Studies on Vitamin E and Meat Quality. 3. Effect of Feeding High Vitamin E Levels to Pigs on the Sensory and Keeping Quality of Cooked Ham

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The objective of this work was to study the influence of vitamin E (α-tocopheryl acetate) supplementation of pig diets on the time-dependent sensory quality of cured and cooked hams. Pigs were fed identical diets until they reached 45 kg live weight. From 45 to 100 kg, six control pigs received a diet containing 8 mg of α-tocopheryl acetate/kg of feed, whereas the supplemented animals received 200 mg/kg of feed. In cured and cooked hams produced from supplemented animals the α-tocopherol levels were 5-fold higher when compared to hams produced from the control animals. After 16 days of storage at 6 °C, the sensory panel detected a significant preference (95%) for the hams produced from pigs fed the supplemented diet. Hams from pigs fed the control diet were significantly more susceptible to lipid oxidation than hams from pigs fed the supplemented diet. GC−MS analyses of the volatile compounds of the cooked hams as a function of storage time (3 weeks at 6 °C and 3 months at −18 °C) indicated higher concentrations of the aldehydes and the sulfur components in the control samples compared to the supplemented samples for both storage conditions.

Keywords: *Cooked ham; vitamin E; sensory quality; volatile composition*

INTRODUCTION

Various attempts have been made to reduce lipid oxidation in fresh meats through the use of antioxidants. In pigs, high levels of vitamin E, supplemented in the animals' feed, reduced lipid oxidation, increased color stability (Buckley et al., 1989; Monahan et al., 1990; Monahan et al., 1992), and reduced drip loss (Asghar et al., 1991a,b).

Lipid oxidation is also one of the primary mechanisms of quality deterioration in cooked meat systems during storage (Monahan et al., 1990). A large number of meat volatiles have been isolated and identified in the literature (Mottram, 1991; Ho et al., 1994). The rapid oxidation of meat products following cooking and subsequent storage is a major concern of precooked meats and is recognized as "WOF" (warmed-over flavor). Development of off-flavors and unpleasant odors depends primarily on the degree of unsaturation of the lipid components of meat (Shahidi, 1989).

Meat preservation by curing involves the addition of salt, nitrite with or without nitrate, and possibly sugars, ascorbates, phosphates, and flavorings. Important work on the difference in volatile composition as a result of curing was performed by Mottram (Mottram et al., 1984; Mottram, 1984). Baloga et al. (1990) isolated volatiles from cured and cooked ham by Likens−Nickerson extraction and dynamic headspace adsorption and used an atomic emission detector for selective detection of nitrogen-, oxygen-, and sulfur-containing compounds. Recently Ramarathnam et al. (1991, 1993) used simultaneous steam distillation−extraction (SDE) and dynamic headspace adsorption for determination of the differences in the volatile composition of uncured and cured cooked pork.

The aim of this study was to evaluate the influence of feeding high vitamin E levels to pigs on the sensory and keeping quality of the resultant cured cooked hams as a function of storage time. Quality evaluations were performed by means of sensory analysis (taste panel) and instrumental techniques, such as induced TBA values and measurement of the α-tocopherol level by high-performance liquid chromatography (HPLC) and of the volatile components by means of gas chromatography−mass spectrometry (GC−MS). This study was designed to investigate the role of vitamin E for delaying oxidation after meat processing by curing and cooking.

MATERIALS AND METHODS

Animals and Dietary Treatments. Samples were obtained from a feeding trial of NV Roche Nederland with the Institute for Animal Science and Health (ID-DLO, Lelystad, The Netherlands). Preparation of the cooked hams was performed at the Department of the Science of Food of Animal Origin (VVDO, University of Utrecht, The Netherlands).

Seventy-two pigs weighing approximately 23 kg were divided into two groups of 36 animals. The pigs were fed a starter diet from 23 to 45 kg (8 mg of α-tocopheryl acetate/kg of feed). At an average weight of 45 kg, they were transferred to finisher diets. One group of 36 pigs was fed a control finisher diet containing 8 mg of α-tocopheryl acetate/kg of feed, and the other group was fed a finisher diet supplemented with 200 mg of α-tocopheryl acetate/kg of feed for at least 70 days. The pigs were fed *ad libitum.* At the end of the period, the pigs were slaughtered at a commercial slaughterhouse. The average weight of the pigs was around 100 kg.

From the fresh meat (the muscles biceps femoris, semimembranosus, and semitendinosus) of both groups, cured and cooked hams (2 hams/animal, left and right sides) were produced using multineedle brine injection. The brine composition (% w/w) was 12% nitrite salt, 3.3% phosphate for injection (Instaphos), 3.3% glucose, 0.6% sodium glutamate, and 80.5% water. No additional spices or preservatives were added. For distribution of the curing ingredients throughout the entire product the hams were tumbled for 90 min, stuffed into plastic casings (content 5 L), and vacuum pressed (vacuum bags). Hams were stored for 1 night at a temperature of 2 °C. The following day heating of the hams was performed by

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increasing temperatures step by step (differential heat treatment) until a core temperature of 70 °C was reached (Reichert et al., 1991).

Hams (right and left sides) of 6 control and 6 supplemented animals were freshly supplied. The hams of the right side were cut into thick slices of around 100 g, frozen immediately at −18 °C, and kept in the freezer at −18 °C for 2 and 3 months. Two hours before chemical analysis, samples were thawed. The hams of the left side were stored in the refrigerator for sensory analysis as a function of storage at 6 °C.

Determination of α-Tocopherol Levels. Slices of 6 control and 6 supplemented cooked ham samples were thawed. Homogenates were prepared with a domestic blender. For analysis, 15 g of each homogenate was used. Extraction of α-tocopherol from the hams was carried out according to the method by Rettenmaier and Schuëp (1992), involving a saponification step, followed by a single extraction of the resulting solution with a mixture of *n*-hexane/toluene. Extracts were injected on a Varian 9002 high-pressure liquid chromatograph (HPLC), equipped with a stainless steel (15 cm × 4.6 mm i.d.) column with Bondesil Si (5 μm) as the stationary phase. Detection and quantitative determination were performed using a fluorescence detector (Fluorichrom II, Varian) operating at excitation and emission wavelenghts of 220 and 260 nm, respectively. The mobile phase was 3% 1,4-dioxane in HPLC grade hexane at a flow rate of 1.6 mL/min. Detector signals were quantified using peak areas and a calibration curve.

Sensory Analysis. Sensory analysis was performed in an air-conditioned room with separate booths and with red light for color masking. The panel was composed principally of researchers, technicians, and students of the research center. They had not been preselected in any way. Standardized meat samples were obtained by cutting slices of equal thickness from each cooked ham. The samples were coded and the order of presentation to the panel was randomized.

A triangle test and a paired comparison test were used. The triangle test was performed to evaluate whether the panel was able to detect a difference between the hams from the control and the supplemented animals.

In the paired comparison test a control and a supplemented sample were presented and the panel had to select the sample with the freshest odor and/or taste. Results of the paired comparison test were used in statistics when the answers of the triangle test were correct.

The experiments were performed on all 6 samples over a 3 week period. There were comparisons of control and supplemented samples after 2, 9, and 16 days of storage at 6 °C. Twenty-four comparisons (4 samples from each ham) were performed on days 2 and 9; on day 16 there were 36 comparisons (6 samples from each ham).

Measurement of Lipid Oxidation. The induced lipid oxidation of the cured cooked hams was measured by the TBA test after 1 week of frozen storage. The TBA method measured a red-colored complex formed by reaction of malondialdehyde, a secondary degradation product of lipid oxidation, and thiobarbituric acid. In the induced TBA method lipid oxidation was stimulated according to a modification of the method of Kornbrust and Mavis (1980). In this method $FeSO_4$, as a catalyst for lipid oxidation, was used. To avoid oxidation proceeding too fast to be measured, the use of $FeSO_4$ in our method was omitted. The determination of the induced TBA values was carried out according to the method of Buege and Aust (1978). The induced TBA values were expressed as micrograms of malondialdehyde/gram of meat.

Measurement of the Volatile Components. Determination of the volatile components was carried out on slices of 2 control and 2 supplemented ham samples after 2 weeks of frozen storage, thawing, and 1, 7, and 14 days of storage at 6 °C. The volatile composition was also determined on slices of 2 control and 2 supplemented samples respectively after 2 and 3 months of storage at −18 °C followed by thawing and 1 day at 6 °C.

The volatile aroma compounds were isolated by Likens−Nickerson extraction (simultaneous steam distillation-extraction) using 100 g of meat (mixture of biceps femoris, semimembranosus, and semitendinosus) in 600 mL of water and 60 mL of dichloromethane as the extraction solvent. The extract was concentrated to a final volume of 0.2 mL; 1 μL of the resultant aroma concentrate was injected into the gas chromatograph.

A Hewlett-Packard Model HP5890 gas chromatograph equipped with a methyl silicone column (50 m × 0.21 mm i.d. × 0.50 μm) was used for separation of volatiles. The gas chromatograph was coupled to a HP 5971A mass spectrometer, which allowed identification of the volatile components. Analysis was carried out by using helium as carrier gas, with the column temperature maintained initially at 40 °C for 5 min and subsequently programmed from 40 to 250 °C at a rate of 5 °C/min, where it was held for 13 min. The injector and transfer line were maintained respectively at 220 and 280 °C. The ionization voltage applied was 70 eV.

Semiquantitative analysis of the different components identified in the aroma concentrates was carried out by spiking the dichloromethane with tetradecane as internal standard (10 μg). The volatile composition was calculated by relating the peak areas to the peak area of tetradecane as internal standard. Results were expressed as nanograms/gram of meat.

Statistical Analysis. The statistical significance of the difference between the α-tocopherol levels and the rate of lipid oxidation in cooked ham from control and supplemented samples was determined by ANOVA (Statgraphics). The

Table 1. Results of Tests and Levels of Significance after 2, 9, and 16 Days of Storage at 6 °C

A. Triangle Test

storage time (days)	no. of tasters	no. of correct answers	significance
2	24	11	none
9	24	11	none
16	36	20	99%

B. Paired Comparison Test (One-Tailed Test)

storage time (days)	no. of tasters	preference for supplemented sample	significance
2	11	7	none
9	11	3	none
16	20	15	95%

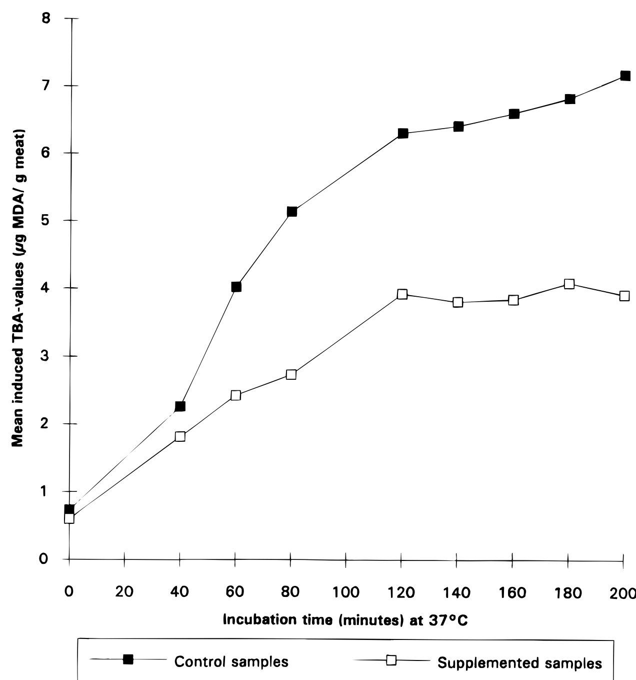

Figure 1. Mean induced TBA values ($n = 5$ samples, μg/g of meat) for control and supplemented samples as a function of forced oxidation time at 37 °C.

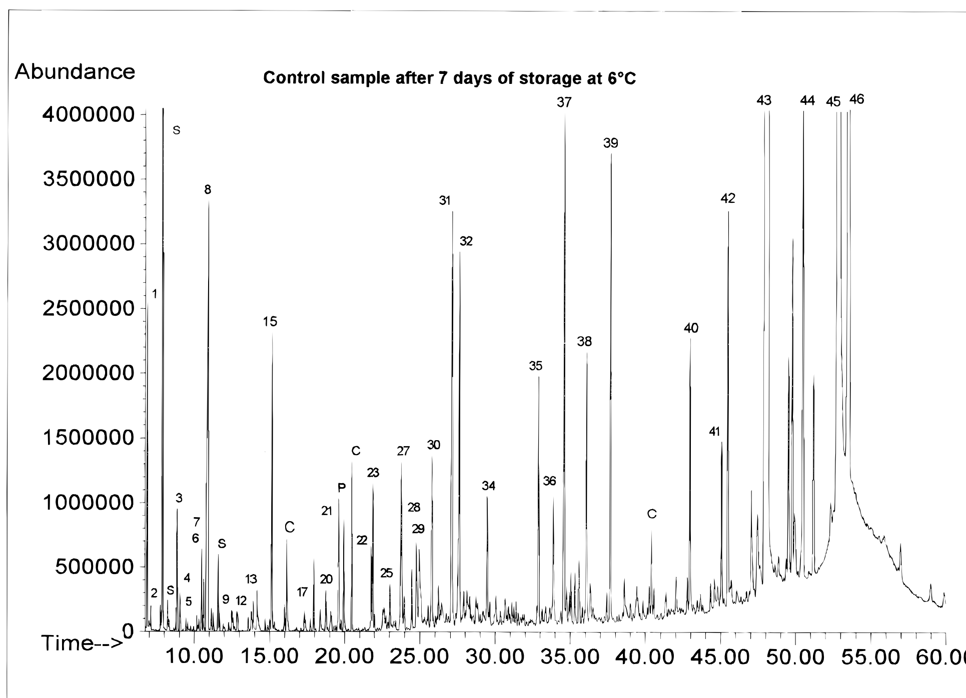

Figure 2. Typical gas chromatogram of the volatile composition of a cooked ham, produced from pigs fed the control diet, after 7 days of storage at 6 °C.

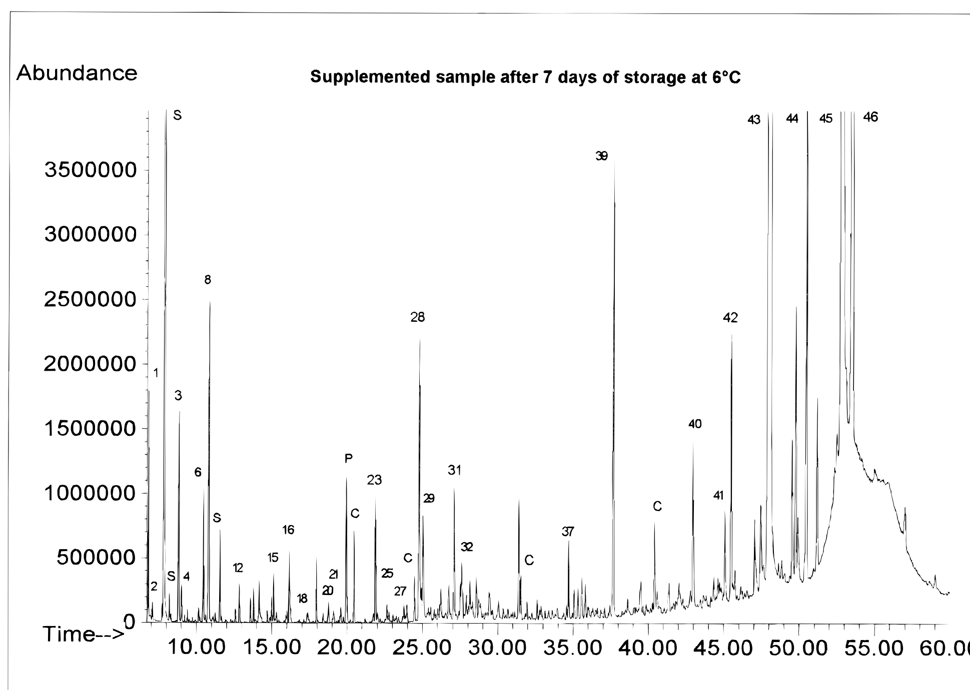

Figure 3. Typical gas chromatogram of the volatile composition of a cooked ham, produced from pigs fed the supplemented diet, after 7 days of storage at 6 °C.

significance of the sensory triangle and paired comparison tests was determined using precalculated tables (Lyon et al., 1992).

RESULTS AND DISCUSSION

The average α-tocopherol levels in cured cooked hams (n = 6 samples, 4 replicates/sample) of pigs fed the control and the supplemented diet increased from 0.54 ± 0.04 μg/g of muscle tissue to 2.87 ± 0.13 μg/g of muscle tissue, respectively, indicating a highly significant difference between both diets. The average α-tocopherol level in hams produced from pigs fed the higher dietary α-tocopherol level was approximately 5 times higher compared to the level in hams of the pigs fed the control diet. The α-tocopherol levels in the fresh meat (longissimus dorsi) increased from 1.3 to 6.7 μg/g of tissue at the higher dietary α-tocopherol level.

Asghar *et al.* (1991b) demonstrated that the deposition of α-tocopherol in the longissimus dorsi muscle of pigs was dependent upon the concentration of vitamin E in the feed. Muscle from pigs supplemented with 134 mg of α-tocopheryl acetate/kg of feed had an α-tocopherol concentration of 4.7 μg/g of tissue, while that from control pigs (6.7 mg of α-tocopheryl acetate/kg of

feed) was 0.5 μg/g of tissue. The α-tocopherol levels of the cooked hams were lower than those obtained on fresh pork. This may be due to some breakdown of vitamin E as a result of the cooking process.

In Table 1 are presented the results of the sensory analyses. Table 1A presents the number of correct answers in the triangle tests comparing control and supplemented samples as a function of storage at 6 °C. When panel members were able to indicate the different sample in the triangle test it was accepted as a correct answer. By comparing the number of correct answers to the minimum number required for significant difference at the 95 or 99% level it can be concluded that after 16 days of storage there was a highly significant difference between both types of ham. As a second part of the sensory session the panel was asked to indicate the sample with the most fresh odor and/or taste. The indications of the paired comparison tests were only used for statistical evaluation if the panel member correctly answered the triangle test. From Table 1B it is clear that after 16 days of storage the cured cooked hams from the supplemented animals had a significantly (95%) fresher odor and taste compared to the hams produced from control animals.

Determinations of induced TBA values were carried out on 5 control and 5 supplemented samples. The mean induced TBA values are presented in Figure 1 as a function of induced oxidation time at 37 °C. Ham samples from animals supplemented with vitamin E were more stable and less susceptible to lipid oxidation than those from the control ham samples. Dietary supplementation with vitamin E resulted in significantly (90%) lower induced TBA values after 80 min of incubation at 37 °C. This is in agreement with our findings on raw pork (Dirinck et al., 1996), which also indicated a significantly faster increase of lipid oxidation as a function of time after disruption of the cells for control samples compared to vitamin E supplemented samples. In comparison with the results on raw pork, induced TBA values of cooked hams reached a lower level and also the difference between control and supplemented samples was lower (Dirinck et al., 1996). This was in accordance with the fact that cooked hams have a longer shelf life compared to raw pork. From these results one may also conclude that measurement of induced TBA values is a quick method for evaluation of oxidative stability in meat and meat products.

Typical chromatograms of the volatile components isolated by Likens−Nickerson extraction from control and supplemented cured cooked hams, stored for 7 days at 6 °C, are presented in Figures 2 and 3, respectively. Comparison of the chromatograms from both types of hams indicated fewer total constituents in the aroma concentrates of samples from pigs fed supplemented levels of α-tocopheryl acetate. This was in accordance with our previous experiments on chicken meat, which demonstrated the use of GC−MS analyses for studying the effectiveness of vitamin E for delaying lipid oxidation (De Winne and Dirinck, 1996).

In cured cooked ham, 46 peaks were identified, and they are presented in Table 2. By referring the intensity of the peaks to the intensity of tetradecane as internal standard, the concentration of all identified components could be determined semiquantitatively. In Tables 3 and 4 the ham volatiles have been classified according to different chemical classes: saturated, higher, and unsaturated aldehydes; alcohols; ketones; furans; aromatics; and sulfur components.

Table 2. Identified Components in the Chromatograms of Cooked Hams Produced from Control and Supplemented Animals

peak no.	component	retention time (min)
1	diacetyl	6.9
2	2-butanone	7.1
3	1-hydroxy-2-propanone	8.8
4	3-methylbutanal	9.0
5	2-methylbutanal	9.4
6	2,3-pentanedione	10.5
7	pentanal	10.6
8	3-hydroxy-2-butanone	10.9
9	3-methylbutanol	12.5
10	2-hexanone	12.6
11	2-methylbutanol	12.7
12	1-(methylthio)propane	12.9
13	1-pentanol	13.8
14	3-hydroxy-2-pentanone	14.8
15	hexanal	15.1
16	furfuraldehyde	16.2
17	2-hexenal	17.3
18	furfuryl alcohol	17.5
19	1-hexanol	18.4
20	methional	19.1
21	heptanal	19.6
22	2-heptenal	21.8
23	benzaldehyde	21.9
24	1-heptanol	22.5
25	1-octen-3-ol	23.0
26	2-pentylfuran	23.7
27	octanal	23.8
28	benzenemethanol	24.8
29	phenylacetaldehyde	25.0
30	2-octenal	25.8
31	1,2,4-trithiolane	27.1
32	nonanal	27.6
33	benzeneethanol	27.9
34	2-nonenal	29.5
35	2-decenal	32.9
36	*cis,trans*-2,4-decadienal	33.9
37	*trans,trans*-2,4-decadienal	34.6
38	2-undecenal	36.1
39	tetradecane	37.7
40	tetradecanal	43.0
41	2-pentadecanone	45.1
42	pentadecanal	45.5
43	hexadecanal	48.1
44	heptadecanal	50.5
45	9-octadecenal	52.8
46	octadecanal	53.5
S	solvent contaminant	
P	package contaminant	
C	hydrocarbon chain	

Aldehydes were the chemical family with the highest concentration in the Likens−Nickerson extracts. A distinction could be made between the low molecular weight saturated and unsaturated aldehydes, which, due to their volatility, should influence the flavor of cured cooked ham, and the higher aldehydes, which could be precursors for the more volatile aldehydes. The straight-chain alkanals (C_5−C_9), alkenals (C_6−C_{11}) and 2,4-decadienals can be produced from oxidation of C_{18} polyunsaturated fatty acids and are typical products of lipid oxidation. Both saturated and unsaturated volatile aldehydes should be considered as the most important contributors to the oxidative rancidity of meat (Belitz and Grosch, 1987). Also 1-octen-3-ol and 2-pentylfuran increased considerably as a function of storage time and were formed as a result of lipid oxidation.

Branched-chain aldehydes, such as 2- and 3-methylbutanal, might arise from the oxidative deamination−decarboxylation of amino acids via Strecker degradation (Garcia et al., 1991), but can also be formed as byproducts during the biosynthesis of valine, leucine, and isoleucine (Belitz and Grosch, 1987). Furfural and

Table 3. Average Concentrations of the Volatile Components of Hams from Control and Supplemented Pigs after 1, 7, and 14 Days of Storage at 6 °C (Expressed as ng/g of Meat)

	day 1		day 7		day 14	
components	con[a]	sup[b]	con	sup	con	sup
Saturated Aldehydes						
3-methylbutanal	14.68	14.87	18.03	15.88	58.92	53.16
2-methylbutanal	4.29	3.64	4.85	3.18	8.42	9.10
pentanal	4.10	0.81	6.37	0.68	4.30	
hexanal	22.89	12.16	38.85	14.20	20.48	9.63
heptanal	8.12	4.04	13.44	5.82	8.27	5.49
octanal	6.05	1.52	10.47	3.32	8.68	4.36
nonanal	17.49	17.91	34.98	21.46	26.08	18.58
sum	77.59	54.94	126.98	64.53	135.13	100.31
Higher Aldehydes						
tetradecanal	23.35	24.85	21.59	26.22	23.42	33.13
pentadecanal	34.46	32.36	30.85	39.78	13.87	46.73
hexadecanal	2078.92	2176.39	2254.44	2727.06	1958.26	2907.51
heptadecanal	75.27	80.38	74.61	93.00	67.76	121.42
octadecanal	384.98	456.37	338.82	546.89	387.80	707.71
9-octadecenal	480.51	578.15	453.51	686.80	401.96	762.60
sum	3077.46	3348.49	3173.81	4119.73	2853.06	4579.09
Unsaturated Aldehydes						
2-hexenal			3.28		1.09	
2-heptenal	2.68	1.96	5.83	2.03	2.55	1.01
2-octenal	8.50	3.80	11.26	5.71	8.76	7.58
2-nonenal	7.61	0.17	9.71	3.70	6.89	4.18
2-decenal	5.39	0.80	8.47	1.24	4.90	1.86
cis,trans-2,4-decadienal	3.55		4.36		4.20	
trans,trans-2,4-decadienal	8.52		11.20	2.30	6.96	0.18
2-undecenal	6.11	0.60	8.25	0.60	6.29	0.69
sum	42.34	7.32	62.35	15.57	41.63	15.50
Alcohols						
3-methylbutanol					222.75	387.84
2-methylbutanol					46.88	69.59
1-pentanol	5.26	5.30	5.83	8.59	2.43	
1-hexanol					4.05	
1-heptanol	3.82				4.77	
1-octen-3-ol	4.90	3.35	15.19	2.91	5.94	4.81
sum	13.97	8.65	21.02	11.50	286.81	462.24
Ketones						
diacetyl	85.76	61.57	95.65	64.85	230.23	313.28
2-butanone	11.01	6.56	8.76	7.04	7.21	6.71
1-hydroxy-2-propanone	77.86	159.45	99.50	126.72	37.97	83.89
2,3-pentanedione	36.58	37.11	46.06	37.49	15.70	26.94
3-hydroxy-2-butanone	312.12	399.15	360.08	363.64	5253.28	9981.55
2-hexanone	4.29	2.95	3.83	2.82		
3-hydroxy-2-pentanone	3.00	0.87	1.54	1.32	5.95	41.34
2-pentadecanone	18.14	11.03	7.55	16.70	8.08	25.17
sum	548.74	678.67	622.96	620.56	5558.41	10478.86
Furans						
furfuraldehyde	8.83	9.38	8.87	6.95	9.51	10.77
furfuryl alcohol	2.86	4.33	4.27	5.19	2.88	4.61
2-pentylfuran	6.79	0.82	4.24	1.69	0.39	
sum	18.48	14.52	17.37	13.82	12.77	15.38
Aromatics						
benzaldehyde	23.22	18.78	20.93	19.32	13.49	10.16
benzyl alcohol	23.71	53.48	8.96	8.85	11.19	16.11
phenylacetaldehyde	27.77	26.73	29.74	25.40	17.34	17.99
benzeneethanol					13.48	17.52
sum	74.69	98.99	59.63	53.57	55.49	61.77
Sulfur Components						
1-(methylthio)-propane	8.57	9.23	11.74	10.84	9.81	10.51
methional	8.19	8.02	8.53	9.02	7.37	6.12
1,2,4-trithiolane	92.24	36.03	114.29	35.29	90.44	22.52
sum	109.00	53.27	134.56	55.14	107.61	39.14
Esters						
ethyl acetate			6.20		265.79	239.60
ethyl propanoate					4.76	
ethyl butanoate					27.87	62.02
ethyl pentanoate					1.07	6.42
3-methylbutyl acetate					1.90	8.63
ethyl hexanoate			5.16		71.97	84.48
ethyl heptanoate						6.72
ethyl octanoate					20.63	7.87
sum	0.00	0.00	11.36	0.00	393.98	415.73

[a] Control samples. [b] Supplemented samples.

Table 4. Average Concentrations of the Volatile Components of Hams from Control and Supplemented Pigs after 2, 8, and 12 Weeks of Storage at − 18 °C (Expressed as ng/g of Meat)

	week 2		week 8		week 12	
components	con[a]	sup[b]	con	sup	con	sup
Saturated Aldehydes						
3-methylbutanal	14.68	14.87	14.14	12.12	11.65	14.50
2-methylbutanal	4.29	3.64	4.14	3.11	4.19	3.91
pentanal	4.10	0.81	15.38	13.46	33.50	14.68
hexanal	22.89	12.16	109.58	115.72	284.30	158.62
heptanal	8.12	4.04	33.73	32.66	73.41	31.83
octanal	6.05	1.52	32.49	29.38	77.60	29.36
nonanal	17.49	17.91	104.70	110.39	189.95	92.02
sum	77.59	54.94	314.15	316.83	674.60	344.92
Higher Aldehydes						
tetradecanal	23.35	24.85	40.83	52.91	38.94	51.93
pentadecanal	34.46	32.36	56.06	79.49	51.57	81.38
hexadecanal	2078.92	2176.39	2626.66	3946.48	2453.11	4110.64
heptadecanal	75.27	80.38	138.40	208.40	46.76	198.53
octadecanal	384.98	456.37	717.67	1094.68	569.30	975.32
9-octadecenal	480.51	578.15	784.07	1211.16	614.65	1022.02
sum	3077.46	3348.49	4363.68	6593.11	3774.33	6439.82
Unsaturated Aldehydes						
2-hexenal			4.15	5.96	8.44	7.06
2-heptenal	2.68	1.96	15.22	17.60	33.78	17.25
2-octenal	8.50	3.80	38.90	47.90	92.88	49.82
2-nonenal	7.61	0.17	25.08	28.88	51.92	25.96
2-decenal	5.39	0.80	41.07	45.74	81.79	43.76
cis,trans-2,4-decadienal	3.55		21.72	29.93	42.01	33.94
trans,trans-2,4-decadienal	8.52		84.32	119.35	165.81	123.85
2-undecenal	6.11	0.60	39.76	46.33	73.27	41.19
sum	42.34	7.32	270.21	341.68	549.90	342.83
Alcohols						
1-pentanol	5.26	5.30	7.80	6.66	14.72	8.26
1-hexanol					7.82	3.85
1-heptanol	3.82		5.04	3.64	10.61	3.35
1-octen-3-ol	4.90	3.35	13.97	15.80	26.66	16.70
1-octanol			16.32	15.81	31.89	13.41
sum	13.97	8.65	43.13	41.91	91.70	45.57
Ketones						
diacetyl	85.76	61.57	65.65	51.21	67.69	59.54
2-butanone	11.01	6.56	6.57	5.52	5.44	6.33
1-hydroxy-2-propanone	77.86	159.45	70.51	74.69	47.38	146.15
2,3-pentanedione	36.58	37.11	34.96	33.52	25.75	58.17
3-hydroxy-2-butanone	312.12	399.15	229.25	167.52	178.00	251.38
2-hexanone	4.29	2.95	3.22	2.81	2.64	5.40
3-hydroxy-2-pentanone	3.00	0.87	1.38	0.85	1.70	1.49
2-pentadecanone	18.14	11.03	21.85	23.04	22.54	31.10
sum	548.74	678.67	433.37	359.14	351.14	559.56
Furans						
furfuraldehyde	8.83	9.38	8.87	8.73	6.07	9.91
furfuryl alcohol	2.86	4.33	3.38	3.47	1.49	5.53
2-pentylfuran	6.79	0.82	15.01	18.41	32.87	21.47
sum	18.48	14.52	27.25	30.60	40.43	36.91
Aromatics						
benzaldehyde	23.22	18.78	23.46	24.02	25.19	21.56
benzyl alcohol	23.71	53.48	33.13	33.97	35.45	35.50
phenylacetaldehyde	27.77	26.73	19.08	19.79	17.38	22.66
sum	74.69	98.99	75.67	138.98	158.88	79.72
Sulfur Components						
1-(methylthio)propane	8.57	9.23	10.91	11.20	13.96	14.95
methional	8.19	8.02	9.35	8.27	11.58	12.20
1,2,4-trithiolane	92.24	36.03	93.21	37.91	118.00	25.60
sum	109.00	53.27	113.46	57.38	143.54	52.75

[a] Control samples. [b] Supplemented samples.

furfurol are typical Maillard reaction products, which were formed from the sugars during heat treatment. Among the ketones, considerable amounts of diacetyl and 3-hydroxy-2-butanone were detected in the chromatograms. These compounds are known to impart buttery notes to food products. The aromatic aldehydes identified, benzaldehyde and phenylacetaldehyde, and the corresponding alcohols were formed from the amino acids phenylglycine and phenylalanine. Low concentrations of sulfur-containing compounds can be found in several food products and, due to their low threshold values, can significantly influence flavor. As sulfur

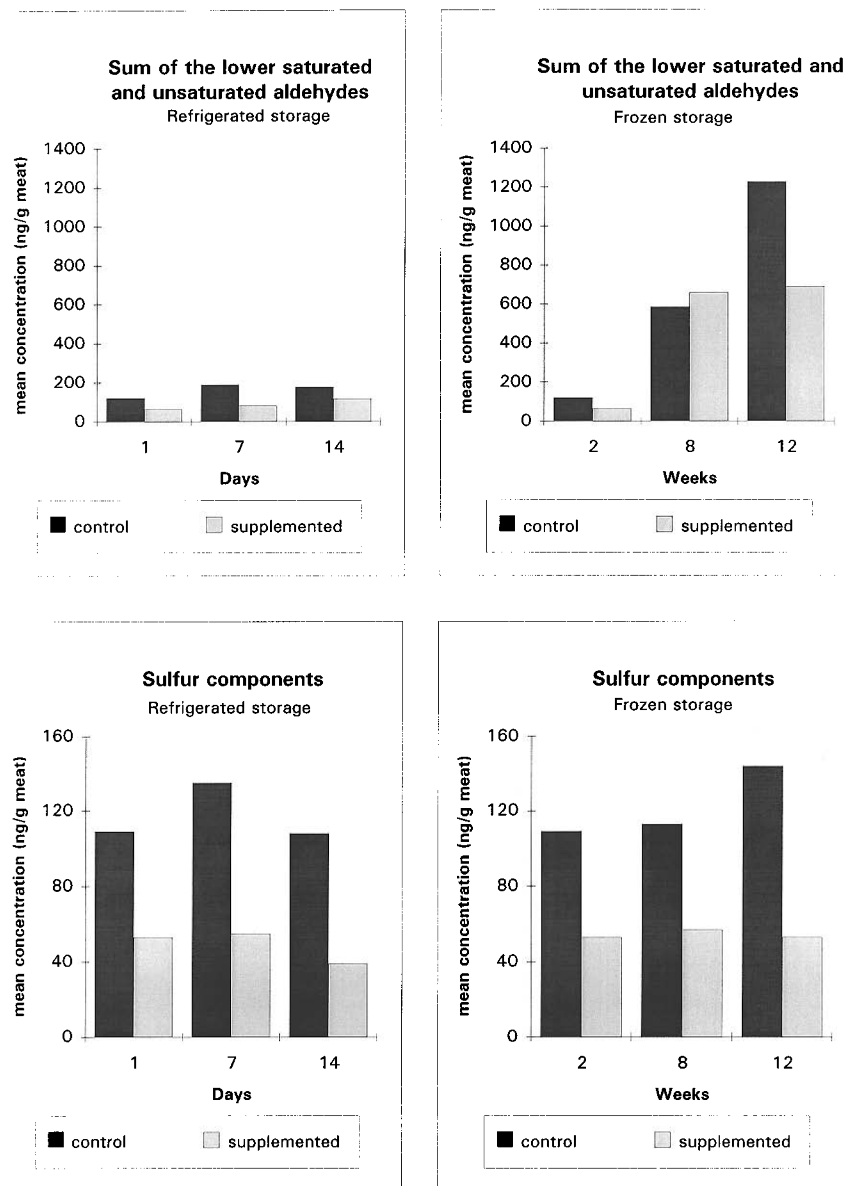

Figure 4. Sum (expressed as ng/g of meat) of the lower saturated aldehydes, the unsaturated aldehydes, and the sulfur components as a function of storage in the refrigerator (6 °C) and the freezer (−18 °C).

compounds are labile and reactive molecules, the compounds identified in the Likens−Nickerson extracts (methyl propyl sulfide, methional, and 1,2,4-trithiolane) of hams could be artifacts and should be considered as indicators for the genuine sulfur volatiles, formed from sulfur-containing amino acids (Barbieri et al., 1992).

By relating the peak intensity of the volatile compounds to the intensity of tetradecane as internal standard, the concentration of all identified compounds could be determined semiquantitatively. The volatile composition of the cured cooked hams was followed as a function of storage in the refrigerator at 6 °C (Table 3; GC−MS analyses at days 1, 7, and 14) and also as a function of storage in the freezer (Table 4; GC−MS analyses after 2, 8, and 12 weeks).

From Table 3 one may conclude that both the volatile saturated and unsaturated aldehydes were present in higher concentrations in the control group compared to the supplemented group. The increase in concentration of the aldehydes from day 1 to day 7 was greater than from day 7 to day 14. The amount of the higher aldehydes was higher in the supplemented samples compared to the control samples, suggesting that the higher aldehydes are precursors for the more volatile lower aldehydes, responsible for rancidity development. The concentration of the alcohols was higher in the control samples compared to the supplemented samples. Especially high concentrations of 3-methylbutanol and 2-methylbutanol, typical fermentation products, were formed after 14 days of storage. This was also the case for the carboxylic esters, of which ethyl acetate was the most abundant. Although cooked ham is a not fermented product, the presence of these components suggested that fermentation occurred after refrigerated storage. The concentration of the ketones (especially 3-hydroxy-2-butanone) was 10−15 times greater after 14 days of storage, probably also related to fermentation in the cooked hams. The concentration of furans and aromatics showed no clear difference between control and supplemented meat samples. The concentration of the sulfur components detected in the control samples was double compared to the concentration in the supplemented samples. Sulfur compounds are potent flavoring substances and even in small traces can contribute a great deal to the flavor of meat. According to Ramarathnam et al. (1991) these are labile constituents, which

are easily transformed into secondary products or can interact with various organic substances present in the meat system. Although the sulfur compounds identified in the Likens–Nickerson extracts could be artifacts, these compounds might be indicators for a higher degree of flavor deterioration in the control samples compared to the supplemented samples.

In Table 4 the results of the storage experiments in the freezer, which measured the volatile composition after 2, 8, and 12 weeks of storage at −18 °C followed by thawing and 1 day at 6 °C, are presented. A qualitative difference with the results in Table 3 was that no fermentation products (3-methylbutanol, 2-methylbutanol, and ethyl esters) were detected in the hams stored in the freezer at −18 °C. However, in accordance with the storage experiments at 6 °C, the compounds related to lipid oxidation and associated with the formation of rancid off-flavor (volatile saturated C_5–C_9 aldehydes, unsaturated C_6–C_{11} aldehydes, and the 2,4-decadienals) were much more important in the control samples compared to the supplemented samples. This was in accordance with the fact that the higher aldehydes were more pronounced in the hams produced from supplemented meat compared to those from control meat. Also the concentration of the sulfur components in the control hams was twice the concentration in the supplemented samples.

In Figure 4 the sums of the lower volatile saturated aldehydes, unsaturated aldehydes, and sulfur compounds are presented for the two types of cooked ham and for both storage experiments. It is visualized that the total sum of saturated and unsaturated aldehydes is far greater in the frozen samples compared to the refrigerated samples, indicating that during storage in the freezer there is a continuous increase of aldehydes as a function of time. Also these carbonyl compounds related to lipid degradation and associated with the formation of rancid off-flavors are higher in concentration in the control compared to the supplemented samples. Except at 14 days of storage at 6 °C for the control samples, a small decrease in the level of aldehydes, which are probably transformed into other products, is observed. Compared to the aldehydes, the sulfur components in the control and supplemented samples showed only slight variation as a function of storage time. However, in both storage experiments, the concentration of the volatile sulfur components in the control samples was constantly higher in comparison with the supplemented samples.

CONCLUSIONS

This work demonstrated by sensory and instrumental techniques that feeding high α-tocopherol levels to pigs suppressed lipid oxidation and had an effect on the time-related flavor characteristics of cured and cooked ham.

Sensory analyses showed that the hams from supplemented animals had a significantly fresher flavor after 16 days of storage at 6 °C compared to hams produced from control animals.

HPLC analyses showed a 5-fold increase in α-tocopherol level in hams from supplemented animals, indicating that dietary vitamin E supplementation was still effective after a curing and heat treatment process.

The sensory results were in correspondence with objective measurements such as induced TBA values for determination of oxidative stability and gas chromatography–mass spectrometry for determination of the aroma compounds. In the cooked hams from supplemented animals there was a consistent lower concentration of lipid degradation compounds responsible for rancidity development as a function of cold and/or frozen storage.

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