirms that the study is not properly classified as a CDC study. Although CDC failed to respond to GMA's follow-up Request for Reconsideration, in a response to Heritage Foundation's Request for Reconsideration that was received May 14, 2015, the CDC explains "To clarify that the numbers resented in the Winnable Battles report came from this paper [Dietz et al.], the report now indicates that the numbers are obtained from the paper by Dietz et al. "12 The letter concludes, "In response to your previous request, the *Winnable Battles Progress Report: 2010-2015* now provides the appropriate reference to the paper."

Public Comments

- …GMA.
- GMA is also concerned about the timeliness and accuracy of the data presented in the opinion
- article published by Dietz et al. It is apparent that the epidemiological data are based on consumer consumption data that are dated and therefore irrelevant to the current situation.
- The reason for the change in relevance is that *trans* fat added to food products has decreased by approximately 86% in recent years.
- In order to gain a more correct understanding of the basis for the risk calculations presented in CDC and FDA communications and to verify the aforementioned presumptions, GMA submitted Freedom of Information Act (FOIA) requests to CDC for the source data used to make the morbidity and mortality figures presented in CDC and FDA communications. So far CDC has failed to respond.
- GMA similarly submitted FOIA requests to FDA for the data underlying the Dietz study. So far, FDA has not provided the source data that has been requested. We will make another request for this information with the expectation that the FDA will either provide the information necessary to verify the correctness of the morbidity and mortality figures or acknowledge the information does not exist.
- These nonvalidated numbers are being used to justify far-ranging government actions that will greatly impact consumers and industry. It is important that any decision involving far-ranging regulatory actions that will greatly impact consumers and the industry be made based on accurate, up-todate exposure information with appropriate risk calculation methodologies.

Public Comments

- The Weston Firm…
- I write to address the possibility of allowing a "multi-year compliance period" for adherence to a rule declaring partially hydrogenated oils (PHOs) non-GRAS and outlawing their existence in our food supply. It would be a grave mistake, and could set dangerous precedent, to allow a lengthy compliance period and risk the health of our country's population. While some food manufacturers have begun to voluntarily reduce PHO usage, there remain many food products with dangerously high PHO and trans fat content. Moreover, these products are often cheaper or sold in discount stores, herefore, the population hardest hit by allowing PHOs to remain in the food supply is America's poor.
- As FDA has recognized, the science regarding PHOs is clear. PHOs, and the artificial trans fat they contain, cause heart disease, type-2 diabetes and multiple forms of cancer. They also affect the brain, increasing the risk of Alzheimer's Disease and accelerating cognitive decline in elderly Americans with diabetes, a demographic that is both growing rapidly and who require large public outlays to treat.
- The extreme dangers of PHOs are unmitigated by any positive trait. A determination that PHOs are no longer GRAS will reap major benefits. There will be no effect on food availability, as seen in the many jurisdictions that have long prohibited artificial trans fat in food, whether they have been banned completely like many parts of Europe, or partially as in California and New York City. There already exist many safe alternatives

Recent Events

- I recently visited the Dollar Tree located at 4200 Kearny Mesa Road in San Diego, California. I was shocked to find a large volume of products with dangerously high trans fat content. Below is a list of some of the worst offenders:

Product Name	Trans Fat Content per Serving
Betty Crocker Easy Bake Fudgy Chocolate Chip Cookie Artificially Flavored Mix	2.5g
Betty Crocker Easy Bake Sugar Cookie & Chocolate Cookie Mixes	3.5g
Fast Bites Breakfast 2-pk Mini Chicken & Biscuits	3.5g
Fast Bites Sausage and Cheese Biscuit	4.5g
Granny's Oven Strawberry Shortbread Premium Bite-Size Cookies	1.5g
La Torre Galleta Chavalin Marshmallow Cookies Covered with Chocolate Flavor and Puffy Rice	1g
Lakeview Farms French Onion Dip	1.5g
Lakeview Farms Unreal!!! Sour Creme	1.5g
Lil' Dutch Maid Iced Oatmeal Cookies	1g
Lil' Dutch Maid Coconut Macaroon Cookies	1.5g
Sunny Acres Mexican Shreds Pasteurized Process Topping	1.5g
Sunny Acres Swiss Slices Pasteurized Processed Sandwich Slices	1g

Recent Events

- …The Weston Firm.
- This visit demonstrates there remain many products available with dangerously high levels of trans fat. It also demonstrates that poor Americans, who can least afford the costs of trans fat consumption, are still buying and consuming large amounts of PHOs.
- As is apparent from the 2006 labeling regulation, waiting for voluntary removal is not effective in keeping trans fat out of our food supply. Nine years past the effective date, high trans fat foods remain on store shelves. For this reason, when the FDA affirms its tentative determination to declare PHOs non-GRAS, it should not delay in instituting requirements to remove trans fat.
- If the tentative determination is adopted, the FDA should require removal of all trans fats as soon as possible. Further, the FDA would set dangerous precedent if it affirmed that PHOs are indeed toxic and declared them non-GRAS, yet continued to allow their existence in our food supply.
- I ask that the FDA be mindful of the legal implications of allowing a substance declared non-GRAS to remain in the food supply. Such a decision could endanger future GRAS determinations and set unfavorable precedent if swift removal of a future food additive is required.

Recent Events

Nutrition Facts:
Serving Size: 5.30 OZ (148 g)
Servings Per Container: 24

Calories / Calories from Fat:	460 / 220
	% Daily Value **
Total Fat 25 g	38%
Saturated Fat 9 g	45%
Trans Fat 4 g	
Cholesterol 35 mg	12%
Sodium 1110 mg	46%
Total Carbohydrate 46 g	15%
Dietary Fiber 1 g	4%
Sugars 5 g	
Protein 12 g	
Vitamin A	2%
Vitamin C	0%
Calcium	15%
Iron	15%

** Percent Daily values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs.

Ingredient Statement: INGREDIENTS: BISCUIT: Enriched Bleached Wheat Flour (Wheat Flour, Niacin, Reduced Iron, Thiamine Mononitrate, Riboflavin, Folic Acid, Enzymes), Water, Partially Hydrogenated Soybean and Cottonseed Oils, Dry Whey, Calcium Sulfate, Buttermilk Solids, Contains 2% or Less of: Dextrose, Sodium Aluminum Phosphate, Salt, Sodium Bicarbonate, Calcium Propionate (Preservative), Methylcellulose, Adipic Acid, Soy Lecithin, Artificial Butter Flavor, Beta Carotene (Color).

FULLY COOKED PORK SAUSAGE PATTY: Pork, Seasoning (Salt, Whey Protein Concentrate, Spices, Corn Syrup Solids, Dextrose, Caramel Color, BHA, Propyl Gallate, Citric Acid).
CHEESE PRODUCT: Water, Palm Oil, Casein, Modified Food Starch, Dairy Product Solids, Maltodextrin, Sodium Citrate, Salt, Natural Flavor, Lactic Acid, Sorbic Acid (Preservative), Artificial Color, Soy Lecithin (Non-Sticking Agent). CONTAINS: WHEAT, MILK, SOY

Recent Events

Amount per serving

Calories	110	
Calories from Fat	110	
*% Daily Value**		
Total Fat	12g	18%
Saturated Fat	3.5g	16%
Trans Fat	0g	
Polyunsaturated Fat	6g	
Monounsaturated Fat	2.5g	
Cholesterol	0mg	0%
Sodium	0mg	0%
Total Carbohydrates	0g	0%
Protein	0g	%

Ingredients

SOYBEAN OIL, FULLY HYDROGENATED PALM OIL, PALM OIL, MONO AND DIGLYCERIDES, TBHQ AND CITRIC ACID (ANTIOXIDANTS).

Recent Events

Nutrition Facts

Serv Size 2 tbsp.(37g)

Calories 200
Fat Cal 110

*Percent Daily Values (DV) are based on a 2,000 calorie diet.

Amount/Serving	%DV*	Amount/Serving	%DV*
Total Fat 12g	**18%**	**Total Carb** 23g	**8%**
Sat. Fat 4g	**20%**	Fiber 1g	**5%**
Trans Fat 0g		Sugar 21g	
Cholest. <5mg	**0%**	**Protein** 2g	
Sodium 15mg	**1%**		

Vitamin A 0% • Vitamin C 0% • Calcium 4% • Iron 4%

INGREDIENTS: SUGAR, PALM OIL, HAZELNUTS, COCOA, SKIM MILK, WHEY (MILK), LECITHIN AS EMULSIFIER (SOY), VANILLIN: AN ARTIFICIAL FLAVOR.

Association of Dietary, Circulating, and Supplement Fatty Acids With Coronary Risk

A Systematic Review and Meta-analysis

- Rajiv Chowdhury, MD, PhD
- Samantha Warnakula, Mphil
- Setor Kunutsor, MD, MSt
- Francesca Crowe, PhD
- Heather A. Ward, PhD
- Laura Johnson, PhD
- Oscar H. Franco, MD, PhD
- Adam S. Butterworth, PhD
- Nita G. Forouhi, RCP, PhD
- Simon G. Thompson, FMedSci
- Kay-Tee Khaw, FMedSci
- Dariush Mozaffarian, MD, DrPH
- John Danesh, FRCP
- Emanuele Di ngelantonio, MD, PhD

- **Background:** Guidelines advocate changes in fatty acid consumption to promote cardiovascular health.
- **Purpose:** To summarize evidence about associations between fatty acids and coronary disease.
- **Data Sources:** MEDLINE, Science Citation Index, and Cochrane Central Register of Controlled Trials through July 2013.

- **Data Synthesis:** There were 32 observational studies (512,420 participants) of fatty acids from dietary intake; 17 observational studies (25,721 participants) of fatty acid biomarkers; and 27 randomized, controlled trials (105,085 participants) of fatty acid supplementation.

- In observational studies, relative risks for coronary disease were 1.03 (95% CI, 0.98 to 1.07) for saturated, 1.00 (CI, 0.91 to 1.10) for monounsaturated, 0.87 (CI, 0.78 to 0.97) for long-chain n-3 polyunsaturated, 0.98 (CI, 0.90 to 1.06) for n-6 polyunsaturated, and 1.16 (CI, 1.06 to 1.27) for *trans* fatty acids when the top and bottom thirds of baseline dietary fatty acid intake were compared.

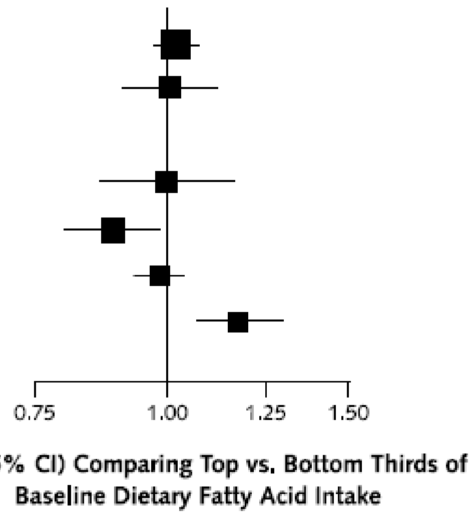
Table. **Summary of Data Included in Current Review***

Data Resource	Studies, *n*†	Participants, *n*	Coronary Events, *n*
Prospective cohort studies of dietary fatty acid intake			
All studies	32	512 420	15 945
Dietary questionnaire‡	21	463 038	11 157
Diet record§	11	49 382	4788
Prospective cohort studies of fatty acid biomarkers			
All studies	19	32 307	7182
Circulating fatty acid composition	17	25 721	5519
Adipose tissue fatty acid composition	2	6586	1663
RCTs of fatty acid supplementation	27	105 085‖	6229¶

RCT = randomized, controlled trial.
* Details of all individual studies are included in **Supplement 1** (available at www.annals.org).
† Five studies reported on both circulating and diet-based exposures, and 1 study reported on both circulating fatty acids and effect of fatty acid supplementation.
‡ Includes food-frequency and diet history questionnaires.
§ Includes open-ended instruments, such as 24-h recall and food diaries.
‖ Includes 52 588 and 52 497 total participants in intervention and control groups, respectively.
¶ Includes 3017 and 3212 coronary events in intervention and control groups, respectively.

Figure 1. RRs for coronary outcomes in prospective cohort studies of dietary fatty acid intake.

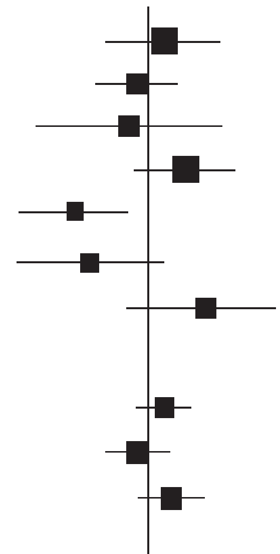
Fatty Acid Intake	Studies, *n*	Participants, *n*	Events, *n*	RR (95% CI)*
Total saturated fatty acids	20	276 763	10 155	1.03 (0.98–1.07)
Total monounsaturated fatty acids	9	144 219	6031	1.00 (0.91–1.10)
Total ω-3 fatty acids				
α-Linolenic	7	157 258	7431	0.99 (0.86–1.14)
Total long-chain ω-3	16	422 786	9089	0.87 (0.78–0.97)
Total ω-6 fatty acids	8	206 376	8155	0.98 (0.90–1.06)
Total trans fatty acids	5	155 270	4662	1.16 (1.06–1.27)



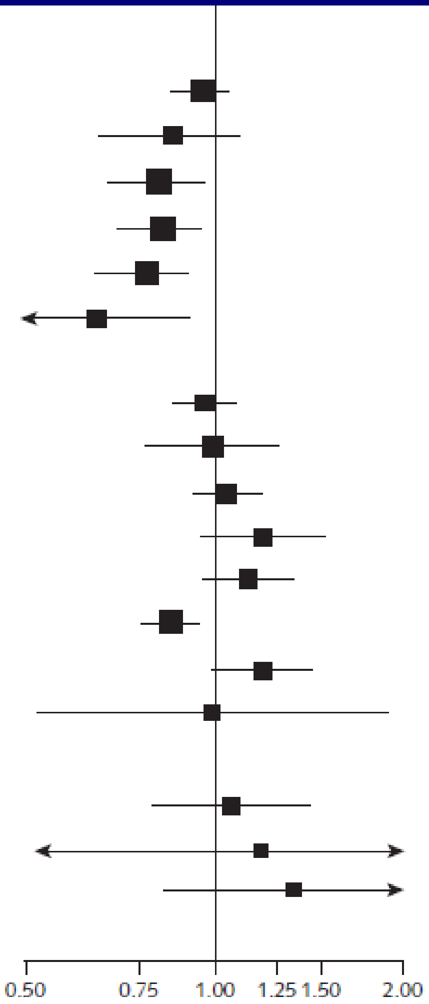
Size of the data marker is proportional to the inverse of the variance of the RR. RR = relative risk.
* Pooled estimate based on random-effects meta-analysis. Corresponding forest plots, I^2 estimates, and pooled RRs based on fixed-effects meta-analysis are provided in **Supplement 1**, available at www.annals.org.

Figure 2. RRs for coronary outcomes in prospective cohort studies of circulating fatty acid composition.

Circulating Blood Fatty Acid Composition	Studies, *n*	Participants, *n*	Events, *n*	RR (95% CI)*
Total saturated fatty acids	8	15 590	3758	1.06 (0.86–1.30)
14:0, Myristic	5	10 598	2932	0.96 (0.83–1.12)
15:0, Pentadecanoic	4	5490	2283	0.94 (0.67–1.32)
16:0, Palmitic	10	25 554	4318	1.15 (0.96–1.37)
17:0, Margaric	4	5490	2283	0.77 (0.63–0.93)
15:0, Pentadecanoic + 17:0, Margaric	4	5490	2283	0.81 (0.62–1.06)
18:0, Stearic	8	22 266	3654	1.23 (0.93–1.61)
Total monounsaturated fatty acids	6	14 356	3236	1.06 (0.97–1.17)
16:1n-7, Palmitoleic	9	17 927	4127	0.96 (0.86–1.08)
18:1cis-9, Oleic	9	22 664	3687	1.09 (0.97–1.23)



Total ϖ-3 polyunsaturated fatty acids				
18:3n-3, α-Linolenic	8	14 945	3426	0.93 (0.83–1.03)
Total long-chain ϖ-3	4	10 558	2753	0.84 (0.63–1.11)
20:5n-3, Eicosapentaenoic	13	23 065	4624	0.78 (0.65–0.94)
22:6n-3, Docosahexaenoic	13	23 065	4624	0.79 (0.67–0.93)
20:5n-3, Eicosapentaenoic + 22:6n-3, Docosahexaenoic	13	20 809	4073	0.75 (0.62–0.89)
22:5n-3, Docosapentaenoic (clupanodonic)	4	7155	2565	0.64 (0.47–0.89)
Total ϖ-6 polyunsaturated fatty acids	2	7432	1877	0.94 (0.84–1.06)
18:2n-6, Linoleic	10	23 022	3866	0.99 (0.77–1.28)
18:3n-6, γ-Linolenic	4	8285	2259	1.03 (0.90–1.17)
20:2n-6, Eicosadienoic	2	4029	1689	1.18 (0.93–1.50)
20:3n-6, Dihomo-γ-linolenic	6	14 189	3214	1.11 (0.93–1.33)
20:4n-6, Arachidonic	10	22 948	3739	0.83 (0.74–0.92)
22:4n-6, Docosatetraenoic	2	4029	1689	1.20 (0.99–1.45)
22:5n-6, Docosapentaenoic (osbond)	2	4029	1689	0.97 (0.50–1.88)
Total trans fatty acids	4	7661	2389	1.05 (0.76–1.44)
18:1, Trans-oleic	2	921	380	1.20 (0.39–3.73)
18:2, Trans-linoleic	2	921	380	1.36 (0.83–2.22)

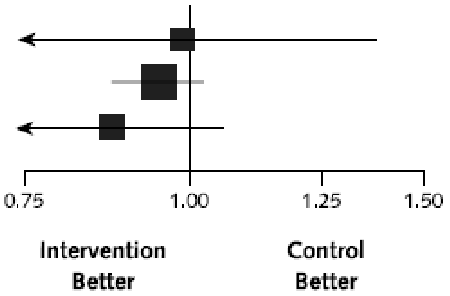


RR (95% CI) Comparing Top vs. Bottom Thirds

Size of the data marker is proportional to the inverse of the variance of the RR. RR = relative risk.
* Pooled estimate based on random-effects meta-analysis. Corresponding forest plots, I^2 estimates, and pooled RRs based on fixed-effects meta-analysis are provided in **Supplement 1**, available at www.annals.org.

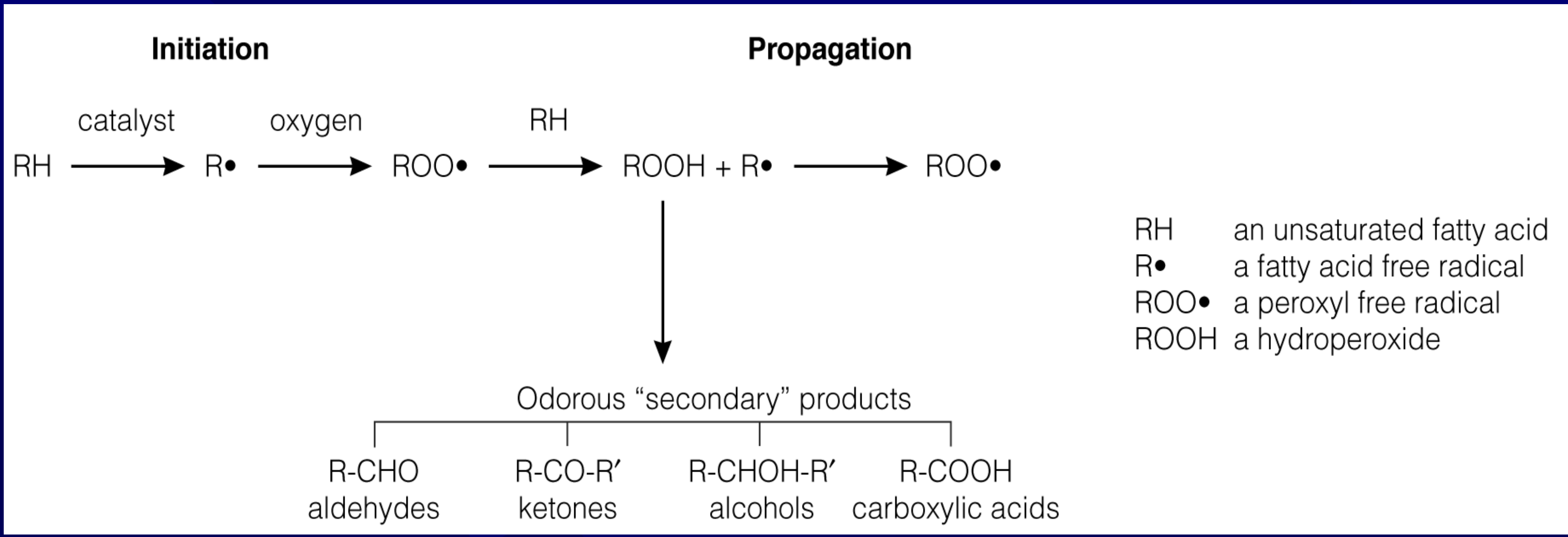
Figure 3. **Effect of fatty acid supplementation on risk for coronary event, derived from available randomized, controlled trials.**

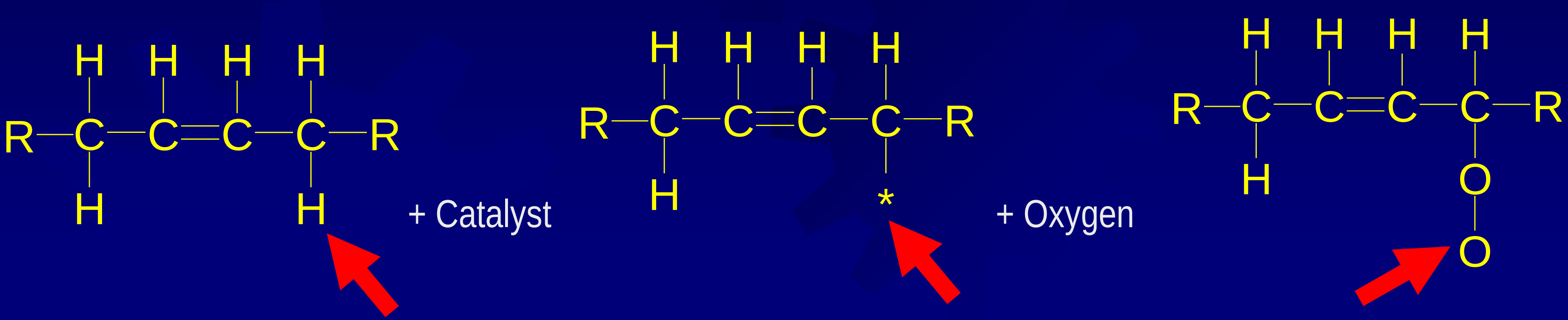
Fatty Acid Supplement	Studies, *n*	Events/Participants, *n/N*		RR (95% CI)*
		Intervention Group	Control Group	
α-Linolenic acid	4	199/9444	220/9422	0.97 (0.69–1.36)
Long-chain ω-3 fatty acid	17	2426/38 303	2548/38 277	0.94 (0.86–1.03)
ω-6 fatty acid†	8	459/7245	515/7231	0.86 (0.69–1.07)



Size of the data marker is proportional to the inverse of the variance of the RR. RR = relative risk.
* Pooled estimate based on random-effects meta-analysis. Corresponding forest plots, I^2 estimates, and pooled RRs based on fixed-effects meta-analysis are provided in **Supplement 1**, available at www.annals.org.
† Includes studies with ω-6–specific intervention and mixed polyunsaturate interventions with linoleic acid as the primary fatty acid.

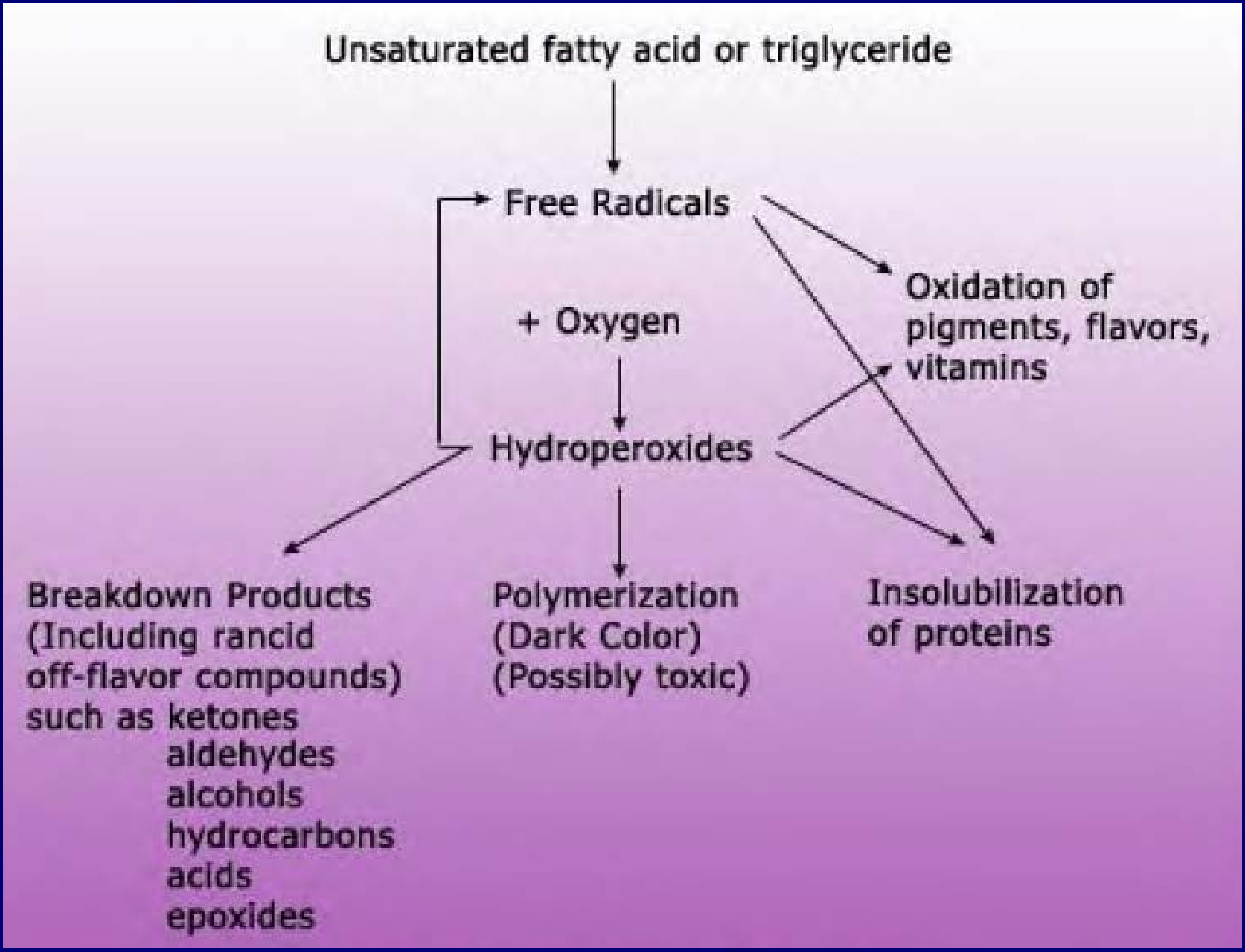
Simplified scheme of lipoxidation



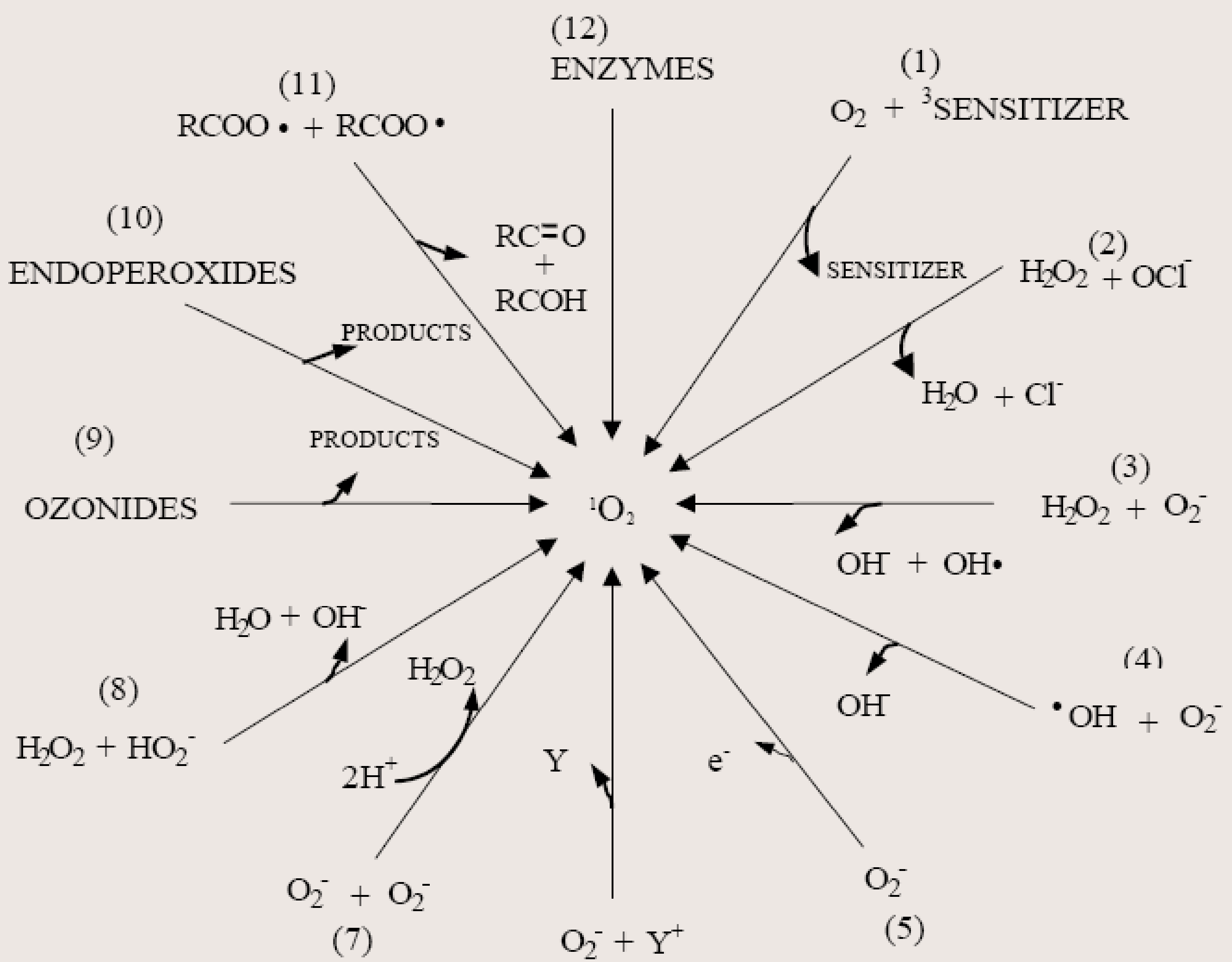


Primary Drivers

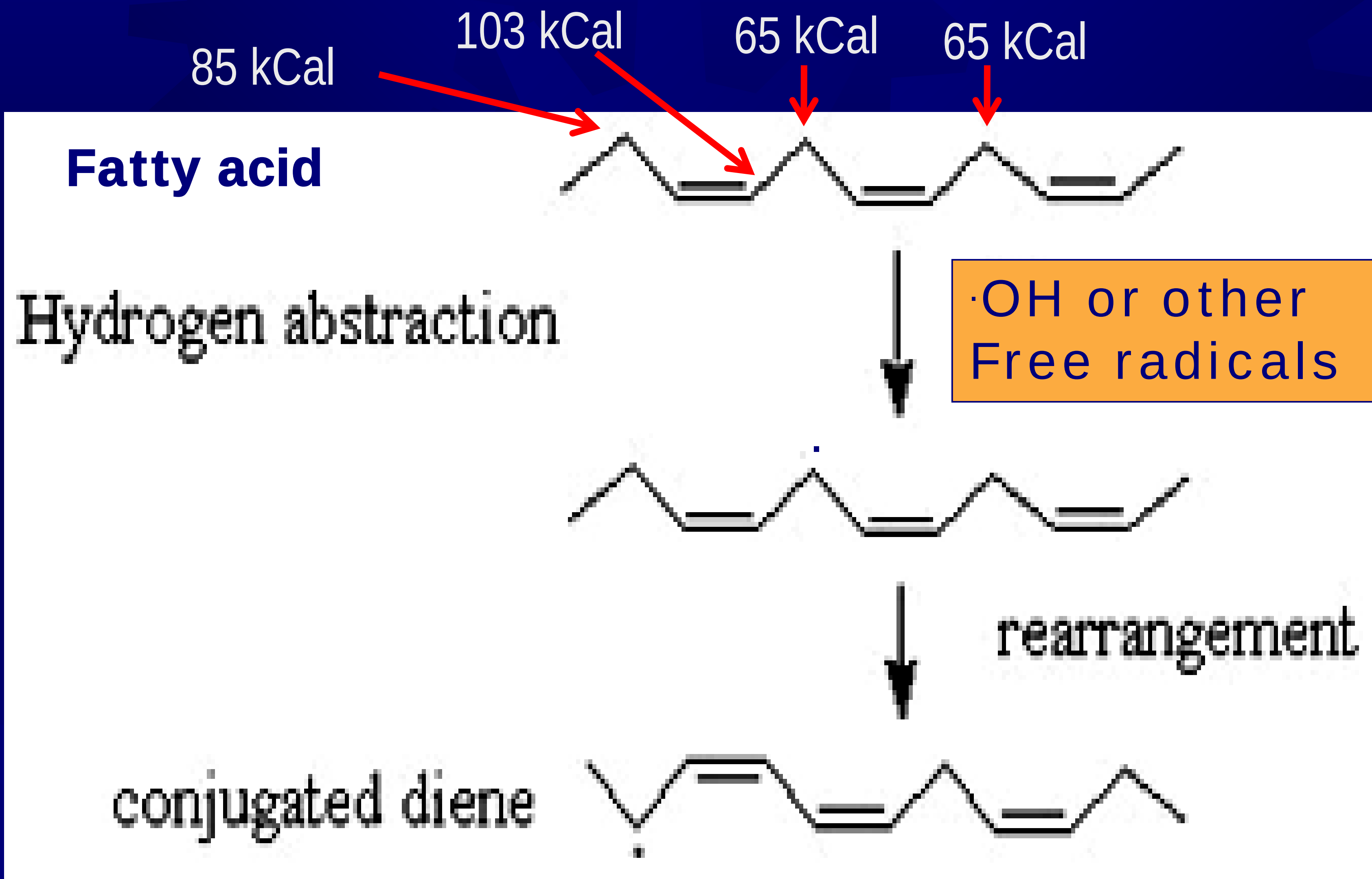
- Temperature-basic rxn kinetics
- Water Activity
  - Both high and low Aw
  - At low Aw, peroxides decompose faster and metal ions are better catalysts in a dry environment
- Metal Ions-catalysts
- Light-energy source
- Singlet Oxygen- ROS, highly electrophilic
  - Reacts 1,500 times faster at C=C than ground state O_2
- Enzymes ie. Lipoxygenase (LOX)


Unsaturated fatty acid or triglyceride
Free Radicals
+ Oxygen
Hydroperoxides
Oxidation of
pigments, flavors,
vitamins
Breakdown Products
(Including rancid
off-flavor compounds)
such as ketones
aldehydes
alcohols
hydrocarbons
acids
epoxides
Polymerization
(Dark Color)
(Possibly toxic)
Insolubilization
of proteins

Production of $^1O_2$ by Photochemical, Chemical, and Biological Systems



Bond Strength



Propagation Reactions

Initiation

Ground state oxygen

Peroxyl radical

Hydroperoxide

New Radical

$$R\cdot + {}^3O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

$$ROOH \longrightarrow RO\cdot + \cdot OH$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot$$

Hydroperoxide decomposition

Alkoxyl radical

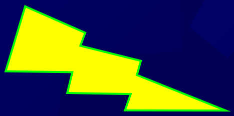
Hydroxyl radical

Start all over again…

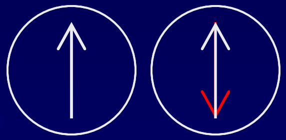
Autoxidation

Mechanism of Photooxidation

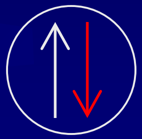
Chlorophyll



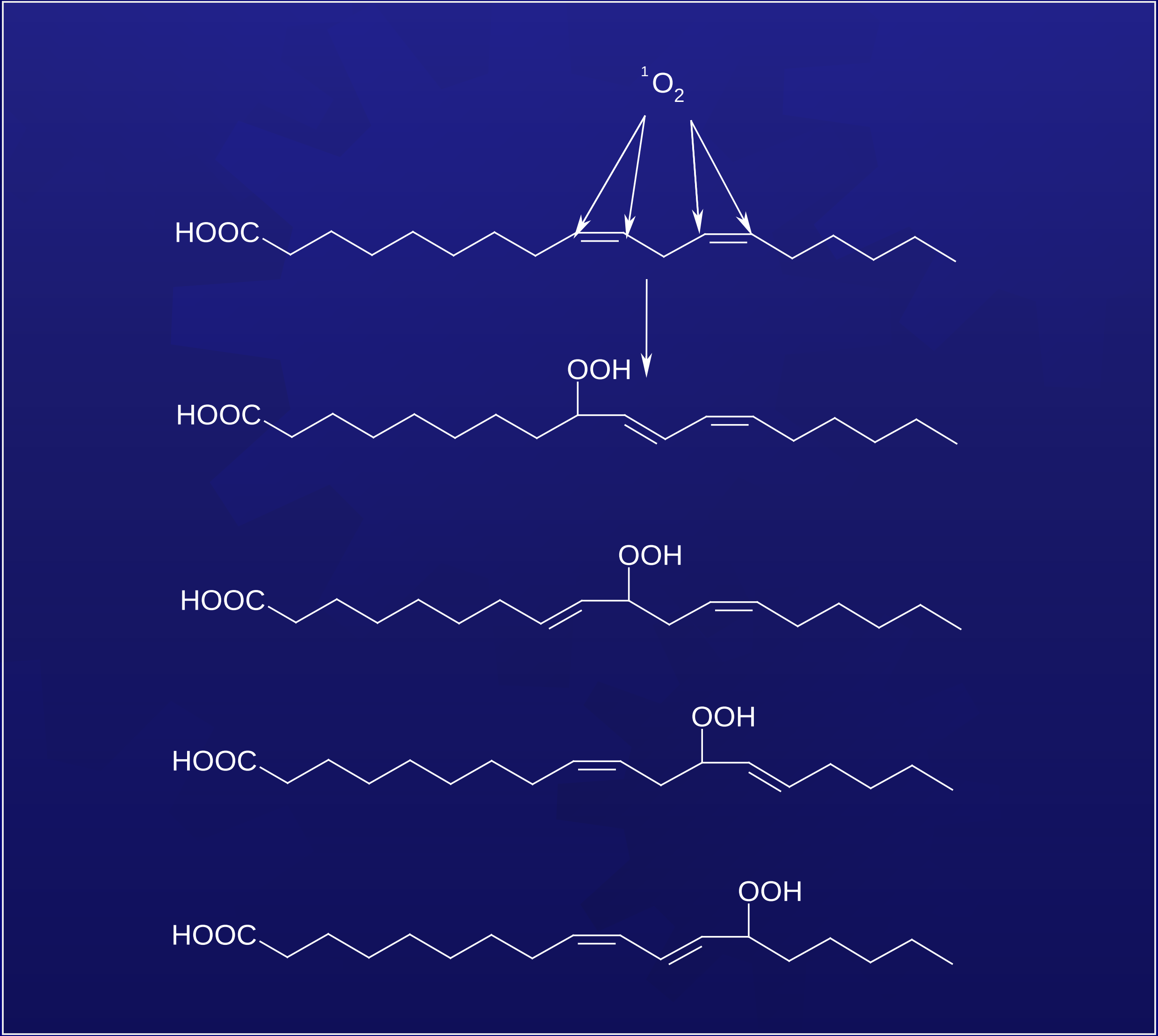
$^{3}O_2$



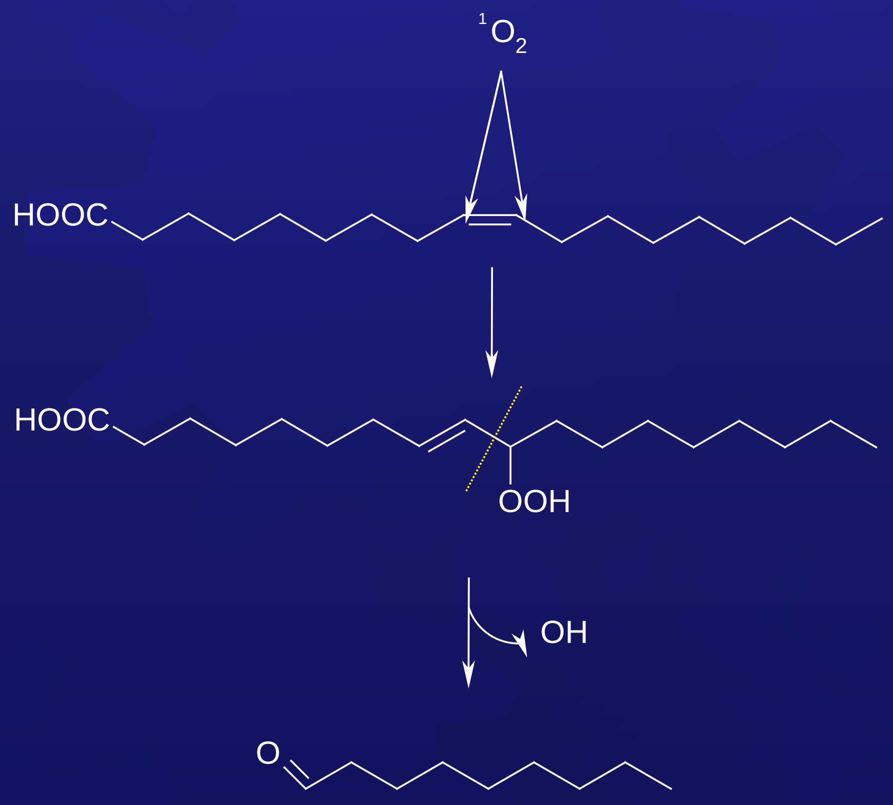
or



Singlet Oxygen Oxidation

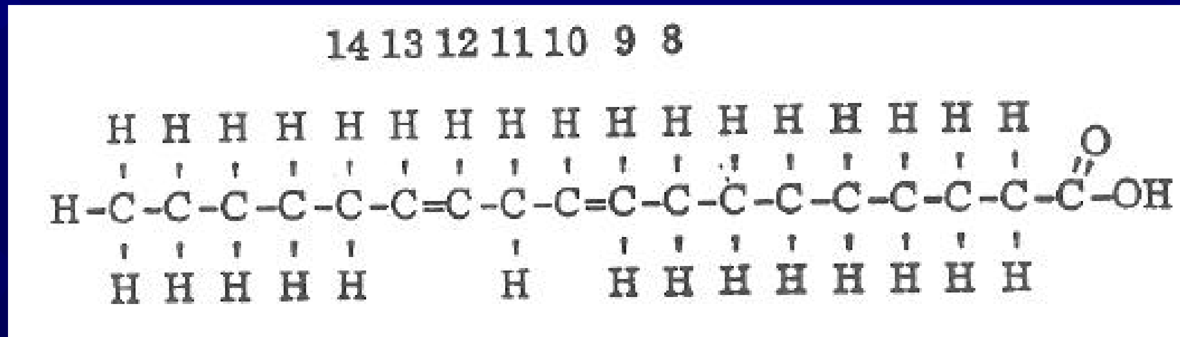


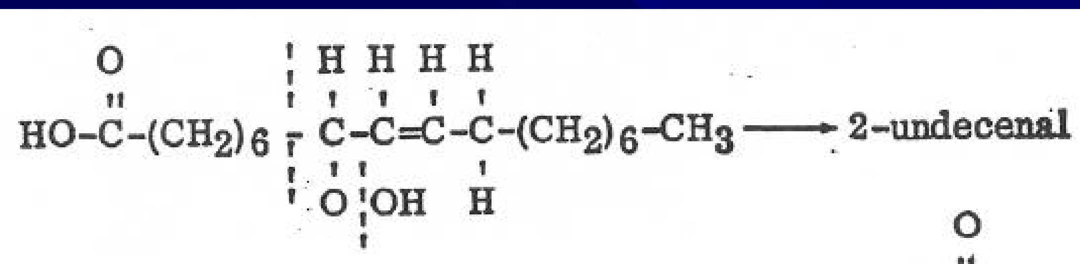
Singlet Oxygen Oxidation

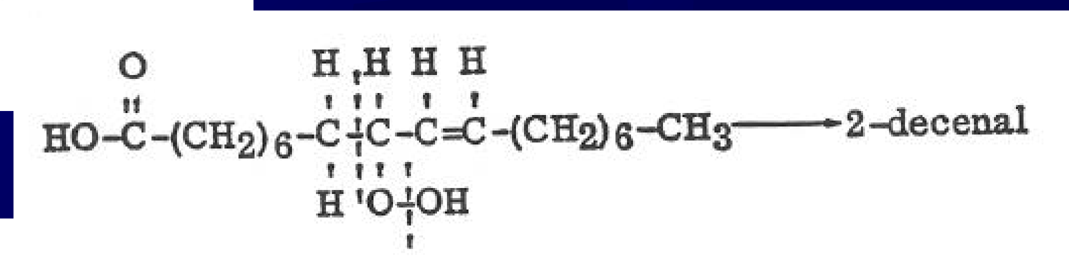


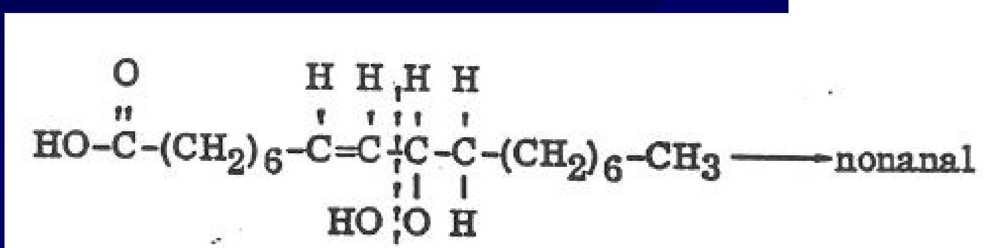
Nonanal

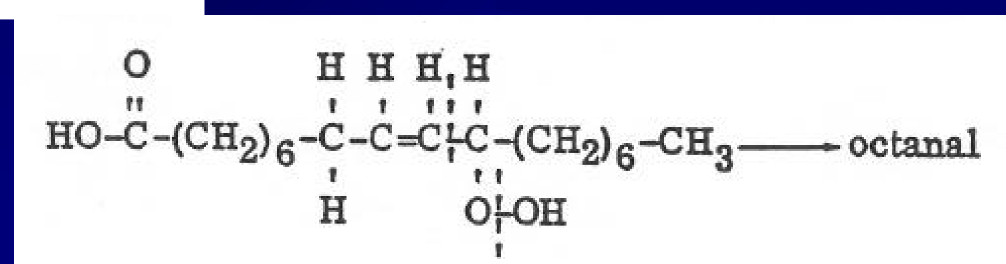
Secondary Products: Aldehydes











Oxidation Rates of Fatty Acids

- Double bonds: number, position, geometry
  - Conjugated db are less reactive then non-conjugated
- Free or esterified
  - Free fatty acids oxidize faster than TAG’s
  - sn-1 and sn-3 oxidize faster then sn-2 positions
- Saturation
  - Saturated fats are generally stable at room temp
- Heating
  - Accelerates everything, creates free fatty acids, increased conjugation, fried foods accelerate

Relative Oxidation Rates

- How fast is lipid oxidation?

Fatty Acid	Relative Rate
Steric acid (18:0)	1
Oleic acid (18:1 n9)	100
Linoleic acid (18:2 n6)	1,200
Linolenic acid (18:3 n3)	2,500

Polar Paradox

Critical Reviews in Food Science and Nutrition
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http://www.tandfonline.com/loi/bfsn20

Role of Physical Structures in Bulk Oils on Lipid Oxidation

Wilailuk Chaiyasit [a] , Ryan J. Elias [a] , D. Julian McClements [a] & Eric A. Decker [a]
[a] Department of Food Science , University of Massachusetts , Amherst, MA, 01003
Published online: 16 Mar 2007.

Surfactants (Emulsifiers)

- Surfactants are molecules that lower the surface tension
  - Part of molecule interacts favorably with water
    - Polar or charged (hydrophilic)
  - Part of molecule interacts unfavorably with water
    - Hydrophobic

→ **Amphiphilic**

Lipid Surfactants

- Fatty Acids

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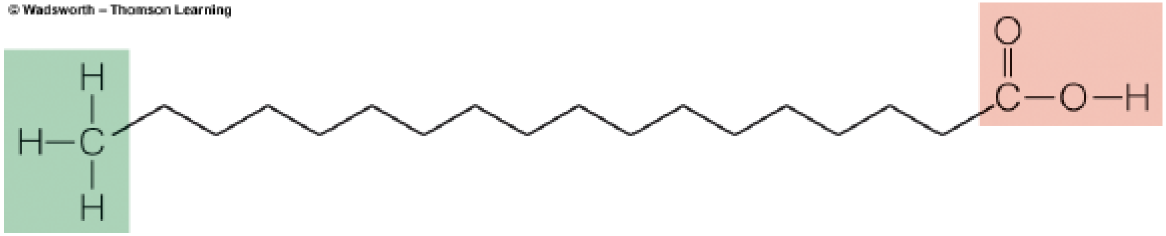
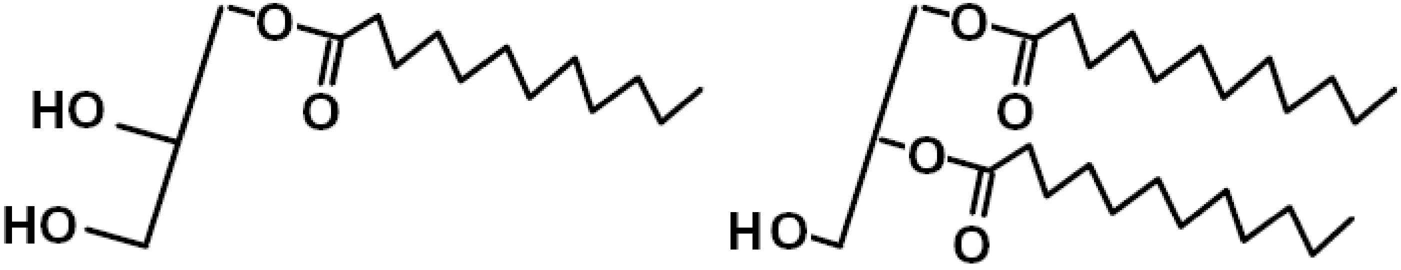
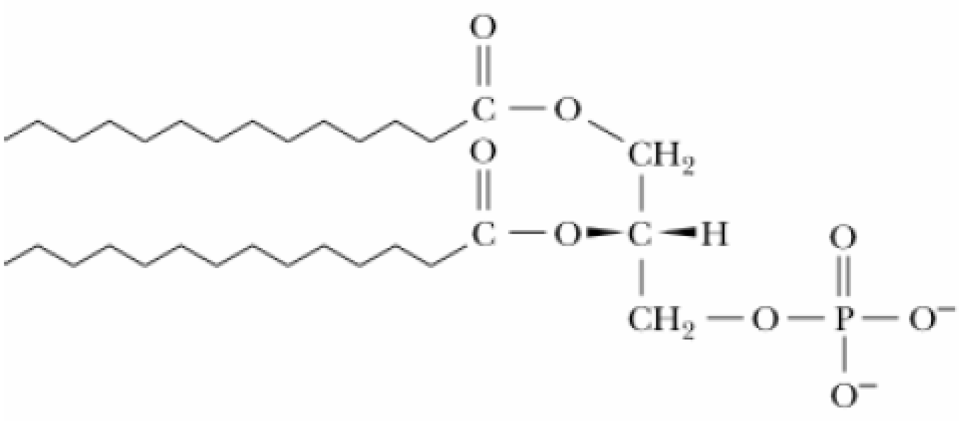


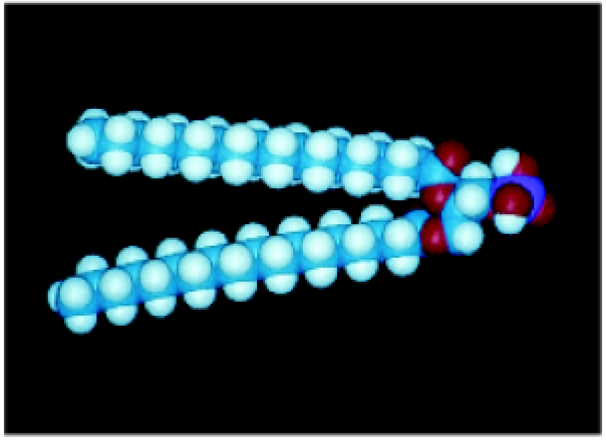
- Monoglycerides and Diglycerides



Lipid Surfactants

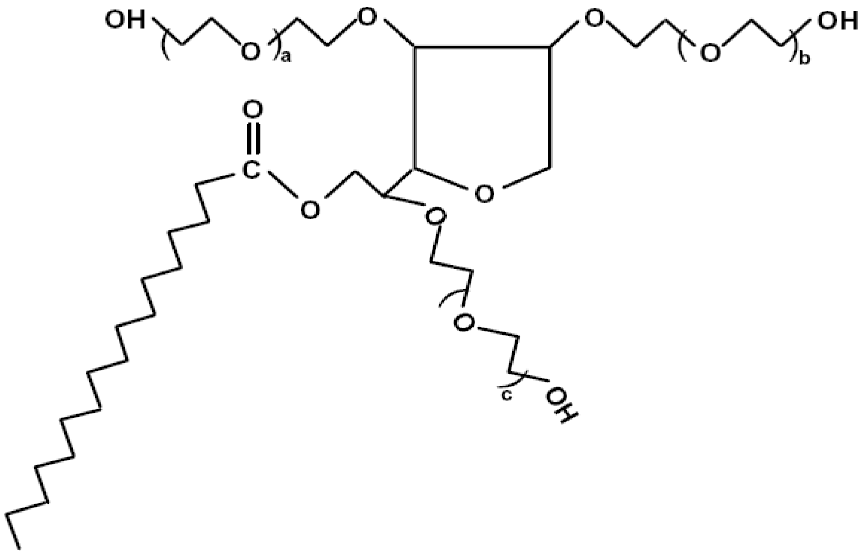
- Phospholipids



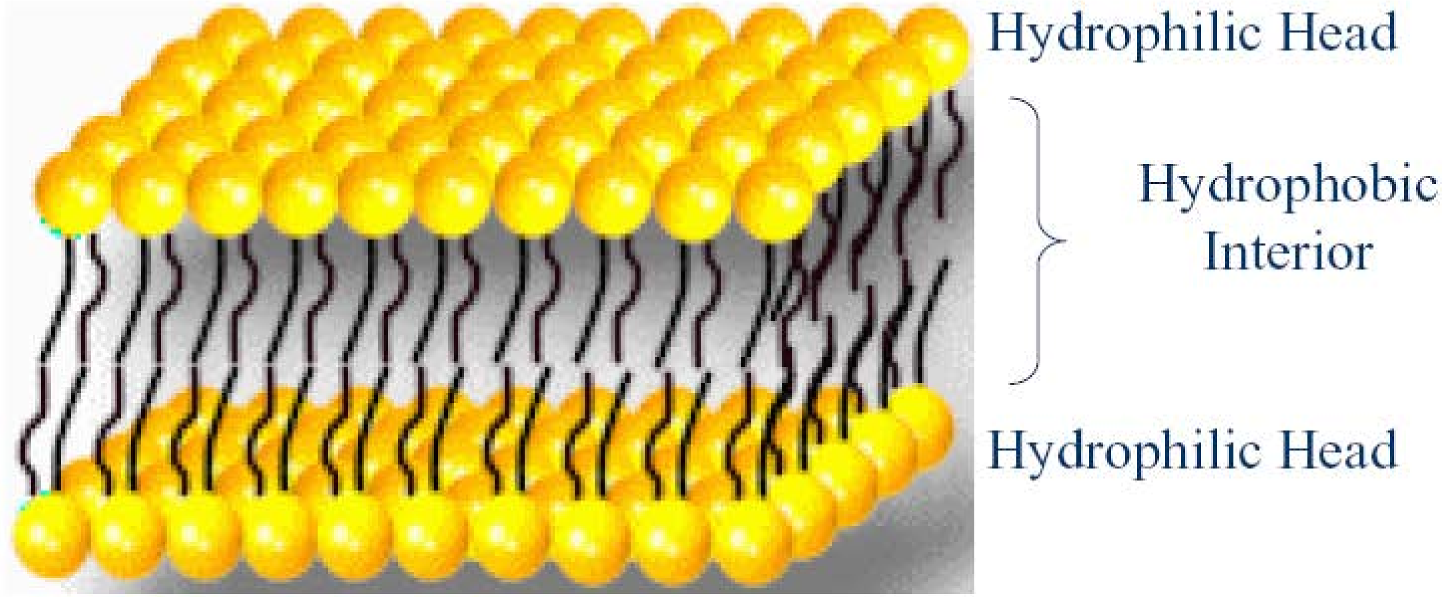


Synthetic Emulsifiers

- Tweens



- Mediates interactions between hydrophobic and hydrophilic phases



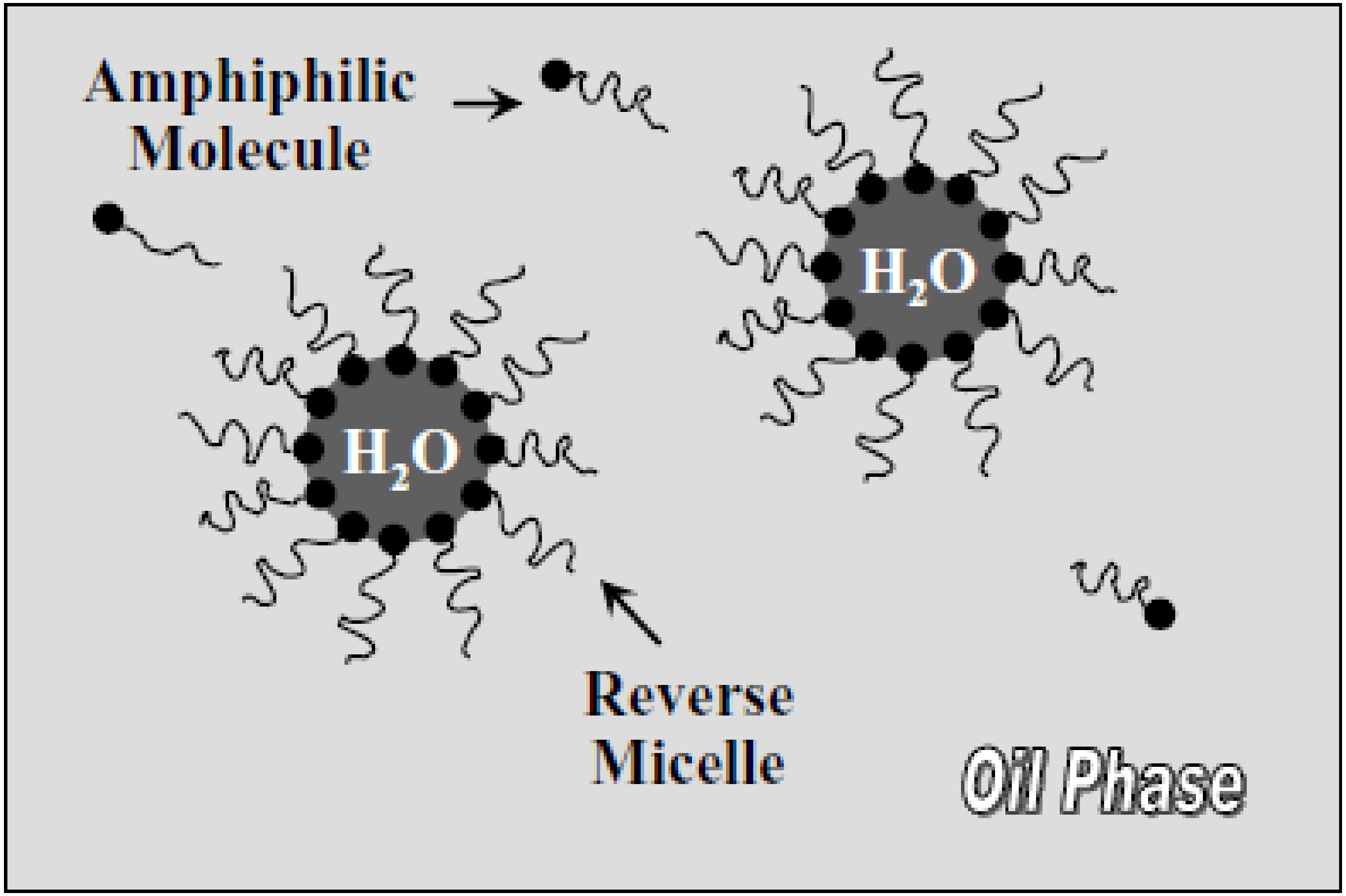
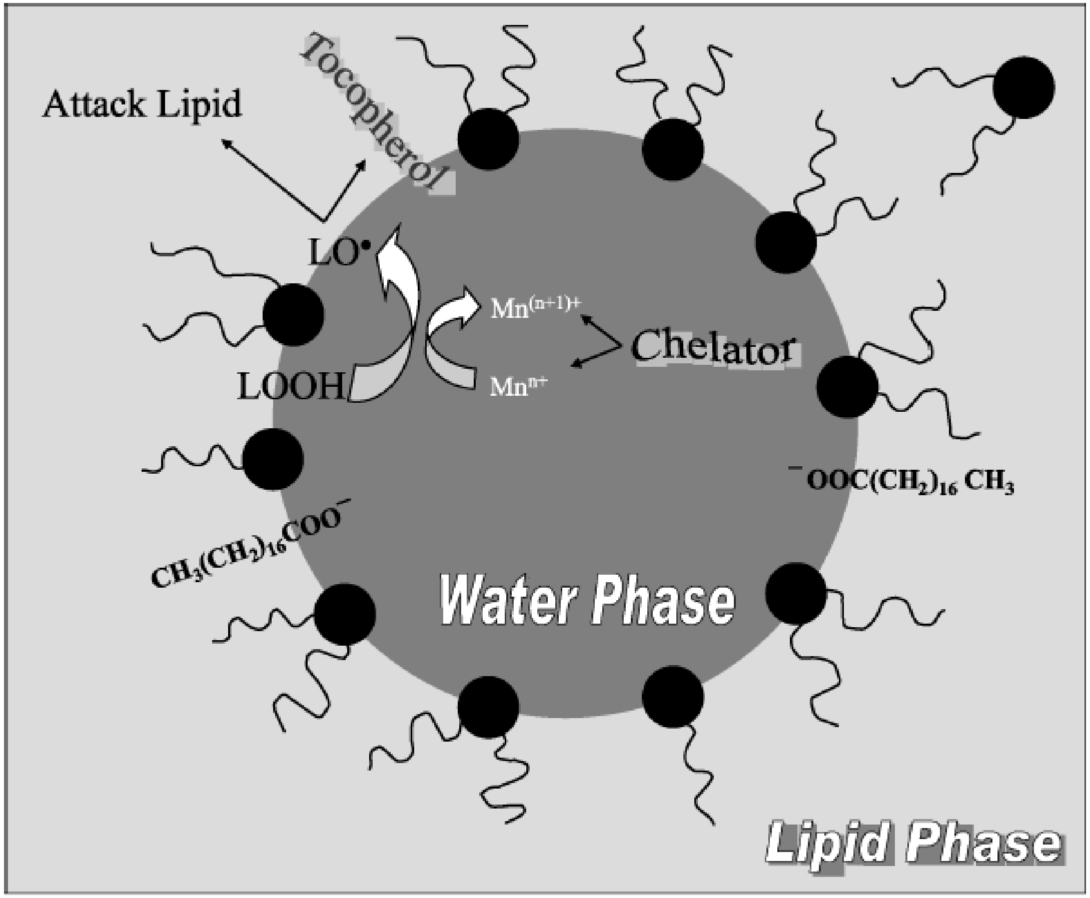


Figure 5 Schematic showing water core in a reverse micelle



LOOH = Lipid hydroperoxide
LO• = Alkoxyl radical
Mn^{n+}, $Mn^{(n+1)+}$ = Transition metals in reduced and oxidized states

 = Amphiphilic molecule e.g. phospholipid

$CH3(CH2)_{16}COO^{-}$ = Fatty acid e.g. stearic acid

Figure 6 Proposed mechanisms of lipid oxidation in bulk oil containing reverse micelles

Interfacial Phenomenon

- Low surface to volume ratio
  - Bulk oils
- High surface to volume ratio
  - Emulsions
- Location:
  - Oil-air
  - Water-oil

Source:
Frankel E, Huang SW, Kanner J, German JB. 1994. Interfactial Phenomena in the Evaluation of Antioxidants: Bulk Oils vs. Emulsions. J. Agric. Food Chem. 42:1054-1059.

The Polar Paradox Theory

- In bulk oils, with water and phospholipids…
- Polar antioxidants are more effective in non-polar or less polar systems
- Non-polar antioxidants are more effective in polar systems
- Due to an "interfacial phenomenon"?

Source:
Porter WL. 1993. Paradoxical Behavior of Antioxidants in Food and Biological Systems. Toxicol. Ind. Health. 9(1):93-122.

*Had to request from library. Email Christina if you would like a copy of the paper.

Interfacial Phenomenon

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  - Bulk oils
- High surface to volume ratio
  - Emulsions
- Location:
  - Oil-air
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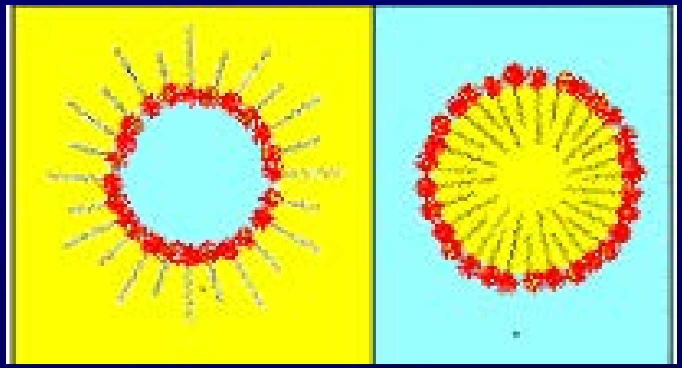
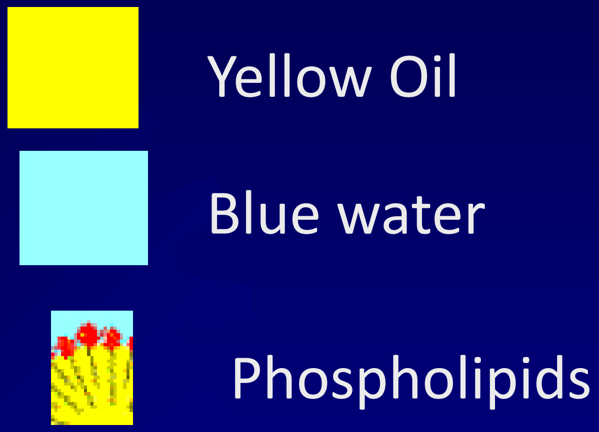
Source:
Frankel E, Huang SW, Kanner J, German JB. 1994. Interfactial Phenomena in the Evaluation of Antioxidants: Bulk Oils vs. Emulsions. J. Agric. Food Chem. 42:1054-1059.

Polar Antioxidants

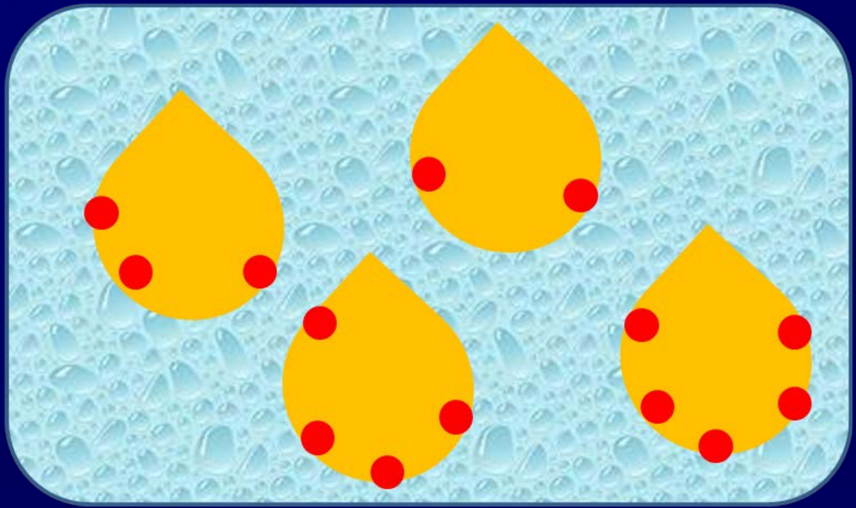
- Most effective in nonpolar or less polar environment
  - Bulk oils
- Located at the oil-air interface or in reverse micelles
  - High amount of oxidants present here





Non-polar Antioxidants

- Most effective in polar environment
  - Oil-in-water emulsions
- Located at the water-oil interface
  - Dissolved in oil droplets of the emulsion
  - Allows access to oxidizing agents located in the water phase
    - Peroxides
    - Oxidizing metals



Crude vs. Partially Refined Açai Oil

- Crude Açai Oil (CAO)
  - Solvent removed
  - 1200-2000 ppm TSP
  - 0.87% Phospholipid

- Partially Refined Açai Oil (RAO)
  - Diatomaceous Earth is rendered
  - Oil and water is then separated
  - 300-400 ppm TSP
  - 0.34% Phospholipid

Experimental Design (cont'd)

- 5 types of oil
  - High Polyphenolic Açai Oil
  - Low Polyphenolic Açai Oil
  - Olive Oil
  - Soybean Oil
  - Canola Oil

Açai Oil Composition

- Fatty acid composition
  - 18:1 – 63%
  - 16:0 – 21%
  - 18:2 – 12%
  - 18:0 – 2%
- Phospholipid
- High Polyphenolic content

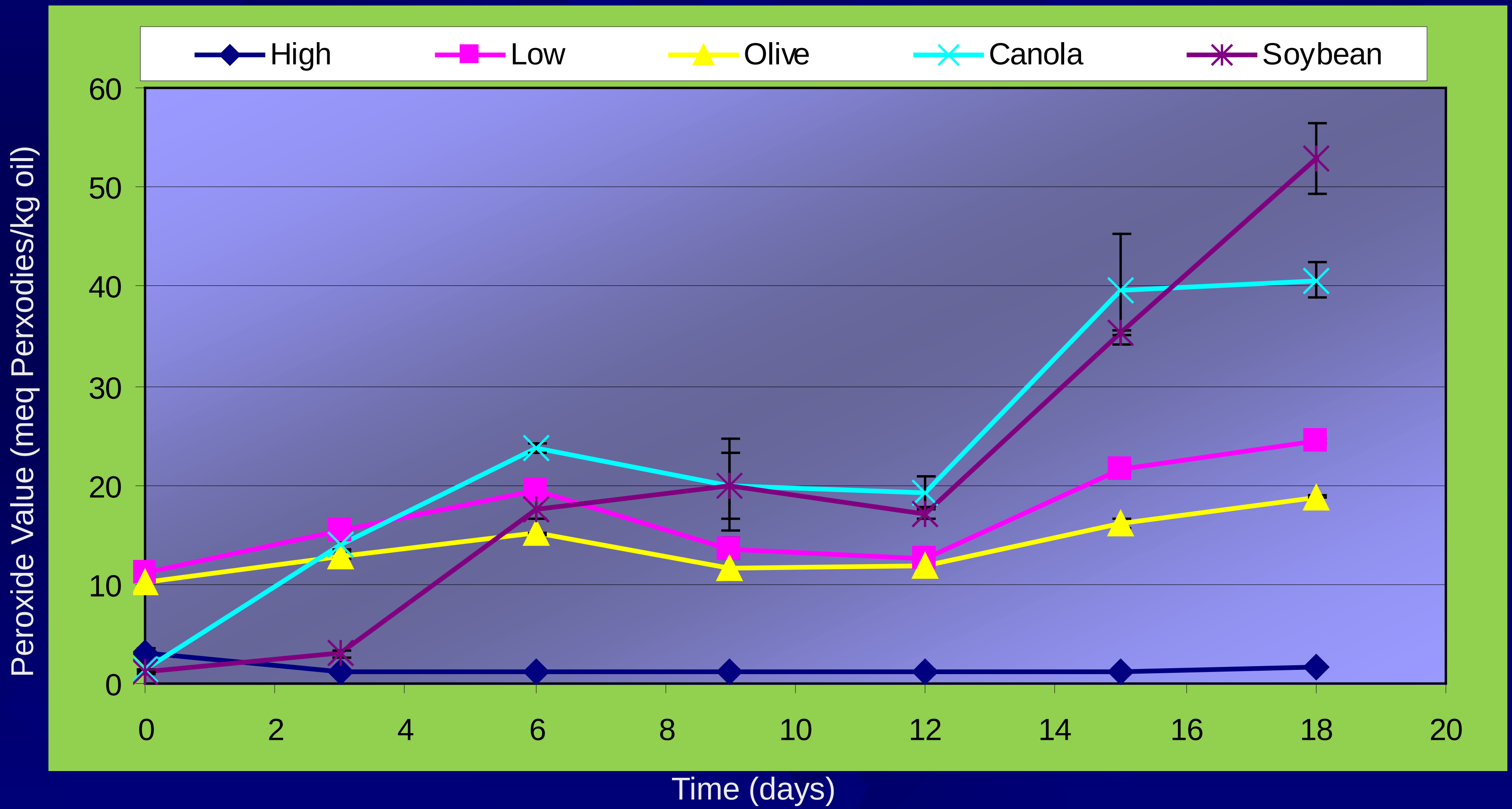
Correlation Between Accelerated and Real-Time Storage for Bulk Oil

Untreated Canola Oil*

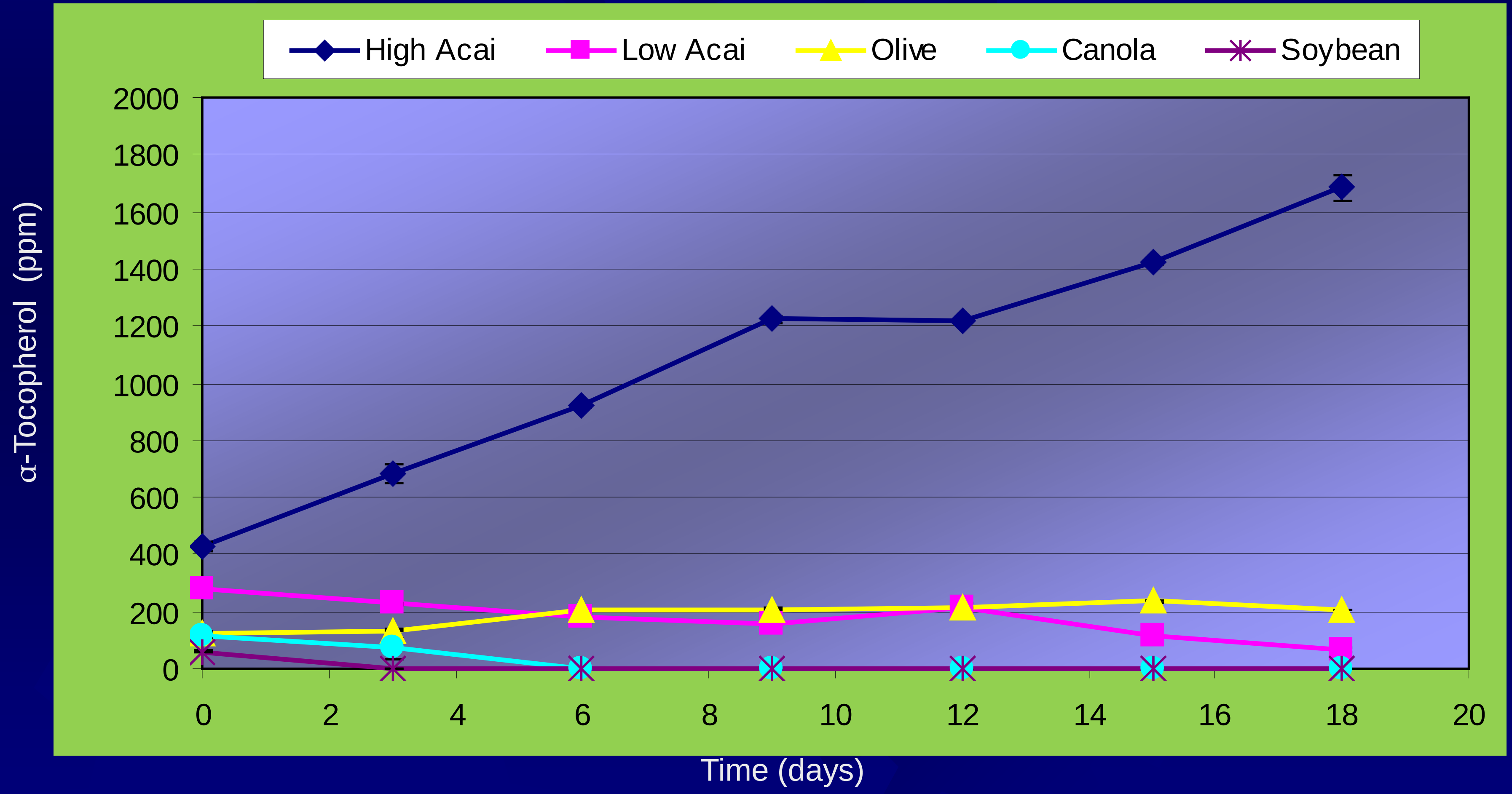
Days at 63°C	Days at Room Temp.
0	0
3	26.6
6	53.3
9	79.9
12	106.6
15	133.2
18	159.8

*Data extrapolated from Hawrysh et al. 1988 and Hawrysh et al. 1989

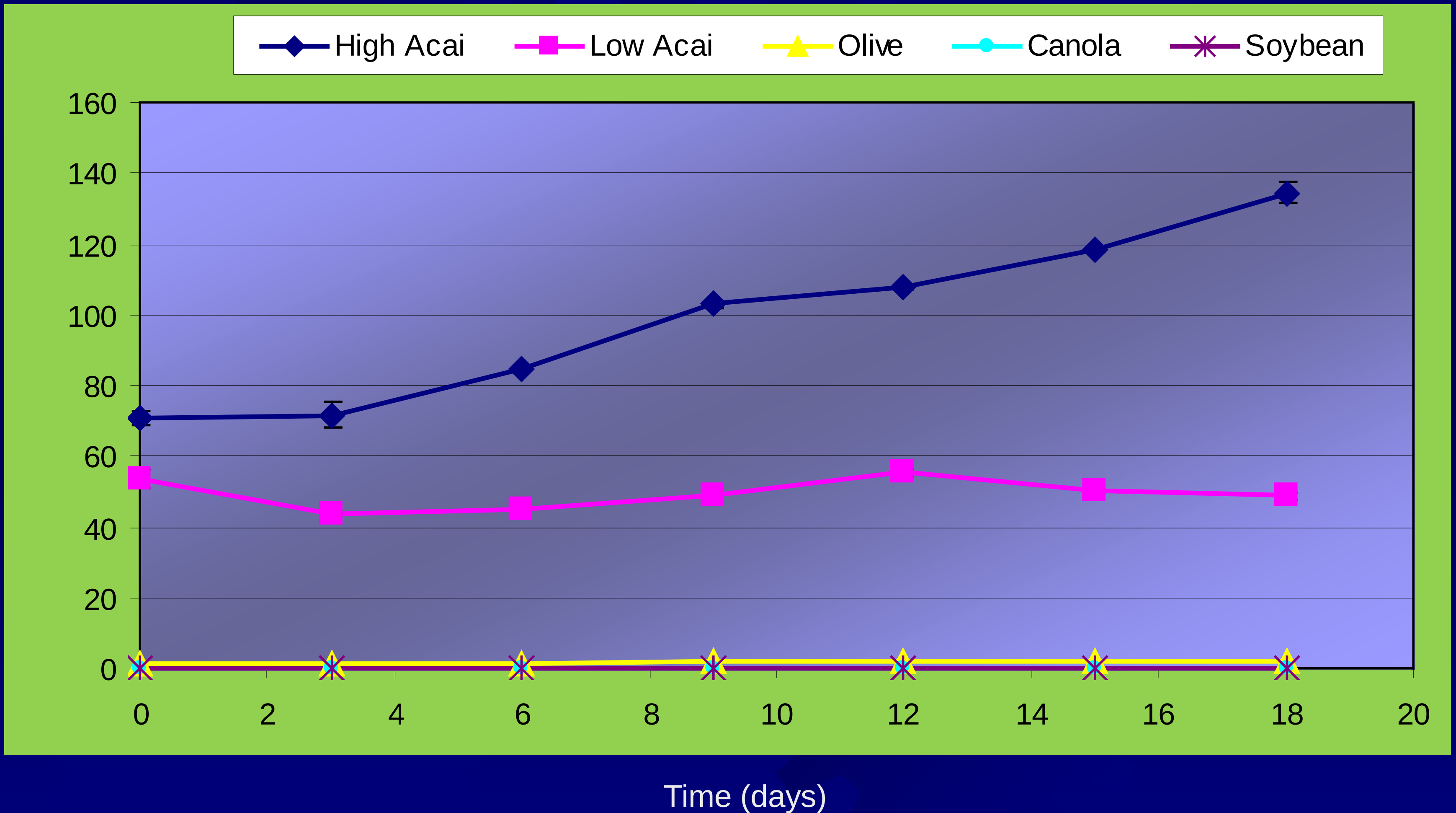
Primary Oxidation Products



Changes in Tocopherol



Changes in β-Carotene



Free Radicals

What are free radicals?

- Any molecular species capable of *independent* existence, which contains one or more unpaired valence electrons not contributing to intramolecular bonding….is a free radical.

The most frequent radicals are oxygen-derived free radicals, also known as reactive oxygen species (ROS):

Superoxide ($O_2\cdot-$)

Peroxyl ($ROO^{\cdot}$)

Alkoxyl ($RO^{\cdot}$)

Hydroxyl ($HO^{\cdot}$)

Nitric oxide ($NO^{\cdot}$)

Other ROS are <u>non-radicals</u> such as singlet oxygen ($^1O_2$), hydrogen peroxide (H_2O_2), and hypochlorous acid ($HClO$).

Where do they come from?

- Free radicals are produced by oxidation/reduction reactions in which there is a transfer of only one electron at a time, or when a covalent bond is *broken* and one electron from each pair remains with each atom.

1) Normal metabolism, ie. the electron transport system in the mitochondria and normally functioning enzymes

2) Environmental factors such as pollution, radiation, smoke, and toxins can produce biologically-derived free radicals.

3) In foods, initiation events are prevalent as well as ROS and non-ROS species

How damaging are free radicals?

- ROS may be very damaging, since they can attack:
  - Lipids in cell membranes
  - Proteins in tissues or enzymes
  - Carbohydrates
  - DNA
  - Vitamins
  - Pigments
  - Natural/Added antioxidants
- Oxidative damage can accumulate with human age and food ageing as well (ie. shelf life).

Our Body vs. Our Food

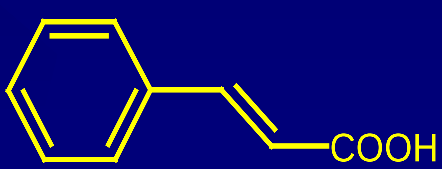
- Biological radicals
- Food-based radicals

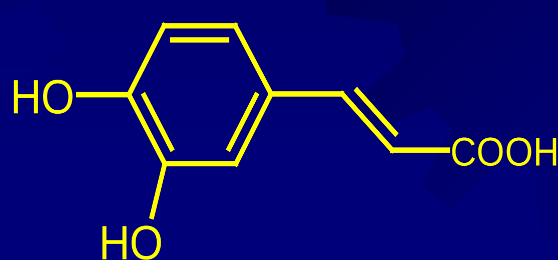
- Where do these 2 areas cross?

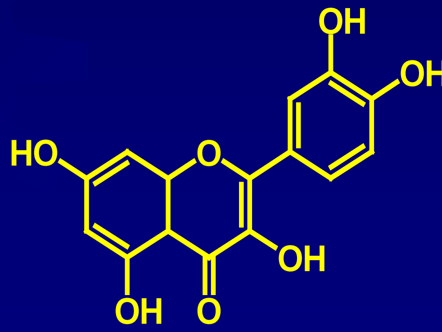
Antioxidants in Food Systems

What Makes a Good Antioxidant?

- **Polyphenolics**- Radical scavengers
  - Number of hydroxy groups (-OH)
  - Location of hydroxy groups (on benzene ring)
  - Presence of a 2-3 double bond (flavylium ring)
  - 4-oxo function (flavylium ring)
- Synergistic/antagonistic reactions with other antioxidant compounds

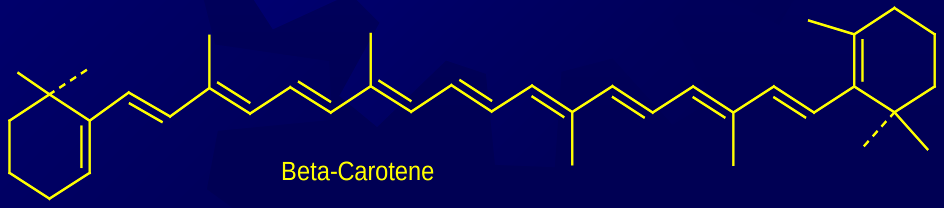






What Makes a Good Antioxidant?

- **Carotenoids**
  - The number of conjugated double bonds (9^+ is best)
  - Substitutions on ß-ionone group (on the end)



- Radical scavengers

  R^* + CAR => R- + CAR^{*+}

- Chain breakers

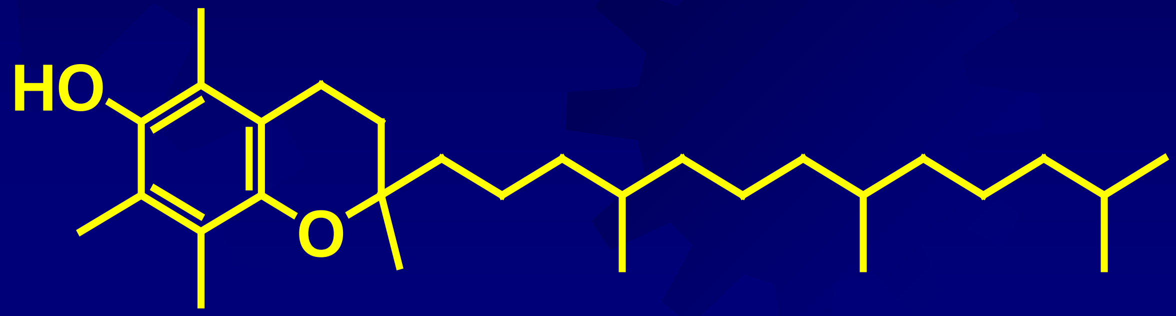
  ROO*+ CAR => $ROO\text{-}CAR^*$

  $ROO\text{-}CAR^*$ + ROO^* => ROO-CAR-ROO

- Singlet oxygen quenchers
  - ${}^1O_2^*$ + ${}^1CAR$ => ${}^3O_2$ + ${}^3CAR^*$

Tocopherol

- Alpha-tocopherol = Vitamin E
  - beta and gamma forms also
- Synergist with carotenoids and selenium and is regenerated by vitamin C
- Efficiency determined by the bond dissociation energy of the phenolic -OH bond
- The heterocyclic chromanol ring is optimized for resonance stabilization of an unpaired electron.



HAT and SET Reactions

- **Hydrogen Atom Transfer (HAT) vs. Single Electron Transfer (SET)**
- Antioxidants can work in one of two ways (HAT or SET).
- End result is the same for both, differing in kinetics and side rxns.
- HAT and SET rxns may occur in parallel
  - Determined by antioxidant structure and properties
  - Solubility and partition coefficient
  - System solvent, system pH

HAT

- *HAT-based methods* measure the classical ability of an antioxidant to quench free radicals by hydrogen donation (AH = any H donor)

$$X^{\bullet} + AH \rightarrow XH + A^{\bullet}$$

HAT assays

- ORAC
  - Oxygen Radical Absorbance Capacity
  - Measures inhibition of peroxyl radical induced oxidations in chain breaking activity by H atom transfer
- TRAP
  - Total Radical-Trapping Antioxidant Parameter
  - Measures the ability to interfere with peroxyl radicals or stable free radicals

SET

- *SET-based methods* detect the ability of a potential antioxidant to transfer one electron to reduce any compound, including metals, carbonyls, and radicals.
- Also based on deprotonation, so pH dependent

$$X^{\bullet} + AH \rightarrow X^{-} + AH^{\bullet +}$$

$$M(III) + AH \rightarrow AH^{+} + M(II)$$

SET assays

- FRAP
  - Ferric Reducing Antioxidant Power
  - The reaction measures the reduction capacity of a ferric compound to a color end-product
- CUPRAC
  - Copper Reduction Assay
  - Variant of FRAP assay using Cu instead of Fe
- Folin-Ciocalteu assay
  - Reduction of oxidized iron and molybdenum

HAT vs SET

HAT

- Selectivity in HAT rxs are determined by the bond dissociation energy of the H-donating group in the antioxidant
- Antioxidant reactivity or capacity measurements are therefore based on competition kinetics.
- Reactions are solvent and pH independent and are very fast
- Common reducing agents (Vitamin C) are an *interference*

SET

- Usually slow and can require long times to reach completion
- Antioxidant reactivity is based on a percent decrease, rather than kinetics
- Very sensitive to ascorbic acid and other reducing agents.
- Trace amounts of metal ions will interfere, and cause over-estimation and inconsistent results.

Antioxidants and Radicals

- Four sources of antioxidants:
  - Enzymes
    - Superoxide dismutase, glutathione peroxidase, and catalase
  - Large molecules
    - albumin, ferritin, other proteins
  - Small molecules
    - ascorbic acid, glutathione, uric acid, tocopherol, carotenoids, phenols
  - Hormones
    - estrogen, angiotensin, melatonin
- Multiple free radical and oxidant sources
  - O_2, O_2·-, $HO^{\cdot}$, $NO^{\cdot}$, ONOO-, HOCl, $RO(O)^{\cdot}$

Method Selections for Antioxidants

- Controversy exists over standard methods for antioxidant determination
- Historical use and peer-review acceptance is critical
- Use my multiple labs to highlight strength, weakness, and effectivness
- New methods take time to adopt and accept
- An “ideal” method:
  - Measures chemistry actually occurring in potential application
  - Utilizes a biologically relevant radical source
  - Simple to run
  - Uses a defined endpoint and chemical mechanism
  - Instrumentation is readily available
  - Good within-run and between-day reproducibility
  - Adaptable for both hydrophilic and lipophilic antioxidants
  - Adaptable for multiple radical sources
  - Adaptable for high-through-put analysis
  - Understanding of the range of use and recognition of interfering agents

HAT assays

- ORAC
  - Oxygen Radical Absorbance Capacity
  - Measures inhibition of peroxyl radical induced oxidations in chain breaking activity by H atom transfer
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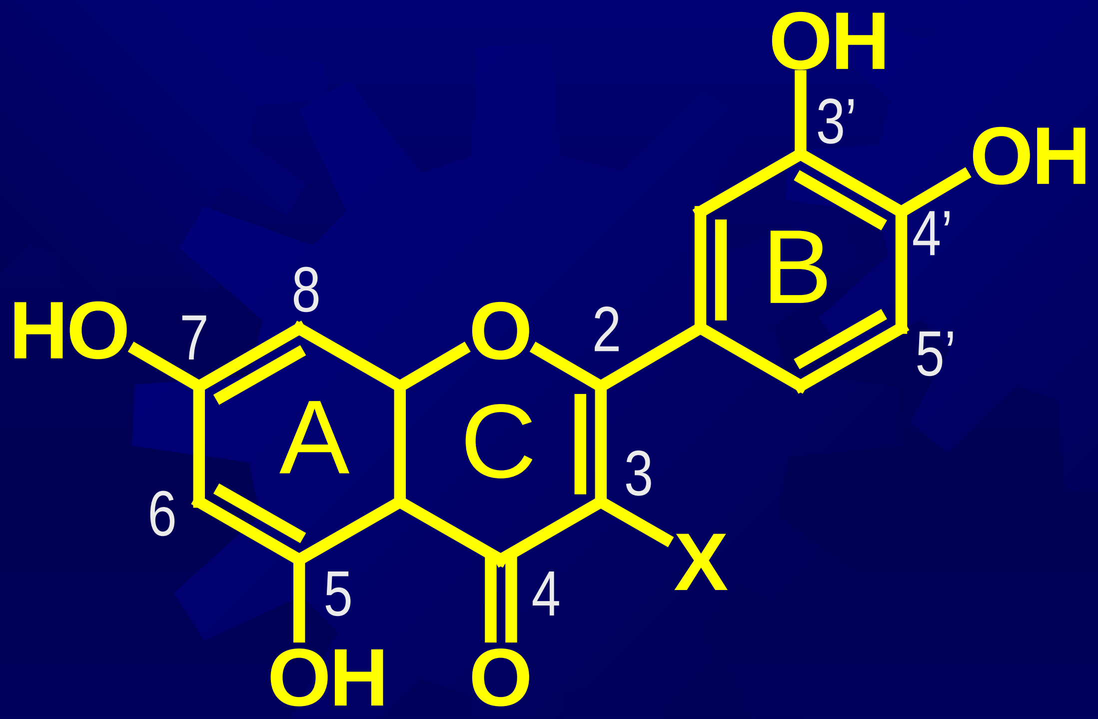
Structure-Based AOX

Polyphenolics

Structure of flavonoids

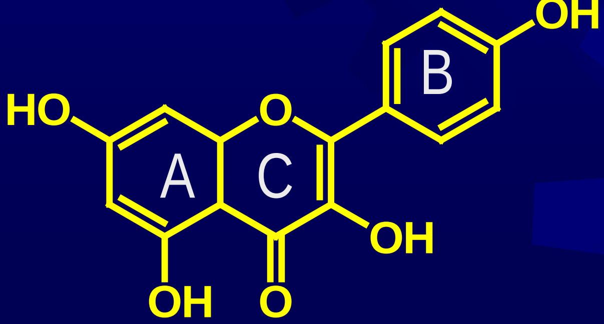


Flavonols: X=OH

Flavones: X=H

Flavanones: No 2-3 db

B-Ring Substitutions

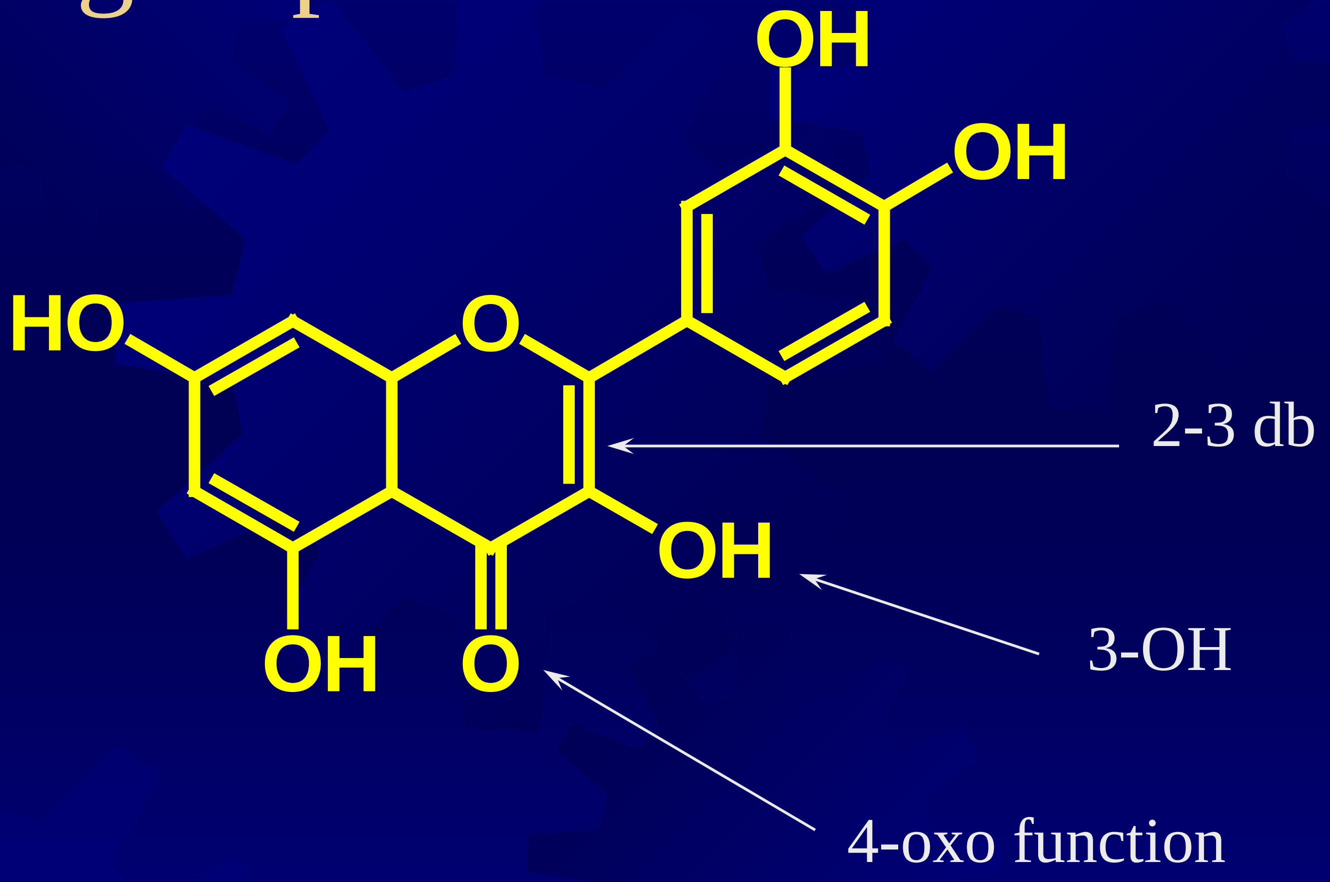


Kaempferol

Quercetin

Myricetin

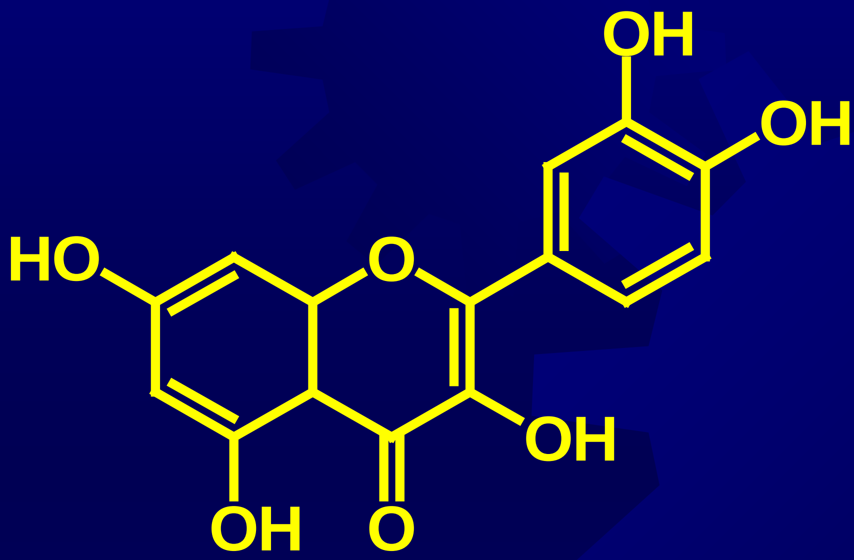
Quercetin
4 –OH groups



Catechin
4 –OH groups

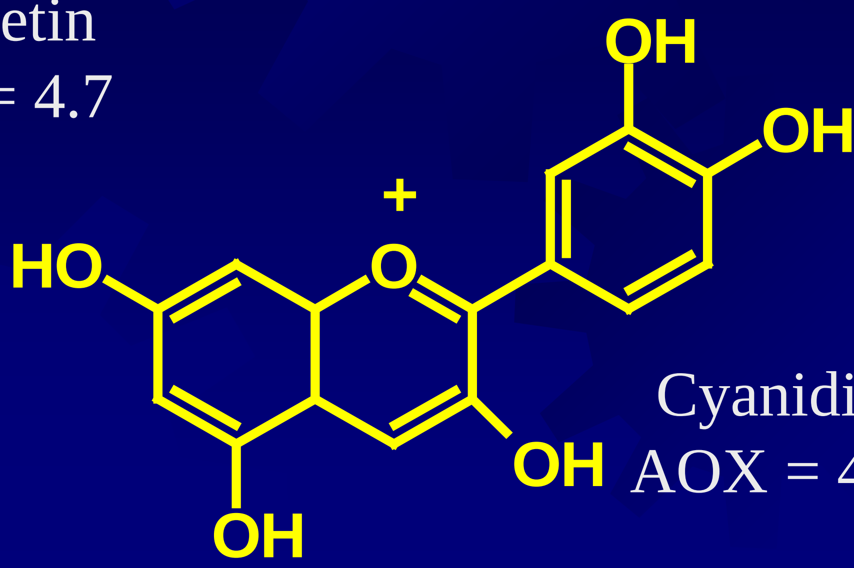
Cyanidin
4 –OH groups

Structurally Similar Compounds



Quercetin
AOX = 4.7

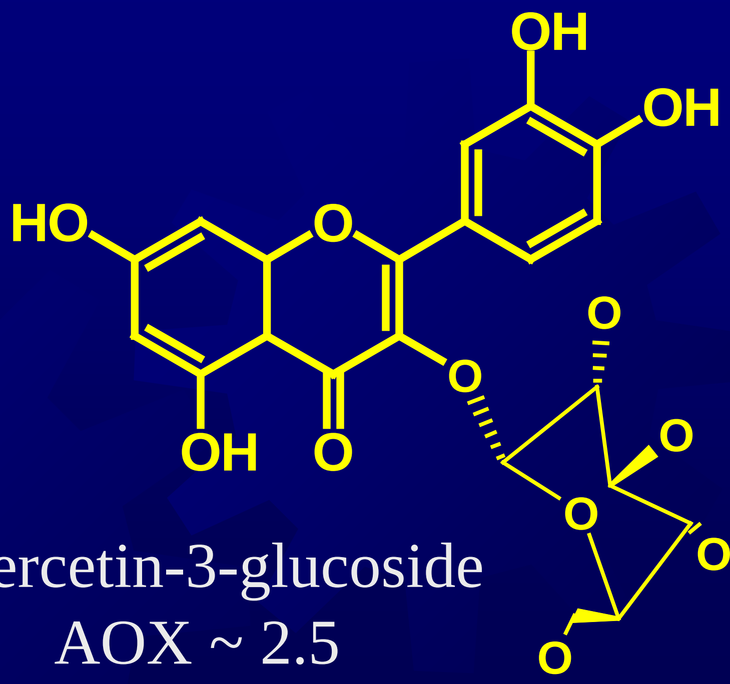
Catechin
AOX = 2.4



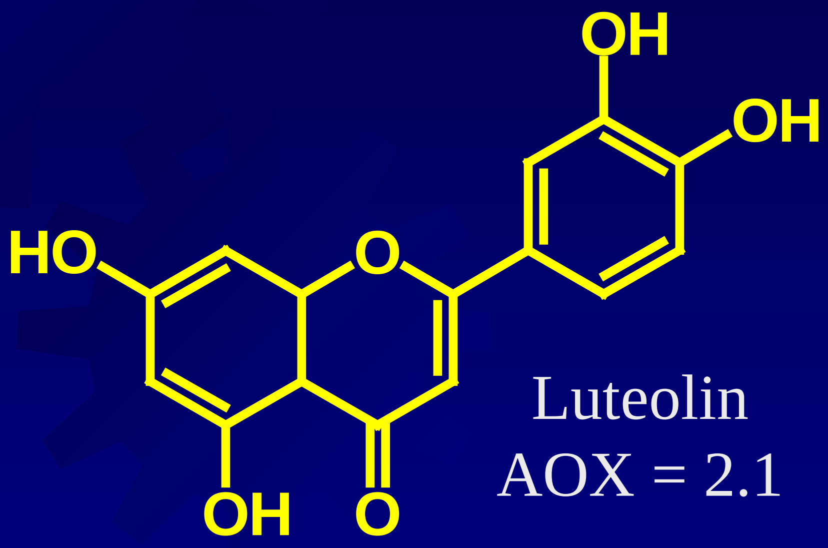
Cyanidin
AOX = 4.4

Importance of the 3-OH group

Quercetin
AOX = 4.7



Quercetin-3-glucoside
AOX ~ 2.5



Luteolin
AOX = 2.1

Importance of the 4-Oxo Function

- Works with the 2-3 double bond in the C-ring and is responsible for electron delocalization from the B-ring.
- 3-OH and 5-OH substitutions with the 4-oxo function are best for maximum AOX properties

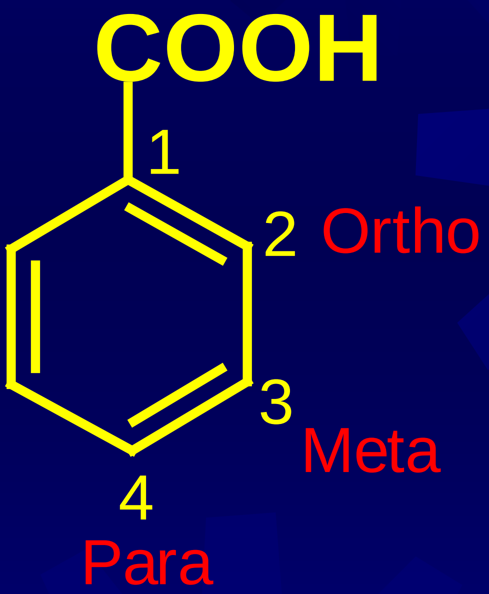
Structurally, quercetin has all the right components to make for the “perfect” antioxidant.

Importance of the 2-3 db

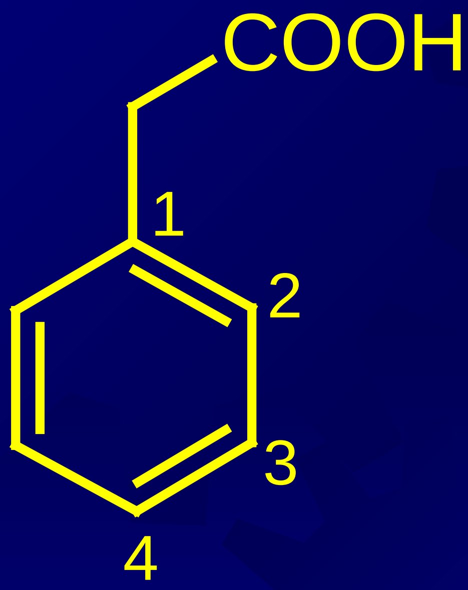
Quercetin
AOX = 4.7

Taxifolin
AOX = 1.9

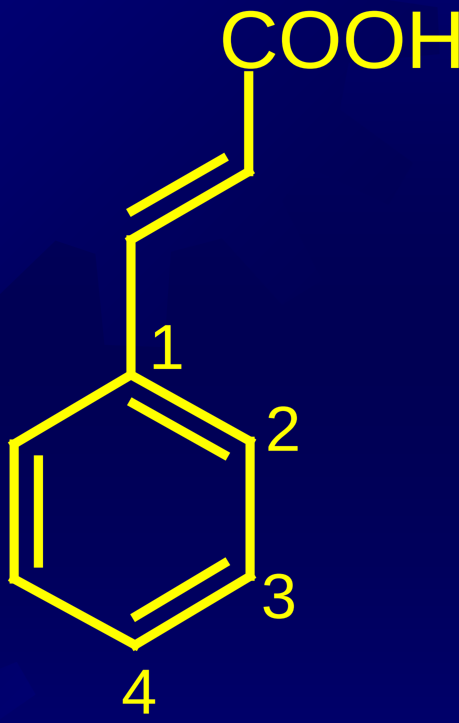
More on the Phenolic Acids



Hydroxybenzoic Acid (HBA)



Hydroxyphenylacetic Acid (HPA)

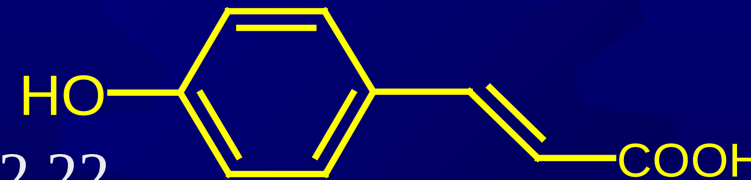


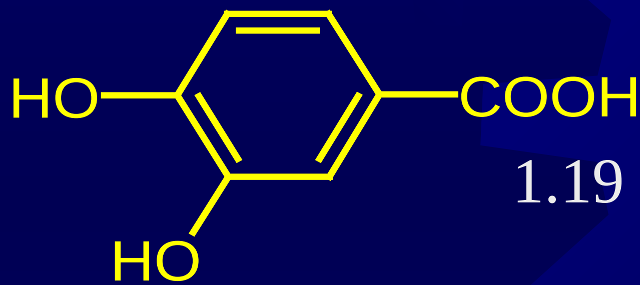
Cinnamic Acid (CA)

0.08

p-OH-benzoic
p-coumaric

2.22

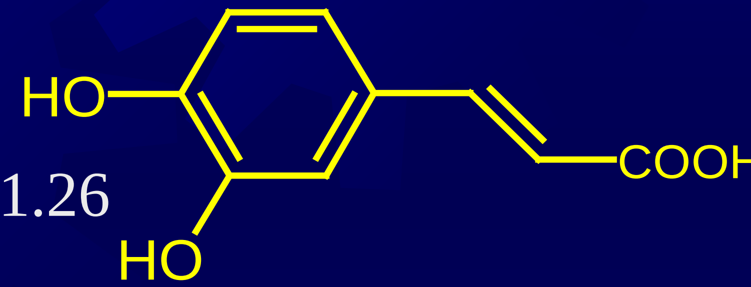




1.19

Protocatechuic
Caffeic

1.26



1.43

Vanillic
Ferulic

1.90

Antagonism-Synergism-Metals

- Many antioxidant work for and against each other
- An antioxidant in a biological system my be regenerated
- In mixed ROS…inefficiency of one antioxidant to quench all the different radicals.
- No way of knowing if the “better” antioxidant for a particular radical is doing all the work or not.
- Will a better antioxidant for a given food system “beat out” a lesser antioxidant (antagonistic response) in order to quench the radicals.

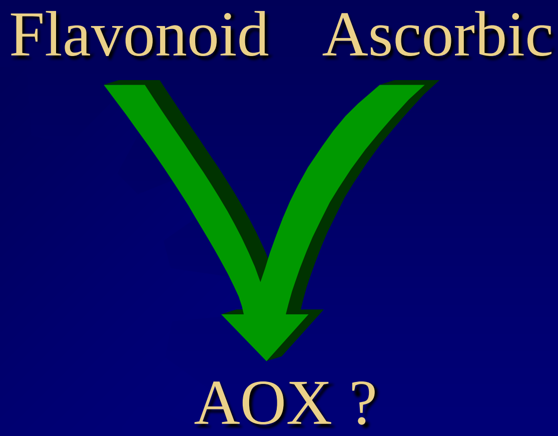
Example: Factors Affecting AOX of Bell Peppers

Chemical interactions

- *In vitro* models
- Find synergistic/antagonistic effects

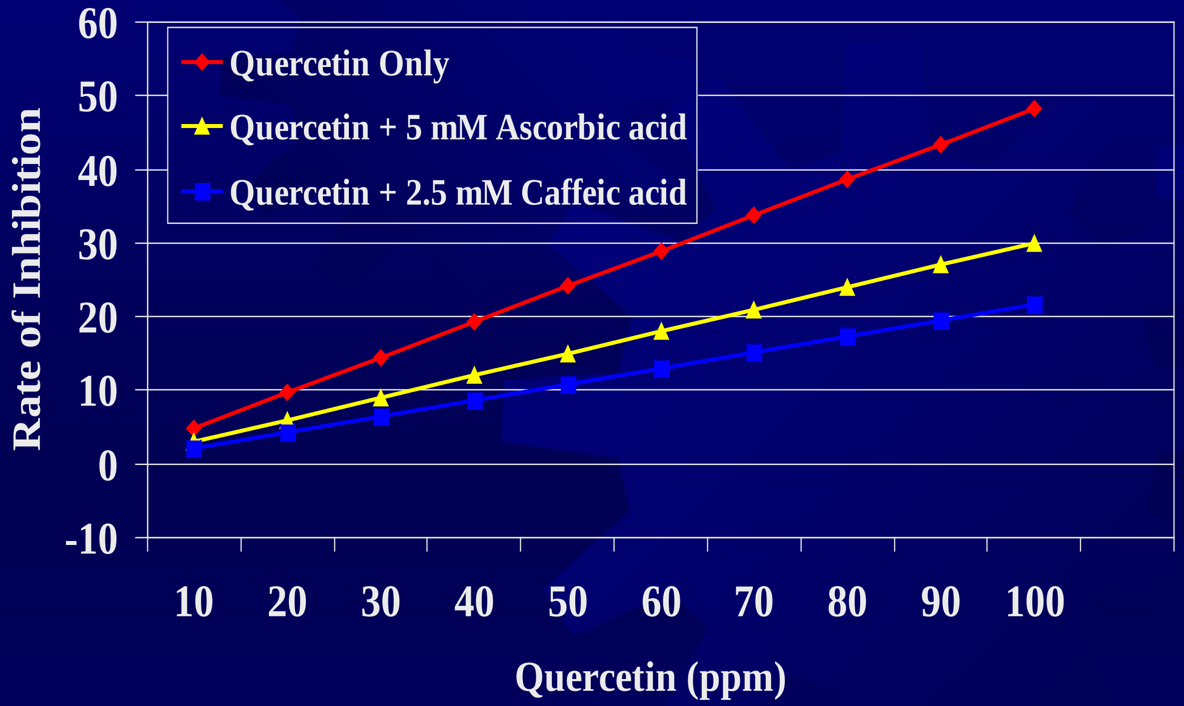
Free metal ions

- Diluted isolates
- Add metal chelator

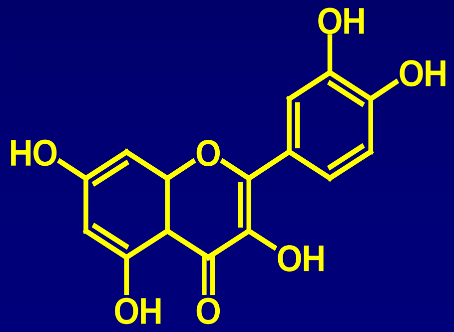


AOX with Quercetin Interactions

(ß-Carotene Bleaching)

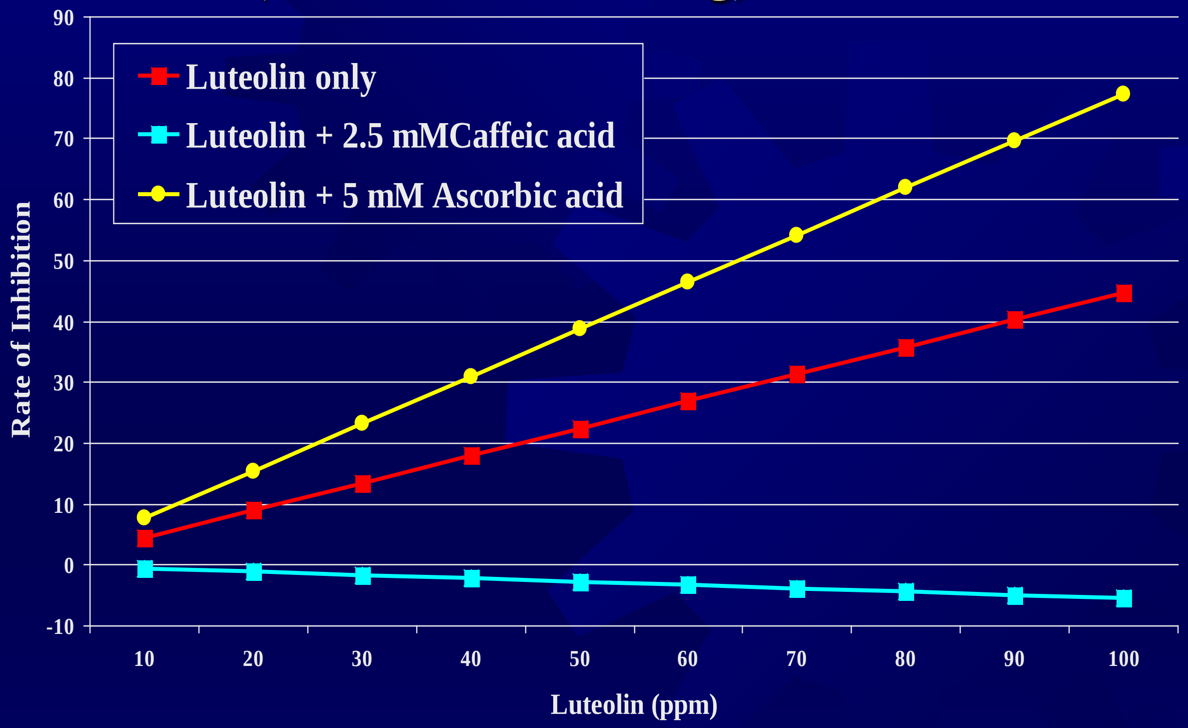


450 ppm Caffeic = 47 %
880 ppm Ascorbic = 15%



AOX with Luteolin Interactions

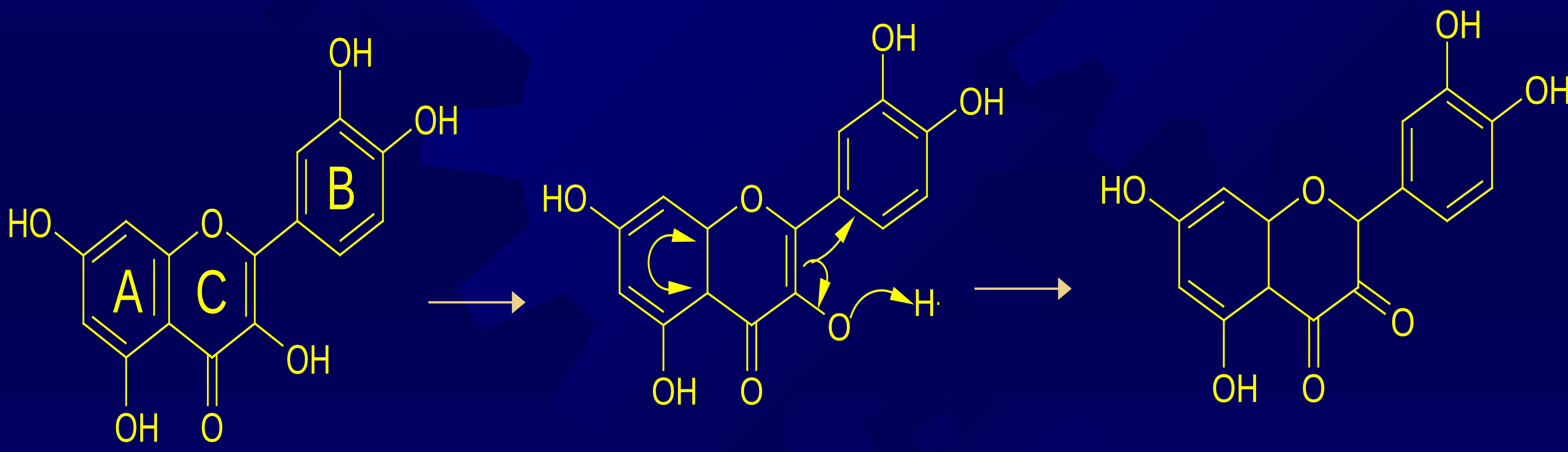
(ß-Carotene Bleaching)



450 ppm Caffeic = 47 %

880 ppm Ascorbic = 15%

Theoretical Quercetin “Regeneration” Scheme

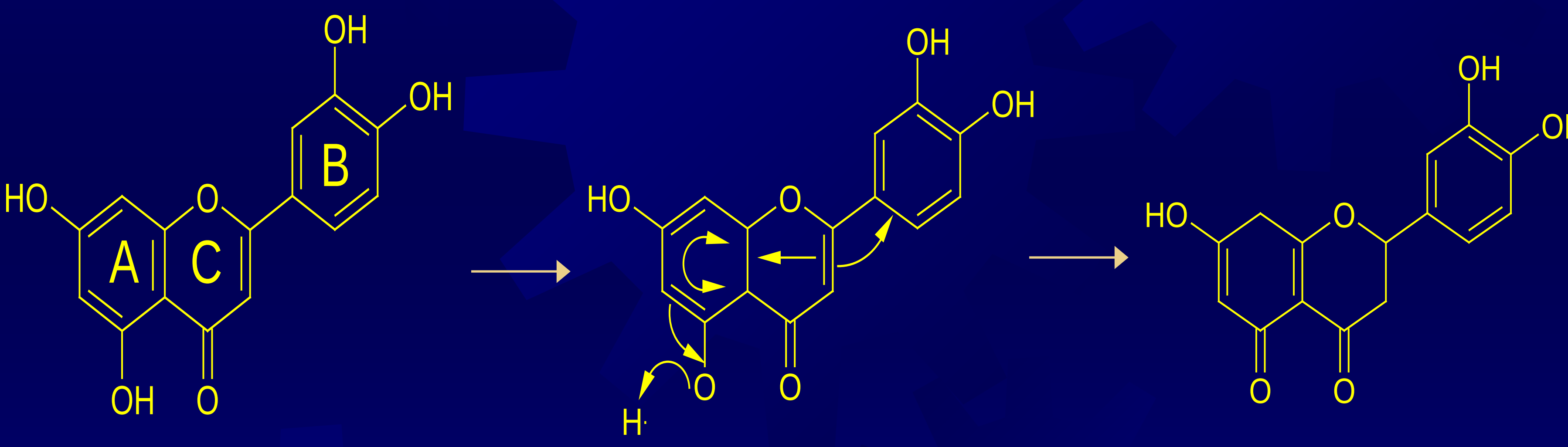


Quercetin

Delocalization of C-ring

Reduced resonation in A and B rings
Minor regeneration by ascorbic acid
Minor regeneration by caffeic acid

Theoretical Luteolin "Regeneration" Scheme

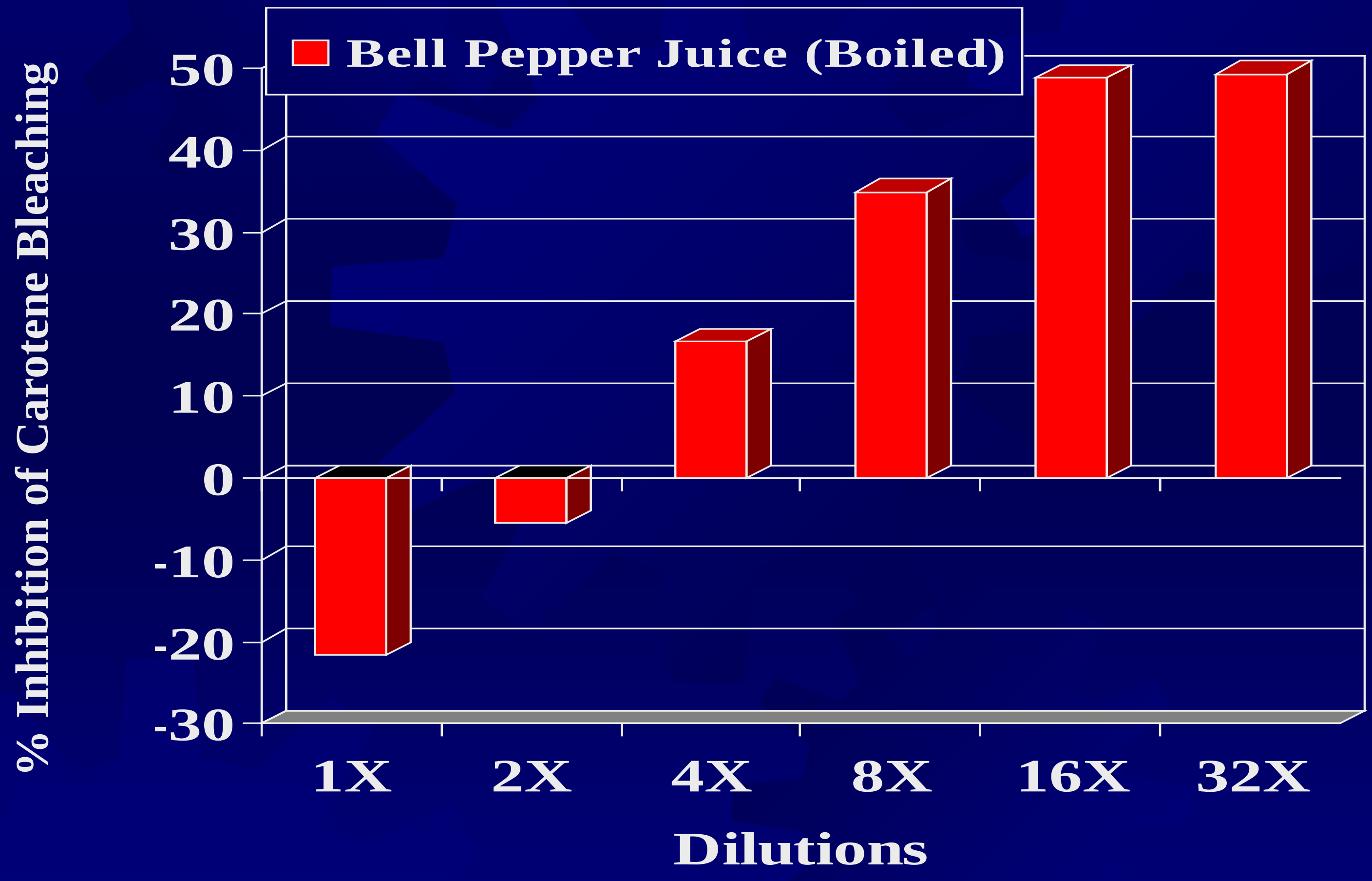


Luteolin

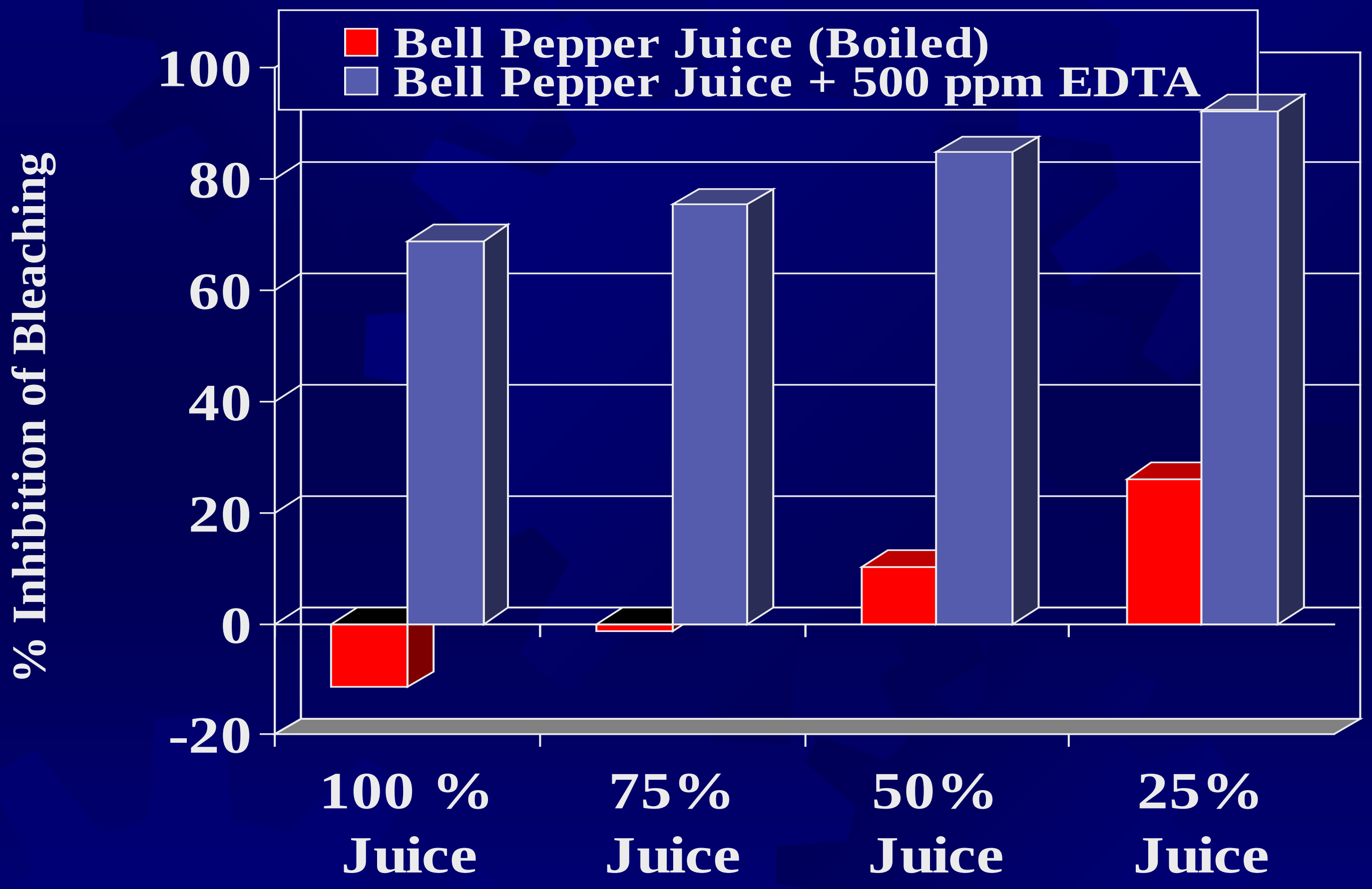
Electron donation by C-ring

Excellent resonance stability in A-ring
Highly regenerated by ascorbic acid
No regeneration by caffeic acid

Antioxidant Activity after Dilution



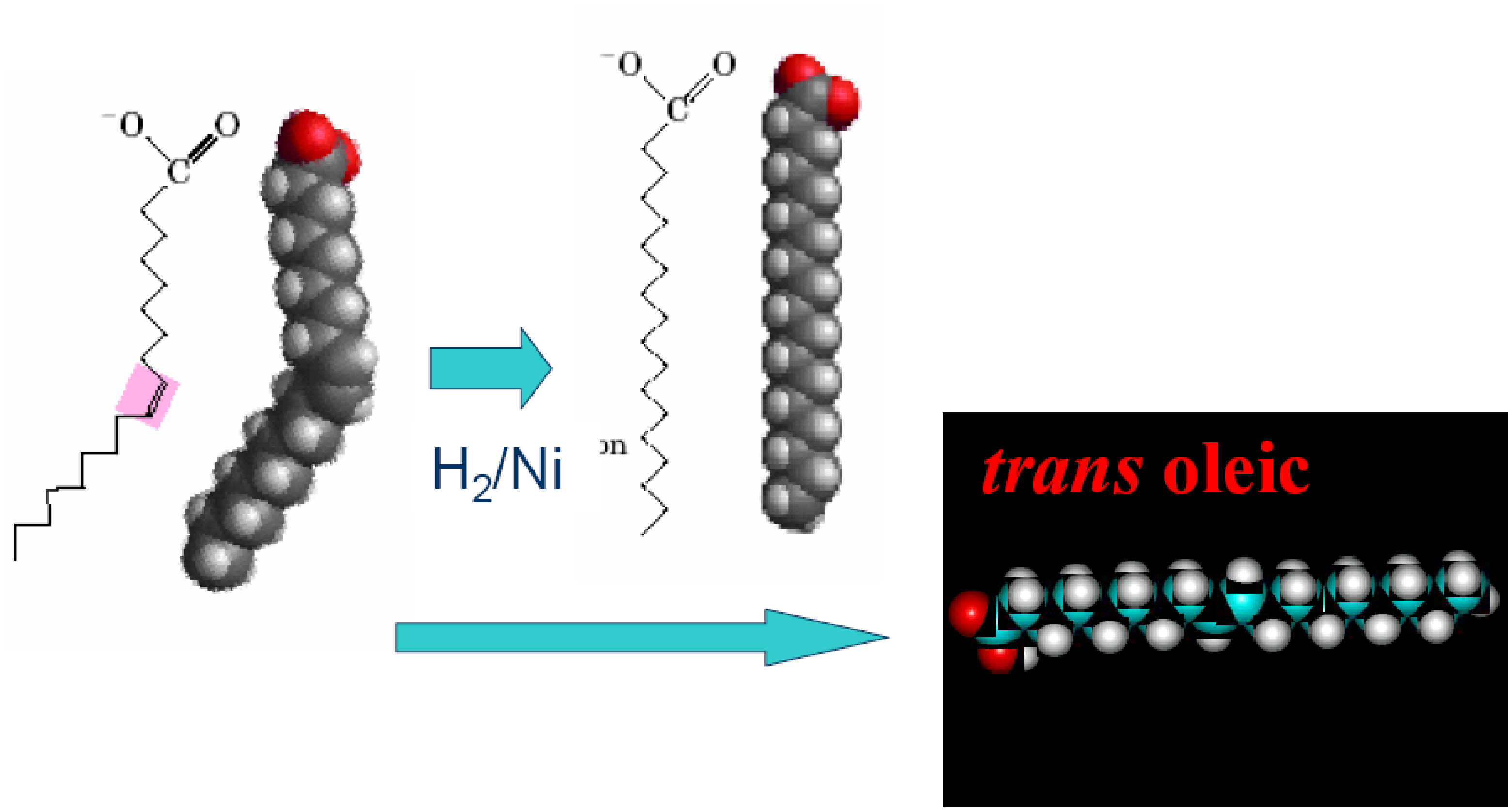
Antioxidant Activity with Chelator



Lipid Modifications

Hydrogenation

- Addition of hydrogen across double bonds



Hydrogenation

- Method

  Oil is heated with catalyst (Ni), heated to the desired temperature (140-225°C), then exposed to hydrogen at pressures of up to 60 psig and agitated.

Hydrogenation - Conditions

- Starting oil must be:
  - Refined
  - Bleached
  - Low in soap
  - Dry
- The catalysts must be:
  - Dry
  - Free of CO_2 and NH_4

Hydrogenation

- Hydrogenation Limitations
  - Selectivity is never absolute
  - Little preference for C18:3 over C18:2
  - *trans*-fatty acids acids may be formed

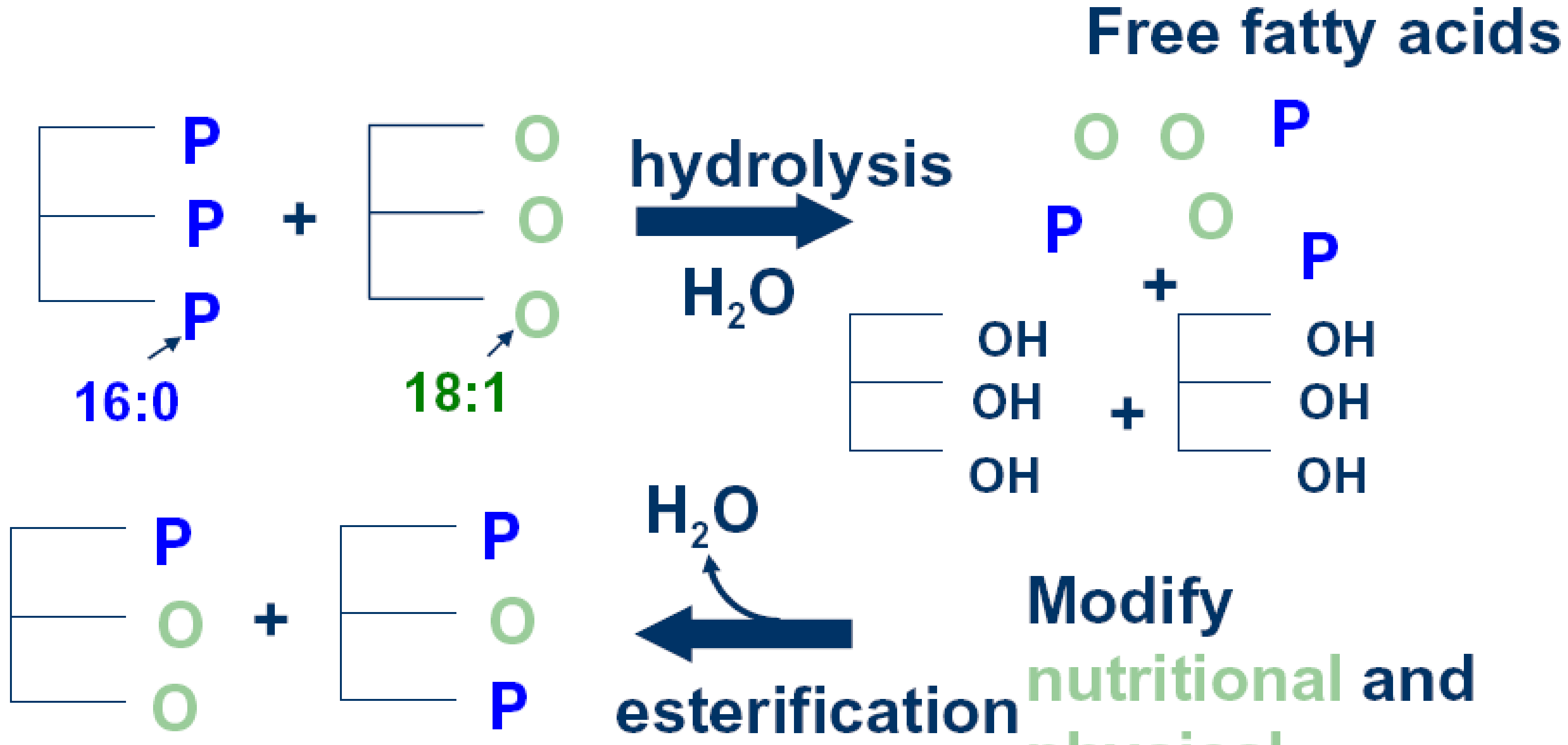
Altering Fats for Oxidative Stability

- Blending solid and liquid fats/oils
- Hydrogenation (full or partial)
- Random inter-esterification to change sn positions
  - Natural re-arrangement
  - Addition of desired fatty acids
- Targeted inter-esterifications
  - 1,3 lipases for a 1, 3 inter-esterification

Interesterification

- Rearrange the fatty acids so they become distributed randomly among triacylglycerol molecules of the fat
- Improves consistency of fats
- Applications:
  - Manufacture of shortenings
  - Lard (want ~10% tri-saturated glycerides)
    - Forms large and coarse crystals
    - Shortenings posses grainy consistency and poor baking performances
    - Randomization improves plastic range
  - Production of high stability margarine blends and hard butters with desirable melting qualities and crystallization behavior

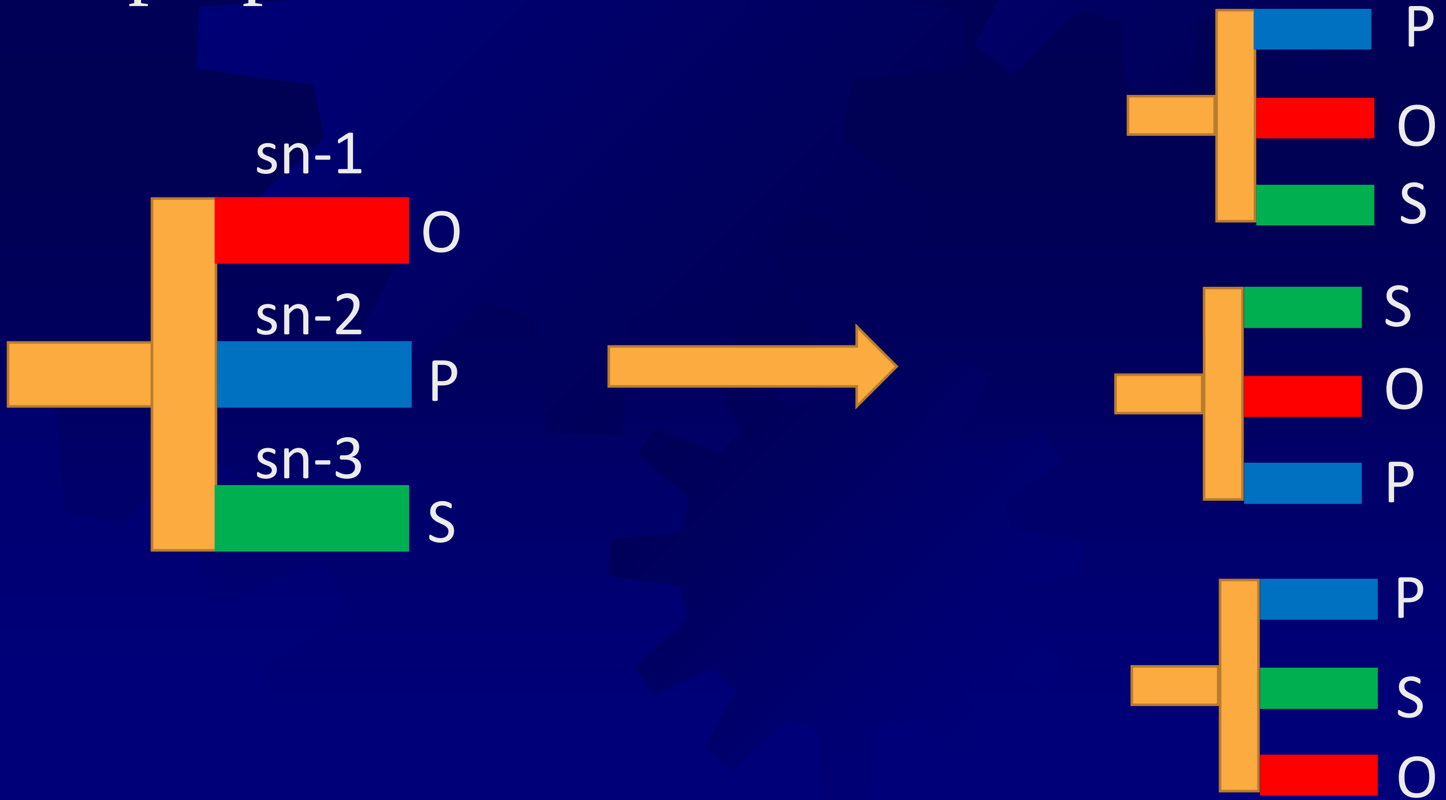
Interesterification



Modify nutritional and physical properties

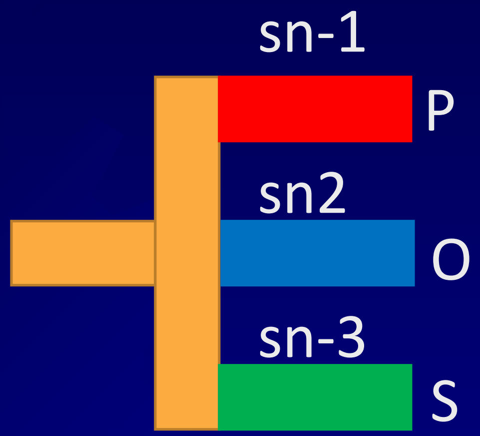
Interesterification

- Exchanging positions from one glyceride to another to alter chemical composition and physical properties



Cocoa butter

- Palmitic, stearic, and oleic acids
  - 95% of the fat
- Predominant sn positions:
  - sn-2 oleic acid
  - sn-1 or 3 palmitic or stearic acid
- P<u>O</u>S: 40%
- P<u>O</u>P: 15%
- S<u>O</u>S: 27.5%



Structured Lipids (SL’s)

Food Reviews International

Structured lipids: Synthesis and applications

Ki-Teak Lee & Casimir C. Akoh

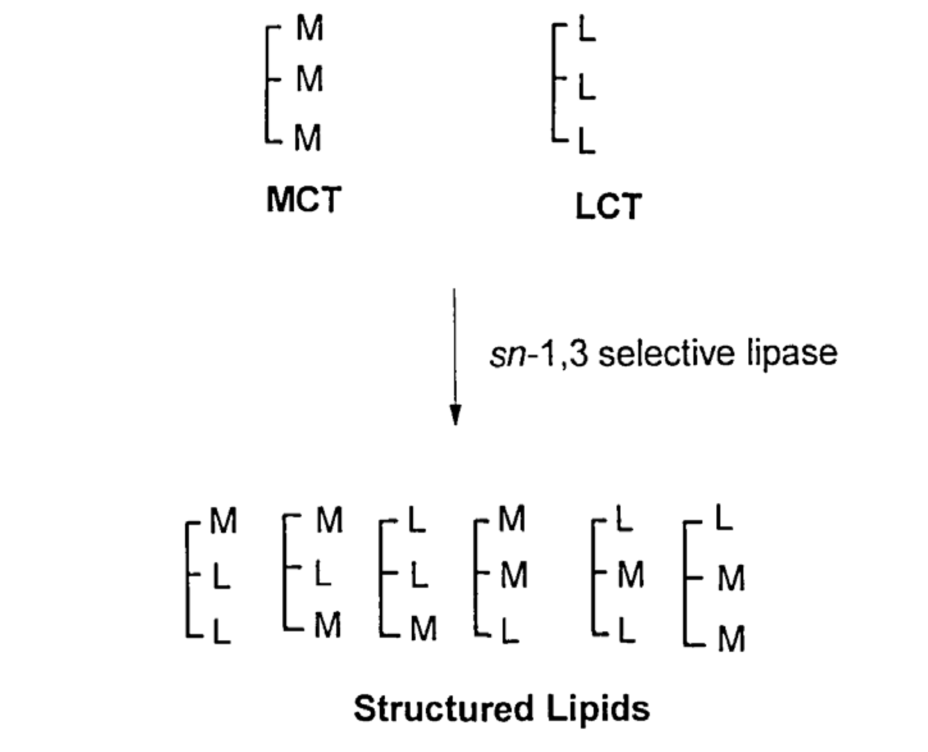
Department of Food Science & Technology , The University of Georgia , Athens, GA, 30602–7610

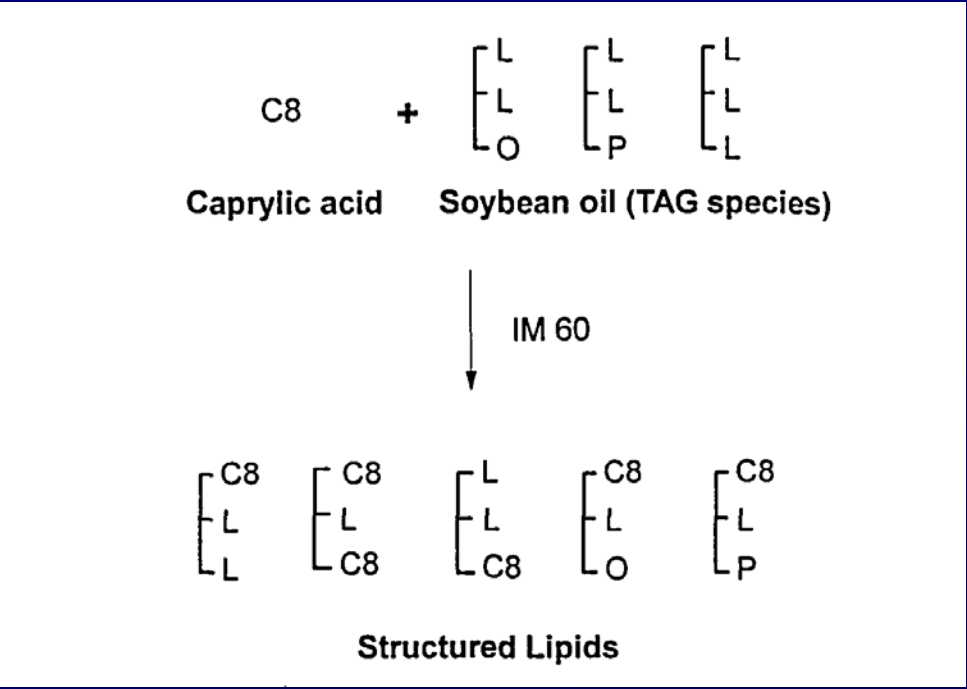
Structured Lipids

- Structured lipids are TAG restructured or modified to change the fatty acid composition and/or their positional distribution in glycerol molecules by chemical or enzymatic processes.
- SL's provide the most effective means of delivering desired fatty acids for nutritive or therapeutic purposes, targeting specific diseases and metabolic conditions.
- SL can also be synthesized to improve or change the physical and/or chemical characteristics of TAG such as melting point, solid fat contents, iodine, and saponification number.
- Because a simple physical mixture results in retention of the original absorption rates of the individual TAG, the different structural composition of TAG between SL and simple physical mixture may lead to different hydrolysis and absorption rates, resulting in different metabolic fates
- There is a need for the enzymatic production of these specialty lipids. They can be produced from short-chain, medium-chain, long-chain TAG, any vegetable or animal fats, through biotechnology by lipase-catalyzed reactions with desirable acyl moieties or their esters, for potential use in food and nutrition.

Structured Lipids

- To produce SL, chemical or enzymatic reactions such as direct esterification, acidolysis, alcoholysis, or interesterification can be used depending on the types of substrates available.
- Direct esterification:
  - R1CO-OH + R-OH -> Ri-CO-OR + H2O
- Acidolysis:
  - R1CO-OR + R2-CO-OH -» R2-CO-OR + R,-CO-OH
- Alcoholysis:
  - R-CO-ORi + R2-OH -> R-CO-OR2 + Ri-OH
- Interesterification (ester-interchange):
  - R1-CO-OR2 + R3-CO-OR4 -> R,-CO-OR4 + R3-CO-OR2
- SL can be produced with lipases in organic solvent, where substrates are soluble, and hydrolysis (reverse reaction) can be minimized.





Trans-esterification = the process of exchanging the organic group R" of an ester with the organic group R' of an alcohol.

- Trans-esterification using *sn-1,3* specific lipase results in the *sn-2* fatty acids remaining almost intact in the resulting TAG. This is significant from a nutritional point of view because the 2-monoacylglycerol produced by pancreatic lipase digestion are the main carriers of fatty acids through the intestinal wall.

Ping-Pong Mechanism: Trans-esterification

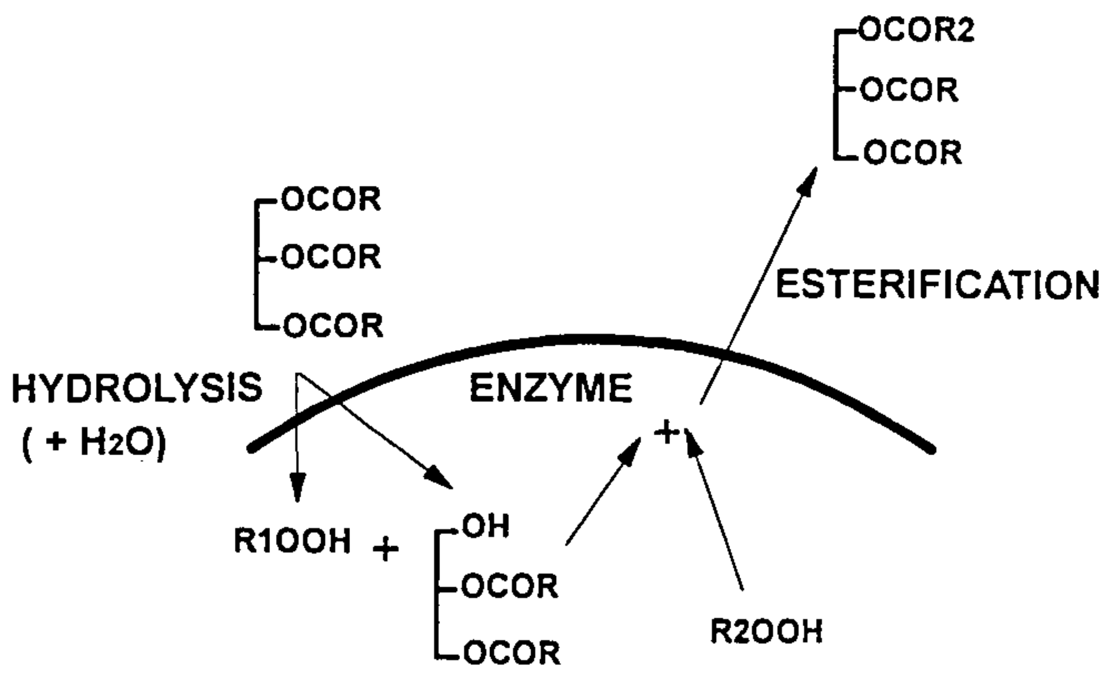


Figure 3. Ping-pong mechanism for transesterification.

Structured Lipids-Species

- Animals
  - Saturated FA in sn-1
  - Unsaturated in sn-2
  - Sn-3 varies
  - Beef = C16:0 in sn-1 and C18:1 in sn-2
- Butter
  - C16:0 is not always in sn-1
  - C16:0 may be in sn-2 ~66% of the time
- Lard
  - C16:0 is in sn-1; sn-2 is variable
  - Unsaturated FA in sn-3

Structured Lipids-Species

- Vegetable Oils
  - C18:1 or C18:2 are exclusively in sn-2
  - C18:3, when present, will be in sn-3
  - Saturated fats are almost always in sn-1
  - Rarely will be sat FA be in sn-3
- Coconut Oil
  - Medium chain FA’s can be in any position (<14 C)
  - C12:0 is mostly in sn-2
- Oleic Acid is almost always in sn-2, but when present in lard it is in sn-1 or sn-3

Chemical Tests for Lipid Characterizations

Iodine Value

- Measure of the degree of unsaturation in an oil or the number of double bonds in relation to the amount of lipid present
- Defined as the grams of iodine *absorbed* per 100-g of sample.
- Target IV is dependent on the characteristics of the lipid you are looking for

Iodine value: g absorbed I_2/ 100 g fat

Iodine Value of some oils (Table 14-2)

Source	I_2 Value
Beef Tallow	<50
Olive, Palm, Peanut	< 100
Corn, Cottonseed	100 - 130
Linseed, Soybean, safflower, conola	> 130
Fish	>150

Highly saturated

High in 18:1

High in 18:1 and 18:2)

18:1, 18:2, 18:3

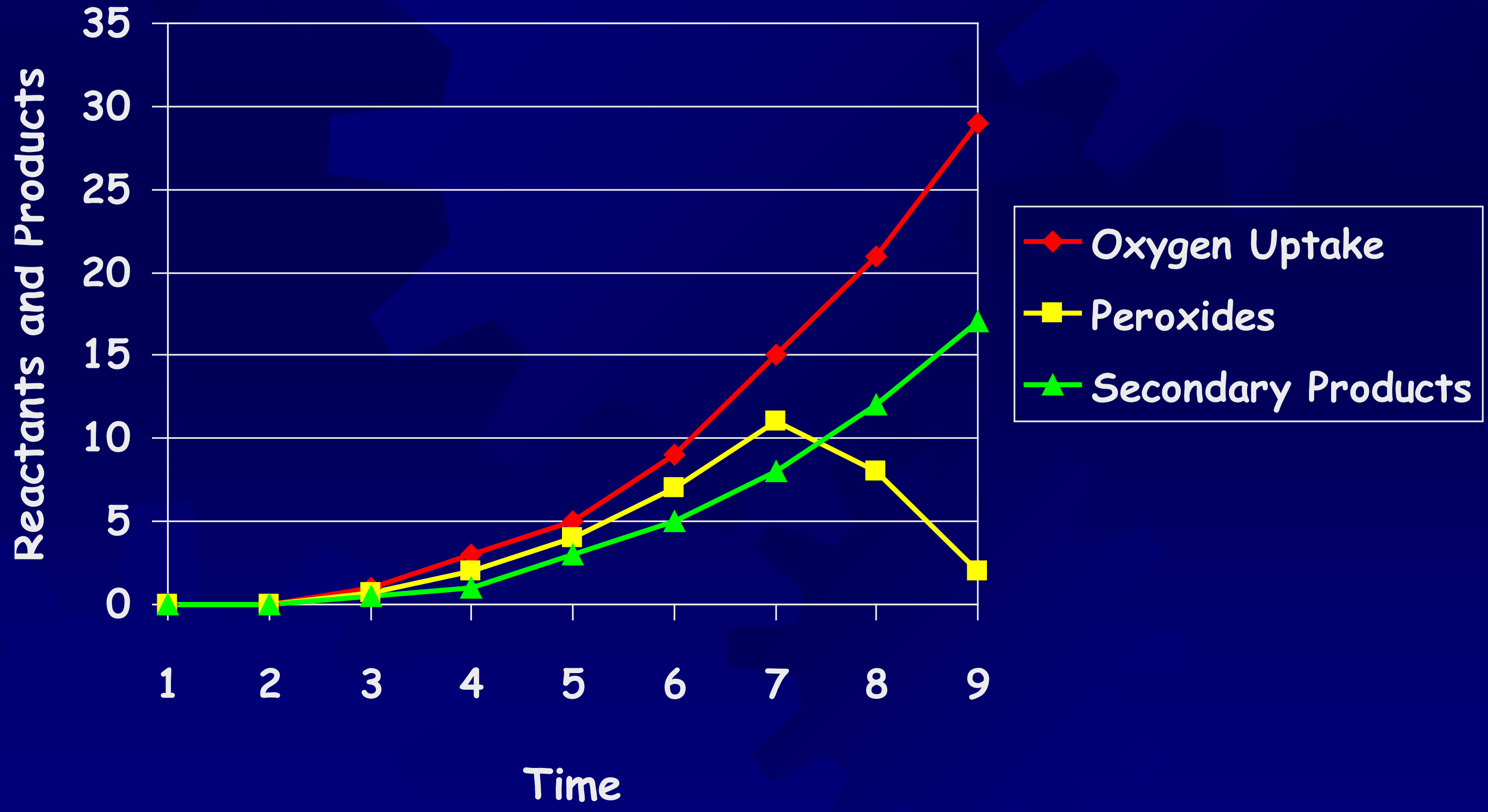
18:1, 18:2, 18:3
(longer chains)

Chemical Tests for Oxidation

- Lipid Oxidation
- Hydrolysis
- Peroxide Value
- Oxidation Tests

LIPID OXIDATION

Lipid System Under Oxidizing Conditions



Thiobarbituric Acid Reactive Substances

Tests for secondary products of oxidation – aldehydes,

Malonaldehyde (primary compound): alkenals, and 2,4-dienals

- A pink pigment is formed and measured at ~530 nm.

TBARS has a strong following in meat research

High TBA = High Oxidative Rancidity

HEXANAL/Nonenal

- Good indictor of the end products of oxidation

- Standard method in many industries.
- Aldehyde formation from lipid oxidation.

- Gas chromatography

Conjugated Fatty Acids

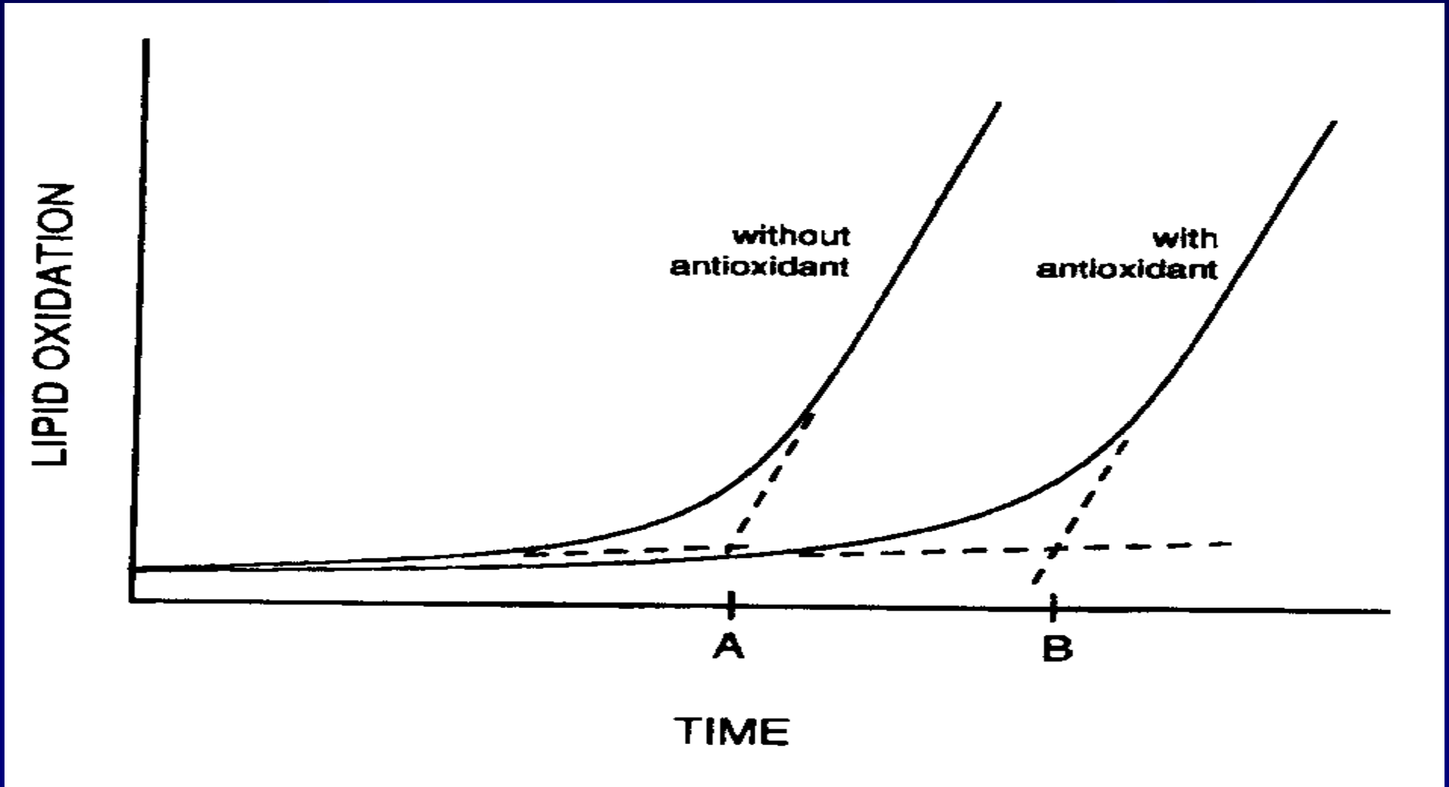
During oxidation, double bond migration occurs and conjugated fatty acids are formed (prior to scission rxns)

They absorb light efficiently and can be monitored in a spectrophotometer.

$$R-C-C=C-C=C-C-C=C-C-R$$

TECHNIQUES OF MEASURING OXIDATIVE STABILITY

Induction Period: is defined as the length of time before detectable rancidity or time before rapid acceleration of lipid oxidation



MEASURING OXIDATIVE STABILITY

- ***Oil Stability Index*** – The Rancimat

- Air is bubbled through oil sample (110°C).
- Oil degrades to acidic volatiles (e.g. formic acid)
- Acids are carried by the air into a water trap.
- Conductivity or pH of the water is measured