Natural Antioxidants in Meat Products

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The Rise of Natural Products in the Meat Industry

- Launches positioned as “natural” increased **26%** from 2008-2009
- Launches in the “no additive/no preservative” category increased **82%** from 2008-2009

“All-natural thinking will remain strong in the future.”
- Leading Ingredients Supplier

Source:
Preservatives/Antioxidants: Consumer Trends Providing Challenges and Opportunities, Euromonitor International, January 2010
U.S. Food Antioxidants Market by Application (2007)

Food Antioxidants

- Meat and poultry: 44%
- Baked goods: 8%
- Fish and seafood: 8%
- Fats, oils, and margarines: 14%
- Snack foods: 6%
- Others: 20%

Herbal Extracts

- Meat & Poultry: 55%
- Other applications: 5%
- Oils, fats & Margarines: 6%
- Fish & Sea food: 6%
- Spices & Condiments: 7%
- Snack foods: 7%
- Baked goods: 14%

Note: All figures are rounded; the base year is 2007. Source: Frost & Sullivan

Source: U.S. Food and Feed Shelf Life Extension Antioxidants Market, N4CC-88, December 2008, Frost & Sullivan
Free Radical Oxidation

Light Metals Enzymes

Heat

INITIATION

RH

R'

O₂

PROPAGATION

ROO⁻ (unstable peroxyl radical)

A'

AH

ROOH

Stable antioxidant radical breaks the cycle

FORTIUM® antioxidants and extracts

EN-HANCE® synthetic antioxidants

Aldehydes, organic acids, alcohols, ketones

(hydroperoxide breakdown products contribute off flavors)
Basic Antioxidant Mechanism

- Chain-breaking antioxidants retard or inhibit oxidation by interfering with either propagation or initiation by donating H to lipid peroxyl radicals
  - \( R^+ + AH \rightarrow RH + A^- \) initiation (low \( pO_2 \), hi temp.)
  - \( ROO^- + AH \rightleftharpoons ROOH + A^- \) propagation
  - \( A^- + ROO^- \rightarrow ROOA \) propagation
Culinary spices used as natural antioxidants

- Various studies report the use of 0.1%-1% dry spices delayed oxidation and warmed over flavor (WOF) in beef, pork, and chicken

- Sensory panels commented that spices imparted characteristic flavors to the meat

- Flavor contribution of some spices may offset the benefit of the increase in oxidative stability
Precooked Chicken Patties with Red Pepper

- Red pepper added at 0.2 and 0.4%, patties frozen (-20 °C) for 9 w
- Capsaicin levels (0.2, 0.4 ppm) < threshold for extreme heat (1 ppm)
- WOF intensity decreased with increasing levels of red pepper
- Pepper is known to interfere with flavor identification. Did it simply mask WOF?

Warmed-over flavor (WOF) evaluation in chicken patties formulated at 3 fat levels and 3 pepper levels

<table>
<thead>
<tr>
<th>Fat (%)</th>
<th>WOF</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>52b</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>54b</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>64a</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Pepper (%)</th>
<th>WOF</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>65a</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>56b</td>
<td>7</td>
</tr>
<tr>
<td>0.4</td>
<td>48c</td>
<td></td>
</tr>
</tbody>
</table>

^aLS means and SE of WOF over 5 storage periods (9 w) as perceived by 12 panelists; no WOF=0, intense WOF=150; (P<0.005).


Image Source: www.wikipedia.org
Precooked Chicken Patties with Red Pepper

- TBA results confirmed WOF differences detected by panelists were attributed to:
  - Decrease in oxidative byproducts due to red pepper
  - Red pepper masked off-flavors associated with oxidation

<table>
<thead>
<tr>
<th>Pepper (%)</th>
<th>Fat level (%)</th>
<th>TBA, mg malonaldehyde/kg meat</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>0</td>
<td>2.06ef</td>
<td>3.05c</td>
<td>4.80a</td>
</tr>
<tr>
<td>0.2</td>
<td>1.80f</td>
<td>2.68d</td>
<td>4.12b</td>
</tr>
<tr>
<td>0.4</td>
<td>1.39g</td>
<td>2.26e</td>
<td>3.20c</td>
</tr>
</tbody>
</table>

aTBA, mg malonaldehyde/kg meat.
bLS means and SE for TBA measured across 5 storage periods; n=45; (P<0.005).


Image source: www.wikipedia.org
Antioxidant Properties of Oriental Nutraceutical Herb Extracts vs. Rosemary

- White peony (Baishaoyao) – root
- Red peony (Chishaoyao) - root
- Sappanwood - heartwood
- Rehmania (Chinese foxglove) - root
- Moutan peony (Mudanpi) - bark of root
- Korean angelica – root
- These traditional herbs are used to decrease species-related flavor of goat meat
- Rosemary – leaves, widespread culinary use, positive control


Image sources: itmonline.com, singaporeitradmarket.com, myhealthspan.com, tradekorea.com,
Active components in red and white peony

- **Paeonia lactiflora**, the common garden peony

- paeoniflorin (monoterpene glycoside) – 3-5%
  - CAS: 23180-57-6, $C_{23}H_{28}O_{11}$, MW = 480.46
  - benzoylpaeoniflorin
  - albiflorin
  - oxypaeoniflorin
  - pentagalloylglucose
  - paeonilactones A, B and C

- No appreciable differences between compounds found in “red” and “white”, likely differentiated due to tradition

Image source: Chemical structure: Tokyo Chemical Industry (TCI) [http://www.tciamerica.com/catalog/P1876.html](http://www.tciamerica.com/catalog/P1876.html), photo: wikipedia.org

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Primary active components in moutan peony – Paeonia suffruticosa

- Known as “tree peony” for its woody branches due to older age
- Contains paeoniflorin - 3-5%
- Unique to moutan peony is paeonol, (2'-hydroxy-4'-methoxyacetophenone)
- ~ 1.5% is found in the root cortex
- CAS 552-41-0, C₉H₁₀O₃, MW:166.18 g/mol

Active compounds peak in trees grown at 600 m elevation which are 5+ years old, and harvested during the first 2/3 of October


**Homoisoflavonoids isolated from ethanolic extracts of sappanwood**

- Protosappanin A and B demonstrated more inhibition of malonaldehyde formation *in vitro*
- Brazilein demonstrated more scavenging of hydroxyl radicals

Performance in Unsalted Raw and Cooked Beef Patties

- Powdered extracts (95% ethanol, 1:4, 3x) added at 0.25%
- Peony, sappanwood, and rosemary were effective in maintaining low TBARS ($P<0.05$) in both raw and cooked beef

Performance in Salted (2%) Raw and Cooked Beef Patties

- 0.25% Red or white peony, sappanwood, Moutan peony, and rosemary extracts counteracted the pro-oxidative effect of 2% NaCl.
- Peony and sappanwood extracts also moderated red color loss ($P<0.05$) in salted and unsalted raw patties.

Reducing the treatment levels revealed distinct differences in antioxidant effectiveness.

At 0.01%, sappanwood was the most effective ($P<0.05$) in maintaining low TBARS during refrigerated storage.

• Cooked, refrigerated, mechanically deboned chicken meat
• 800 ppm cocoa leaf (CL) extract and 200 ppm green tea (GT) demonstrated the best performance
• Cocoa leaves are typically discarded during tree pruning, and are a good source of catechins

Image source: www.skyfieldtropical.com
Cloudberry Extract

- Cloudberries (Rubus chamaemorus) grow mostly above 55°N (boreal circumpolar distribution)
- Predominantly found in Finland, Norway, Alaska, and Newfoundland and Labrador
- Cultivated in peat bogs, pH 3.5-4.5, with groundwater 30 cm below the surface
- Also grows in moist tundra
- Rich in ellagic acid (150 ppm)


Image source: www.wikipedia.org
Performance in Refrigerated Cooked Pork

- Ground pork patties, 30% fat, were cooked, then stored at 4 °C under light
- 100 ppm of either cloudberry extract or quercetin most effectively suppressed TBARS on d 3


Image source: www.wikipedia.org
Performance in Refrigerated Cooked Pork

- Similar results were seen for hexanal formation.
- At 500 ppm, willow herb (*Epilobium angustifolium*), known as Fireweed, performed as well as cloudberry and quercetin.


Image source: www.wikipedia.org
Yerba Mate - *Ilex paraguariensis*

- Subtropical evergreen
- Requires >120 cm annual rainfall, distributed throughout the year
- Cultivated in Argentina
- Active compounds are caffeoyl derivatives ~9%/dry wt:
  - chlorogenic acid,
  - 3,5-dicaffeoylquinic acid,
  - 4,5-dicaffeoylquinic acid,
  - 3,4-dicaffeoylquinic acid,
  - caffeic acid

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<table>
<thead>
<tr>
<th>Table 1—Polyphenols in green tea, black tea, and Mate tea.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polyphenol</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Caffeic acid</td>
</tr>
<tr>
<td>Caffeine</td>
</tr>
<tr>
<td>Caffeoyl derivatives</td>
</tr>
<tr>
<td>Caffeoylshikimic acid</td>
</tr>
<tr>
<td>Catechin</td>
</tr>
<tr>
<td>Catechin gallate</td>
</tr>
<tr>
<td>Chlorogenic acid</td>
</tr>
<tr>
<td>Coumaric acid</td>
</tr>
<tr>
<td>Epicatechin gallate</td>
</tr>
<tr>
<td>Epigallocatechin</td>
</tr>
<tr>
<td>Epigallocatechin gallate</td>
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<tr>
<td>Feruloylquinic acid</td>
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<td>Gallic acid</td>
</tr>
<tr>
<td>Galloatechin gallate</td>
</tr>
<tr>
<td>Kaempferol</td>
</tr>
<tr>
<td>Myricetin</td>
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<tr>
<td>Procyanidin</td>
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<tr>
<td>Quercetin</td>
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<tr>
<td>Quinic acid</td>
</tr>
<tr>
<td>Rutin</td>
</tr>
<tr>
<td>Theaflavin</td>
</tr>
<tr>
<td>Theobromine</td>
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</table>

*Adapted from Carini and others (1998); Chandra and de Mejia Gonzalez (2004); Atou and others (2005); Bastos and others (2007); Bravo and others (2007).*
0.1% dried mate leaves were more effective ($P<0.05$) than rosemary leaves in salted (0.5%), cooked, refrigerated chicken.

- Sensory (aroma, flavor) results indicated 0.05% mate extract was the optimum level.
Performance of Green Tea Catechins in Beef and Chicken

- 200 and 400 ppm green tea catechins reduced \( P<0.05 \) lipid oxidation in raw and cooked beef (1% salt), and were more effective than sodium ascorbate in cooked beef.

Sensory Acceptability in Cooked Chicken Patties

- Although tea catechins effectively reduced lipid oxidation, they caused discoloration (darkening) in cooked meat which reduced the overall acceptability as judged by the panel.

Principal Active Components in Nonpolar Rosemary Extract

- Phenolic diterpenes, 1-3% (w/w leaf)
- Various factors contribute to efficacy in meat products
  - Form, solubility, flavor, point of application

Carnosic acid

Carnosol
Rosemary Oleoresin in Raw Turkey Sausage – 1985

- 75% hand deboned/25% mechanically deboned turkey breakfast sausage
- 20 ppm rosemary oleoresin
- Spice blend delivered 1.7% salt
- TBARS improvement in D vs. C illustrates the impact of the rosemary oleoresin
- TBARS and sensory testing concluded rosemary oleoresin was comparable to BHA/BHT/CA

In raw frozen pork sausage, 510 ppm (R1500) and 850 ppm (R2500) rosemary extract maintained lower TBARS ($P < 0.05$) than BHA/BHT from d 42 and 28, respectively.

For color retention, 510 ppm (R1500) and 850 ppm (R2500) rosemary extract were more effective ($P < 0.05$) than BHA/BHT from d 98 and 84, respectively.

Maximizing the Benefits of Rosemary Extract – Stage of Addition During Ground Beef Processing

Effect of rosemary extract treatments applied to different stages of ground beef on mean ± standard error (SE) of CIE $L^*$, $a^*$, and $b^*$ values, 630/580 nm reflectance values, saturation index, hue angle, and TBARS through 144 h of simulated retail storage

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Treatment</th>
<th>Trim</th>
<th>Cube</th>
<th>Coarse</th>
<th>Fine</th>
<th>SE</th>
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</thead>
<tbody>
<tr>
<td>CIE $L^*$</td>
<td>Control</td>
<td>46.68b</td>
<td>46.67ab</td>
<td>49.54a</td>
<td>47.96b</td>
<td>0.70</td>
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<tr>
<td>CIE $a^*$</td>
<td>23.17b</td>
<td>25.68a</td>
<td>24.72a</td>
<td>22.82b</td>
<td>22.15b</td>
<td>1.76</td>
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<tr>
<td>CIE $b^*$</td>
<td>21.92b</td>
<td>23.74a</td>
<td>23.48a</td>
<td>22.37b</td>
<td>22.02b</td>
<td>1.23</td>
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<tr>
<td>630/580 nm</td>
<td>3.28bc</td>
<td>3.86a</td>
<td>3.54ab</td>
<td>3.10c</td>
<td>3.01c</td>
<td>0.29</td>
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<tr>
<td>Sat. index</td>
<td>32.19b</td>
<td>35.16a</td>
<td>34.33a</td>
<td>32.23b</td>
<td>31.47b</td>
<td>2.03</td>
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<tr>
<td>Hue angle</td>
<td>45.88ab</td>
<td>44.22c</td>
<td>45.22bc</td>
<td>46.49a</td>
<td>46.85a</td>
<td>1.17</td>
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<tr>
<td>TBARS</td>
<td>4.75a</td>
<td>0.78c</td>
<td>0.83c</td>
<td>1.15c</td>
<td>2.77b</td>
<td>0.38</td>
</tr>
</tbody>
</table>

*Means within row not having a common letter are significantly different ($p<0.05$)

0.3% dilute, oil soluble rosemary extract was applied at various stages prior to 6 d simulated retail storage

Red circles indicate improvement over control ($P<0.05$)

Effect of Display Time on Ground Beef TBARS

- Significant difference at 0 h indicated the immediate activity of rosemary extract
- Improvement ($P<0.05$) in TBARS was maintained through 144 h for all treatments

0.01-0.02% Grape seed extracts (89% proanthocyanidins) were highly effective at maintaining low TBARS in beef.

This dilute rosemary extract used at the typically recommended rate (0.2%) would have likely yielded better results.

Performance in Refrigerated Cooked Pork

- Grape seed extract was also effective in cooked pork
- Use of rosemary extract at an appropriate level would likely have yielded performance comparable to grape seed extract

Important Considerations When Using Natural Extracts

• Consult the extract supplier for application advice

• Test the flavor threshold
  – Alleviates generating results with no commercial applicability
  – Allow time for flavors to blend during storage/retail distribution

• Product solubility and form
  – Dispersion is key
  – Dilute products often outperform concentrated products
  – Use appropriate products for enhancement solutions