The Effect of Natural Antioxidants on the Colour and Lipid Stability of Paprika Salami

Bo-Anne ROHLÍK, Petr PIPEK and Jan PÁNEK

Department of Food Preservation, Faculty of Food and Biochemical Technology, Institute of Chemical Technology Prague, Prague, Czech Republic

Abstract

Rohlík B-A., Pipek P., Pánek J. (2013): **The effect of natural antioxidants on the colour and lipid stability of paprika salami**. Czech J. Food Sci., **31**: 307–312.

The typical red colour of paprika salamis is a very important quality attribute but it is also very susceptible to oxidation. Rosemary extracts and lycopene appear to be efficient antioxidants for dry fermented sausages. The complicated structure of dried sausages with different kinetics of colour changes was evaluated using VIA software NIS-Elements 2.20 and lightness L^*, redness a^*, yellowness b^*, mean red (R), mean green (G), and mean blue (B) were measured; the ratio of red $r = R/(R + G + B)$ and hue $h = \text{arctg}\,(a^*/b^*)$ were calculated. The addition of rosemary extract has positively affected the colour and suppressed lipid oxidation in both meat and lard particles in the paprika salami. Even more satisfactory results were obtained by adding both the rosemary extract and lycopene. Video image analysis enabled to perform colour measurements of meat and lard particles separately, which could not be done by any available method (reflective spectrophotometry).

Keywords: video image analysis; dried sausage; oxidation; rosemary; lycopene

The typical red colour of paprika salamis is a very important quality attribute and it is an important parameter to evaluate. The red colour intensity of this meat product depends not only on the concentration of haem pigments, but also on the added paprika and it is further affected by technological processes and storage conditions.

Many undesired chemical reactions can take place among which lipid oxidation is the most unfavourable and can negatively affect the colour of the meat product. Lipid oxidation reactions usually also interacts with haem pigments and so can turn their red colour brown. These chemical reactions inducing discoloration of meat products are dependent on various factors like ambient temperature, addition of antioxidants (in the presence of spices), applied smoke, haem pigment concentration and other.

For the above-mentioned reasons producers are developing more efficient antioxidant of natural character, among which lycopene, paprika, and rosemary extracts are classified, to minimise the impact of undesired oxidative reactions.

The benefits of lycopene added to meat products have been tested in several studies. Østerlie *et al*. (2005) studied the colour stability of minced meat with added lycopene from tomato paste. They concluded that lycopene efficiently decreased lipid oxidation and successfully stabilised the red colour of the meat product during the storage period. They further found out that the addition of lycopene decreased the pH of the meat product and thus contributed to the slower growth of microorganisms in the meat product. A similar experiment was done by García *et al.* (2009), who added dried

Supported by the Ministry of Industry and Trade of the Czech Republic, Project No. FT-TA3/059.

tomato peels to hamburger patties and come to the same conclusion as Østerlie *et al.* (2005).

Even other two recent researches, which studied the effect of lycopene on frankfurters, obtained similar results. First Deda *et al.* (2007) added lycopene to frankfurters in the form of tomato paste and secondly Eyiler & Oztan (2011) added dried tomatoes in a powder form. These two studies showed that the meat product had a better lipid and colour stability against their oxidation. The addition of lycopene was also tested in fermented sausages. The study of Calvo & Salvador (2008) showed a positive effect of lycopene on the colour and lipid stability of fermented meat products.

However, the ability of lycopene to quench singlet oxygen depends on its concentration; the study of Liu *et al.* (2008) showed that higth concentrations of lycopene significantly reduce its ability as an antioxidant. Thus the quenching constant of lycopene was found to be more than double that of β-carotene and even ten times higher than that of α-tocopherol, which makes its presence in the diet of considerable interest (Shi 2008).

Lycopene is a relatively stable molecule and does not undergo any significant changes during current food technology operations. However, extreme conditions (e.g. hight temperature or long-term heat treatments, long-term exposure to light and long-term storage) can contribute to the degradation of the molecule (Shi 2008).

On the other hand, paprika has one of the lowest redox potentials and has been shown to have antioxidant properties. However, during paprika processing and storage the concentration of antioxidant compounds remarkably decreases due to oxidative processes and the loss of the typical orange pigment is incurred. Oxygen easily oxidises the hydroxyl group in the cyclopentane circle of capsanthin, which turns into diketone, capsanthone, and is further decomposed to β-citraurin from which 3-oxo-β-apo-8'-carotene is formed. Products containing a carbonyl group undergo reactions of non-enzymatic browning, which results into the change of the paprika red colour to brown. These changes in stored paprika may further influence the colour of meat products it is added to. For this reason it might be interesting to add natural antioxidants, such as rosemary, to meat products containing paprika (Gómez *et al.* 2008; Velíšek & Hajšlová 2009).

Another solution seems to be the addition of paprika seeds to pulverised paprika. The degree of stabilisation depends on the content of antioxidants in the seed, which is tested among different types of paprika (Klieber & Bagbato 1999).

The greatest level of attention among herbs and spices as sources of antioxidants has been focussed on rosemary. Spices from rosemary (*Rosmarinus officinalis*) are made from dried leaves of the evergreen bush plant. Rosemary is widely used as a spice and as a natural antioxidant agent.

The antioxidant activity of rosemary extracts has been associated with the presence of several phenolic diterpenes such as carnosic acid, carnosol, rosmanol, rosmariquinone, and rosmaridiphenol, which break free radical chain reactions by hydrogen atom donation and form chelates, by scavenging peroxide radicals (Sánchez-Escalante 2001; Yanishlieva 2006; Georgantelis 2007; Erkan 2008). The effectiveness of spice extracts is often higher than that of synthetic antioxidants in dependence of the medium which they should affect (water, oil) (Yanishlieva *et al.* 2006). Rosemary extracts appear to be an efficient antioxidant for dry fermented sausages (Dragojev *et al.* 2007), they suppress the lipid oxidation processes during the production of fermented sausages and cooked/dried sausages (Dragojev & Balev 2006; Rohlík *et al.* 2010).

The complicated structure of dried sausages (a rough chopped meat product) with different kinetics of colour changes in separate layers of the sausage makes it very hard to measure and evaluate these changes using classical reflectance spectrophotometry. Therefore video image analysis is used to divide the sausage into precise parts and to measure and evaluate the colour of the muscle and fat tissue particles separately applying a suitable threshold (Pipek *et al.* 2004, 2007).

The goal of this study was to evaluate the effect of natural antioxidants, namely lycopene and rosemary extract, on the oxidation of haem and paprika pigments, and lipid oxidation and colour.

MATERIAL AND METHODS

Material. Three series of model fermented paprika sausages were developed and made in a pilot plant. To accelerate oxidation processes in the sausages and to study the antioxidant properties of used additives in a shorter time line, intentionally rancid lard was added to the fermented sausages. The first and second series consisted of standard

Table 1. Raw material composition of the model paprika sausages

Raw material	Proportion of raw material (%)
Beef	6.7
Frozen lard	53.3
Lean pork	36.35
Salt mixture	2.5
Spices	1.1
Additives	see Table 2

paprika sausages to which natural antioxidant (rosemary extract) was added. The third series also consisted of standard paprika sausages some without any antioxidants and some containing either rosemary extract, lycopene or their combination.

Model paprika sausages were made of beef, pork, and back lard (Table 1). First the beef (–1°C) along with the pork were cut in a cutter until the particles were 2–3 cm in diameter. Then the starter cultures, a part of the nitrite salt mixture, and a mixture of spices containing paprika and antioxidants (rosemary extract or lycopene) were added (Table 2) depending on the produced batch. Frozen lard, which was standardised (in size and fat rancidity), was also added and cut into the meat dough until all the particles were smaller than 6 mm in diameter. During the last three turns in the cutter the second part of the salt mixture was added and thoroughly mixed into each batch.

Final sausage mixtures were stuffed into collagen casings (ø 55 mm), while the final length of each sausage was 30 cm. Stuffed sausages were put into a drying chamber (22°C, 85–90% relative air humidity) to start the fermentation process. The sausages were then stored in a dark chamber (25°C). The sausages were analysed from the fourth day of production and then further in specified intervals.

Before analysis to all the studied sausages, which were cut into slices (12 mm in thickness); one part of the sliced sausages was analysed directly after slicing and the other part was exposed to different light and temperature conditions, of which one part was exposed to light of 4100 K colour temperature at 4°C and the other part was exposed to dark at 4°C.

Table 2. Additives added to the paprika sausage

Sample		Rosemary extract (g/kg)	Lycopene (g/kg)
Control	C	–	–
Rosemary	R	0.5	–
Rosemary and lycopene	RL	0.5	0.5
Lycopene	L	–	0.5

Methods*. Colour evaluation using VIA*. The surface of the exposed slices was scanned using an HP Scanjet 5470c scanner and the images were evaluated using VIA software NIS-Elements 2.20 (Laboratory Imaging, Prague, Czech Republic). First of all it was necessary to eliminate the background and prepare the picture for a further analysis. After threshold of muscle particles their colour was measured and expressed as lightness L^*, redness a^*, yellowness b^*, mean red (I), mean green (G), and mean blue (B); the ratio of red $r = R/(R + G + B)$ and hue $h = \text{arctg}\,(a^*/b^*)$ were calculated.

TBARS. Lipid oxidation in meat samples was determined via thiobarbituric acid reactive substances following Tarladgis *et al.* (1960). The extent of lipid oxidation was determined through thiobarbituric acid reactive substances (TBARS), giving the concentration of 1,3-propandial in mg/kg of the meat sample as described by the following equation:

$$(\text{TBARS}) >> C_{\text{MA}} = 78 \times \text{A} \times n^{-1}$$

where:
78 – coefficient
A – absorbance
n – sample weight (g)

RESULTS AND DISCUSSION

Colour stability

Colour changes in the paprika salami were monitored by VIA, which enabled to evaluate these changes in muscle particles separately from fat particles. Concerning the muscle particles, in the intact sausage, they have a more complex colour than fat particles, since both haem and paprika pigments are defining their colour. The value of redness a^* of muscle particles in the paprika sausage slices increased during the storage time due to the drying process which influenced the concentration of haem pigments (Figure 1). It is also obvious that the redness is higher in samples containing the rosemary extract (R and RL) due to the capability of this antioxidant to inhibit oxidative reactions, which affects the paprika pigment.

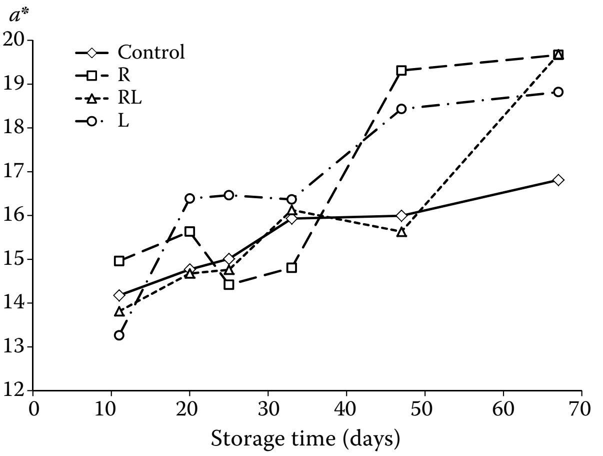

Figure 1. Redness *a** (VIA) of meat particles in the fresh cut of intact sausages during their storage in a drying chamber

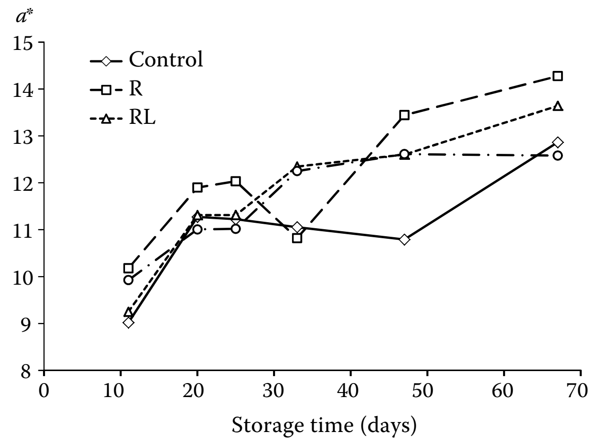

Figure 2. Redness *a** (VIA) of fat particles in intact sausages during their storage in a climate chamber

This phenomenon can be seen perspicuous in the lard particles, where the colour is ensured by the paprika pigment (Figure 2). The redness *a** of fat particles in the sausage slices, where the rosemary extract was added, had a more increasing trend, than seen in the slices of control sausage (without any antioxidants).

On the other hand the colour of slices exposed to light and air for 48 hours showed a substantial fall, due to the degradation of the haem and paprika pigments (Figure 3a). While the colour of meat particles in sausage slices exposed to light showed a remarkable decrease, the colour of meat particles in sausage slices exposed to dark was relatively stable (Figure 3b).

The redness *a** of meat particles in sausage slices, with rosemary extract and lycopene (R and L), which were exposed to light, decreased much faster than in samples without antioxidants. This might be due to the exhausted antioxidant capacity used for suppressing oxidative reactions in lard particles (see Lipid stability) of the sausage or to the overdosed concentration of these antioxidants, which may lead to prooxidative reactions. The precise reason for this phenomenon is still the subject to be examined.

Lipid stability

The stability of lipids against oxidation was supported by the rosemary extract, especially the sausage with 0.5 g/kg of the extract (R) showed lower TBARS values than lycopene and its combination with the rosemary extract. In the study of Balev *et al*. (2005) the rosemary extract was also found to be a positive antioxidant in fermented sausages and it is even considered that synergistic effects with other antioxidants might occur.

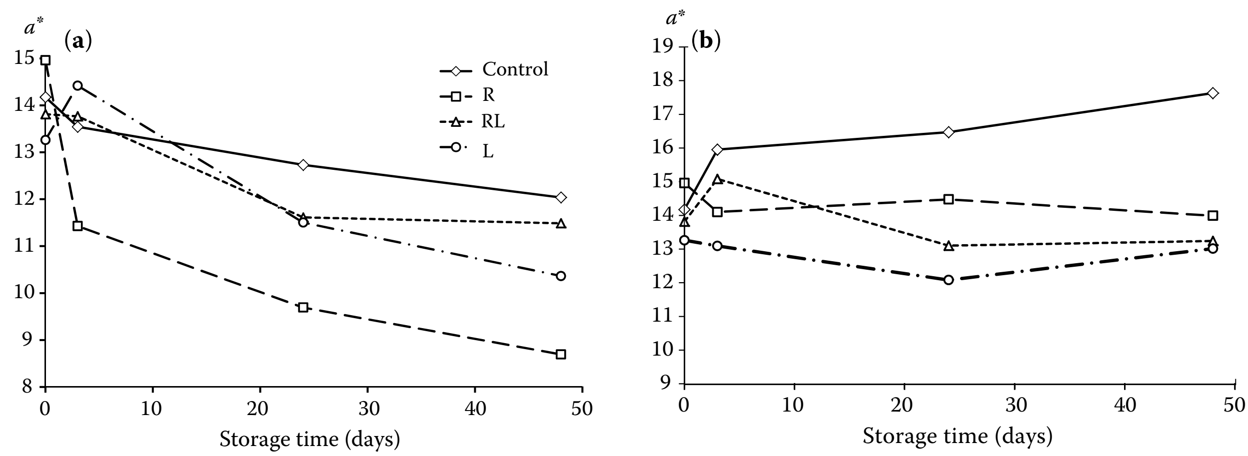

Figure 3. Redness *a** (VIA) of meat particles in sausage slices exposed to light (**a**) and to dark (**b**) at 4°C 11 days after production

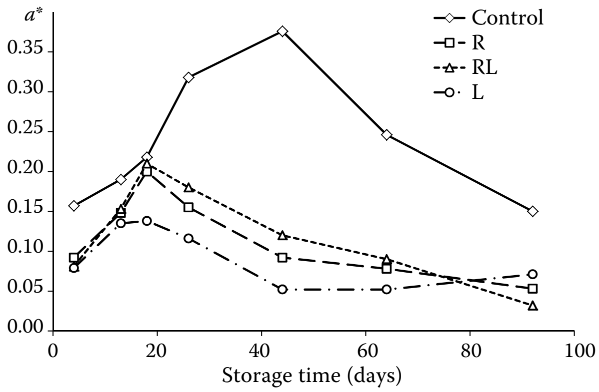

Figure 4. TBARS of paprika salami during storage time

Sausages with added lycopene (L) also showed relatively low TBARS and it could be considered that the lipid oxidation in this case was successfully reduced also in this case. The TBARS values were even lower than at the control sausage (without any antioxidants), due to the antioxidant capacity of lycopene itself (Figure 4).

The rosemary extract, as an antioxidant, experts a positive effect on TBARS values (slows down fat oxidation) in the fermented paprika salami. In samples without any antioxidants, the oxidation of fat particles was more obvious. Lycopene had also a positive effect on reducing the fat oxidation.

Interesting data were obtained by measuring the overall red coloured area, by paprika, of the lard particles. It was found that during the first approximately 20 days the red area of lard particles was increasing most probably due to the diffusion process of the lipophilic paprika colorant into the lard particles. However, during the following 40 days the overall area was decreasing (Figure 5). The bleaching process

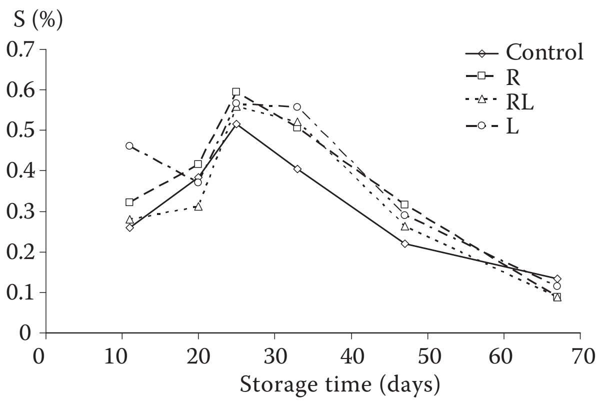

Figure 5. Size of red coloured area of fat particles (are coloured by the paprika pigment)

generally started from the middle of the lard particle and proceeded to its outer part. This mechanism might be explained by the different rates of fat oxidation and by the diffusion of both paprika colorant and lycopene.

CONCLUSIONS

Based on the above measured results, the addition of rosemary extract has positively affected the colour and suppressed the lipid oxidation in both meat and lard particles in the paprika salami. Even more satisfactory results were obtained by adding both the rosemary extract and lycopene.

Video image analysis enabled to perform colour measurements of meat and lard particles separately, which could not be done by any available method (reflective spectrophotometry). It was possible to detect the dynamics of lipid oxidation on lard particles, especially the diffusion of the paprika pigment into the lard particle and its gradual oxidation during the storage time.

References

Balev D., Vulkova T., Dragoev S., Zlatanov M., Bahtchevanska S. (2005): A comparative study on the effect of some antioxidants on the lipid and pigment oxidation in dry fermented sausages. International Journal of Food Science and Technology, **40**: 977–983.

Calvo C., Salvador A. (2008): Dry fermented sausages enriched with lycopene from tomato peel. Meat Science, **80**: 167–172.

Deda M.S., Bloukas J.G., Fista G.A. (2007): Effect of tomato paste and nitrite level on processing and quality characteristics of frankfurters. Meat Science, **76**: 501–508.

Dragojev S., Balev D. (2006): Effect of natural antioxidants on lipolysis and pH of dry-fermented sausages "Lukanka" type. In: Proceeding 52nd International Congress of Meat Science and Technology, August 13–18, 2006, Dublin, Ireland. Wageningen Academic Publishers, Wageningen: 451–452.

Dragojev S., Balev D., Vulkova-Jorgova K. (2007): Inhibition of lipid oxidation in dry-fermented sausages using rosemary extracts, In: Proceeding 53rd International Congress of Meat Science and Technology, August 5–10, 2007, Beijing, China. China Agricultural University Press, Beijing: 421–422.

Erkan N., Ayranci G., Ayranci E. (2008): Antioxidant activities of rosemary (*Rosmarinus officinalis L.*) extract, blackseed (*Nigella sativa L.*) essential oil, carnosic acid, rosmarinic acid and sesamol. Food Chemistry, **110**: 76–82.

Eyiler E., Oztan A. (2011): Production of frankfurters with tomato powder as a natural additive. LWT-Food Science and Technology, **44**: 307–311.

García, M.L., Calvo M.M., Selgas M.D. (2009): Beef hamburgers enriched in lycopene using dry tomato peel as an ingredient. Meat Science, **83**, 45–49.

Georgantelis D., Blekas G., Katikou P., Ambrosiadis I., Fletouris D.J. (2007): Effect of rosemary extract, chitosan and α-tocopherol on lipid oxidation and colour stability during frozen storage of beef burgers. Meat Science, **75**: 256–264.

Gómez R., Alvarez-Orti M., Pardo J.E. (2008): Influence of the paprika type on redness loss in red line meat products. Meat Science, **80**: 823–828.

Klieber A., Bagnato A.T. (1999): Colour stability of paprika and chilli powder. Food Australia,. **51**: 592–596.

Liu D., Shi J., Ibarra A.C., Ibarra Y., Xue S.J. (2008): The scavenging capacity and synergistic effects of lycopene, vitamin E, vitamin C, and β-carotene mixtures on the DPPH free radical. LWT-Food Science and Technology, **41**: 1344–1349.

Østerlie M., Lerfall J. (2005): Lycopene from tomato products added minced meat: Effect on storage quality and colour. Food Research International, **38**, 925–929.

Pipek P., Lojková A., Bělková B.-A., Staruch L. (2007): Analýza obrazu při hodnocení kvality masa a masných výrobků. In: Zborník XVI. Medzinárodnej konferencie LABORALIM 2007. Banská Bystrica, 7.–8. 2. 2007. STU, Bratislava: 16–21.

Pipek P., Jeleníková J., Sarnovský L. (2004): The use of video image analysis for fat content estimation. Czech Journal of Animal Science, **49**: 115–120.

Rohlík B.-A., Pipek P., Pánek J. (2010): The effect of natural antioxidants on the colour of dried/cooked sausages. Czech Journal of Food Sciences, **28**: 249–257.

Sánchez-Escalante A., Djenane D., Torrescano G., Beltrán J.A., Roncalés P. (2001): The effects of ascorbic acid, taurine, carnosine and rosemary powder on colour and lipid stability of beef patties packaged in modified atmosphere. Meat Science, **58**: 421–429.

Shi J., Dai Y., Kakuda Y., Mittal G., Xue S.J. (2008): Effect of heating and exposure to light on the stability of lycopene in tomato pureé. Food Control, **19**: 514–520.

Tarladgis B.G., Watts B.M., Younathan M.T., Dugan L. (1960): A distillation method for the quantitative determination of malonaldehyde in rancid foods. Journal of the American Oil Chemists' Society, **37**: 44–52.

Velíšek J., Hajšlová J. (2009): Chemie potravin II. 3rd Ed. OSSIS, Tábor.

Yanishlieva N.V., Marinova E., Pokorný J. (2006): Natural antioxidants from herbs and spices, European Journal of Lipid Science and Technology, **108**: 776–793.

Received for publication August 17, 2012
Accepted after corrections December 21, 2012

Corresponding author:

Bo-Anne Rohlík, Ph.D., Vysoká škola chemicko-technologická v Praze, Fakulta potravinářské a biotechemické technologie, Ústav konzervace potravin, Technická 5, 168 28 Praha, Česká republika; E-mail: bo-anne.rohlik@vscht.cz