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Chemometric Modeling to Relate Antioxidants, Neutral Lipid Fatty Acids, and Flavor Components in Chicken Breasts

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ABSTRACT Relationships among quality factors in retailed free-range, corn-fed, organic, and conventional chicken breasts (9) were modeled using chemometric approaches. Use of principal component analysis (PCA) to neutral lipid composition data explained the majority (93%) of variability (variance) in fatty acid contents in 2 significant multivariate factors. PCA explained 88 and 75% variance in 3 factors for, respectively, flame ionization detection (FID) and nitrogen phosphorus (NPD) components in chromatographic flavor data from cooked chicken after simultaneous distillation extraction. Relationships to tissue antioxidant contents were modeled. Partial least square regression (PLS2), interrelating total data matrices, provided no useful models. By using single antioxidants as Y variables in PLS (1), good models (r^2 values > 0.9) were obtained for α-tocopherol, glutathione, catalase, glutathione peroxidase, and reductase and FID flavor components and among the variables total mono and polyunsaturated fatty acids and subsets of FID, and saturated fatty acid and NPD components. α-Tocopherol had a modest (r^2 = 0.63) relationship with neutral lipid n-3 fatty acid content. Such factors thus relate to flavor development and quality in chicken breast meat.

(*Key words*: α-tocopherol, antioxidant enzyme, free range, organic, partial least squares regression modeling)

INTRODUCTION

Essential lipids contribute to the nutritional quality of chicken, specifically n-3 polyunsaturated fatty acids (PUFA) C20:5 (eicosapentanoic acid; EPA) and C22:6 (docosahexanoic acid; DHA) (Verbeke et al., 1999; Jahan et al., 2004b). Breast meat has a healthy image, desirable flavor and texture (Barker and Bruce, 1995), and is convenient to prepare. Good flavor is considered important, and application of chemometrics to understanding food quality has been recently reviewed (Martens and Martens, 2001).

Muscle fat is a primary source of meat flavor (Mottram, 1998), and lipid composition influences muscle firmness and shelf life (Wood et al., 2004). In pig meat, triacylglycerols of neutral lipids form >99% total lipids and fatty acid contents influence flavor (Gandemer, 2002), but phospholipids also have an influence on lipid storage stability. Chicken meats with abundant unsaturated fatty acids are susceptible to oxidation, impairing flavor quality and acceptability (Rhee et al., 1996; Tang et al., 2001), as cooking yields volatile flavor components that influence sensory characteristics (Sañudo et al., 2000). St. Angelo et al. (1987) reported that n-3 PUFA are positively correlated with aroma, active secondary lipid degradation products, saturated and unsaturated aldehydes (Byrne et al., 2002), alcohols, and ketones.

Maintaining chicken quality is a challenge. Natural antioxidants can influence unsaturated fatty acids (Melton, 1990), protecting n-3 fatty acids (Huang, 1996), and dietary supplements extend shelf life (Wood et al., 2004). α-Tocopherol is particularly effective, is accepted by consumers (Sheehy et al., 1993), and has positive effects on the sensory quality of chicken meat (Opstvedt, 1984; Sheehy, 1994). Such antioxidants may protect by providing oxidative stability and reducing off-flavor development.

The term chemometrics [(Hopke, 2003), coined by Wold in 1971] is defined as use of mathematics, statistics, and formal logic to provide maximum relevant information from analysis of chemical data and is of value in food quality studies (Martens and Martens, 2001). Understanding relationships between lipid components, antioxidants, and chicken flavor requires study of influences of multiple components and possibly nonlinearities. Univariate data treatments impose selectivity and search only for linear relationships.

Abbreviation Key: DHA = docosahexanoic acid; EPA = eicosapentanoic acid; FID = flame ionization detector; FM = chicken from farmers' market; GC = gas chromatography; LD = standard/conventional; MO = organic; NPD = nitrogen phosphorus detector; PCA = principal component analysis; PLS = partial least squares regression; PUFA = polyunsaturated fatty acids; SFA = saturated fatty acids; SR = rare breed; TC = corn-fed; TF = frozen conventional; TO = organic.

TABLE 1. Fatty acid classes in the neutral lipid (NL) of chicken breast meat from different product categories (%mean + SD)

Product Code	Product category	Treatment	SFA	MUFA	PUFA	n-3	n-6	n-6/n-3
TS	Conventional	Chilled	37.77 ± 3.21	46.30 ± 1.65	15.93 ± 2.02	2.87 ± 0.83	13.06 ± 1.21	4.71 ± 0.88
MS	Conventional	Chilled	34.60 ± 2.21	46.05 ± 3.50	19.34 ± 1.38	3.21 ± 0.34	16.14 ± 1.18	5.06 ± 0.46
TF	Conventional	Frozen	35.72 ± 0.67	40.75 ± 2.96	23.54 ± 3.55	4.87 ± 1.47	18.67 ± 2.10	3.97 ± 0.68
TC	Corn-fed conventional	Chilled	30.95 ± 2.02	42.77 ± 3.72	26.28 ± 1.7	3.50 ± 0.87	22.78 ± 0.82	6.68 ± 1.42
LD	Conventional	Frozen	37.09 ± 0.63	37.45 ± 0.95	25.46 ± 0.89	2.05 ± 0.20	23.41 ± 0.71	11.48 ± 0.91
MO	Organic	Chilled	38.50 ± 1.28	36.80 ± 2.30	24.69 ± 3.57	2.23 ± 0.43	22.46 ± 3.14	10.12 ± 0.54
TO	Organic	Chilled	35.07 ± 2.06	38.14 ± 1.91	26.79 ± 2.16	2.46 ± 0.28	24.33 ± 1.88	9.93 ± 0.38
FM	Farmers' market Free range	Chilled	36.92 ± 1.8	46.45 ± 2.63	16.63 ± 3.06	1.90 ± 0.41	14.73 ± 2.65	7.79 ± 0.34
SR	Rare breed Free range	Chilled	36.06 ± 1.07	44.61 ± 1.52	19.33 ± 0.45	2.45 ± 0.75	16.88 ± 0.30	7.25 ± 2.36

Principal component analysis (PCA) seeks reduced numbers of linear combinations or factors, facilitating data interpretation (Bro, 2003) and summarizing important variations in data, and allows development and exploration of models as product spaces. Predictive modeling using partial least squares regression (PLS) (Martens and Martens, 2001) can develop relationships from calibration data and test for validity even when interference is present.

Chemometric methods offer noise reduction and detection of outliers in exploring compositional data sets used in food research by minimizing bias (Martens and Martens, 2001), but these methods can be met with skepticism when used for complex data analysis (Hopke, 2003).

The aim of the current study was to relate storage lipid fatty acids and antioxidants in breast meat to flavor volatiles in cooked chicken. An earlier report (Jahan et al., 2004a) examined total lipids and antioxidants. In this study neutral lipid composition was related to antioxidants and data on cooked chicken flavor volatiles from Likens-Nickerson extraction followed by gas chromatography. Relationships within flavor volatiles were studied using PCA, and relationships with other data sets modeled using PLS.

MATERIALS AND METHODS

Product Analysis

Nine (Table 1) raw chicken breast products with 2 or more breasts per pack were purchased from local retailers in triplicate and had the same sell-by date. Total lipids were extracted with cold chloroform:methanol (2:1, vol/vol) (Bligh and Dyer, 1959; Jahan et al., 2004b) and neutral lipids obtained by sorbent extraction (Kaluzny et al., 1985). By using capillary gas chromatography (GC), fatty acid methyl esters were identified and quantified (Christie, 1989; Jahan et al., 2004b).

Breast meat (1-cm cubes) at ambient temperature was cooked for 7 min using a microwave (800 W) and browning plate, preheated for 2 min was cooled to ambient, and then transferred to a glass simultaneous distillation extractor (Likens and Nickerson, 1964; Chaintreau, 2001). Extraction flasks (500 mL) contained chicken (80 g) in 100 mL of water, solvent (25 mL) flasks, and 10 mL of hexane. Extraction was for ≥3.5 h using an electrical heating mantle with an oil bath holding hexane at 80°C and a condenser temperature of –5°C. With oxygen-free nitrogen, hexane was evaporated, and the residue was redissolved in 20 μL of hexane. Aliquots (1 μL) were processed on a GC[2] with flame ionization detection (FID) and nitrogen-phosphorus detectors (NPD) using Carbowax 20M on a fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm) with the following temperature gradient: 40°C for 30 min, increasing by 5°C/min to 180°C; 0.5°C/min to 196°C; and 2°C/min to 240°C and held for 30 min. For NPD detection 2.7 A and 3.5 V were used to favor nitrogen detection over phosphorus compounds (Braithwaite and Smith, 1985). FID components were integrated by peak height, and NPD was integrated by area using Chromperfect software.[3]

Data Analysis and Modeling

Antioxidant and total lipids data have been reported in a previous study (Jahan et al., 2004b): α-tocopherol, glutathione, catalase, glutathione peroxidase, and reductase. Neutral lipid and flavor data determined for this modeling were subjected to 1-way ANOVA.[4]

Four quantitative data matrices were obtained: antioxidants (2 chain-breaking and 3 enzymes), neutral lipid fatty acid compositions, and GC data on 58 FID volatile flavor components and 11 NPD. Flavor variables were selected as significant ($P < 0.05$) in differences but common to all products and matrix components selected by ANOVA from 108 FID and 26 NPD peaks. Chemometric modeling used PLS1 and PLS2 protocols (Martens and Martens, 2001) in Unscrambler software.[5] Latent variables modeling with PCA and PLS estimated relevant and noise components of data (Piggott and Sharman, 1986; Kettaneh et al., 2003). In each case multivariate factors seek to explain the maximum of variance from all original variables simultaneously, and significance of successive factors is established by ANOVA (Bro, 2003). Triplicate samples were averaged for plotting after PLS assisted visualization of product spaces.

[2]Carlo-Erba 5300 gas chromatograph, Fisons Instruments, Leicester, UK.
[3]Chromperfect, Version 2, Justice Laboratory Software, Denville, NJ.
[4]MINITAB, version 11. 1, Minitab, Inc., State College, PA.
[5]Version 7.0, Camo Process A/S, Oslo, Norway.

TABLE 2. Saturated (SFA) and monounsaturated (MUFA) fatty acid components in the neutral lipid (NL) of chicken breast meat from different product categories (% mean + SD)

Product code	SFA			MUFA			
	C14:0	C16:0	C18:0	C16:1	C18:1	C20:1	
TS	1.0 ± 0.22	27.34 ± 2.9	9.43 ± 0.69	3.33 ± 0.88	38.65 ± 1.1	4.31 ± 1.7	
MS	0.96 ± 0.34	25.67 ± 1.2	8.53 ± 1.57	3.82 ± 0.86	36.88 ± 5.9	3.22 ± 1.1	
TF	0.92 ± 0.13	23.20 ± 4.3	10.19 ± 1.95	2.40 ± 1.30	30.68 ± 7.28	1.95 ± 1.12	
TC	0.85 ± 0.16	23.86 ± 2.2	7.96 ± 1.17	4.78 ± 1.6	36.93 ± 1.3	1.16 ± 0.87	
LD	1.01 ± 0.43	26.26 ± 1.9	10.17 ± 0.6	2.85 ± 0.76	31.98 ± 1.52	2.77 ± 0.23	
MO	0.52 ± 0.02	28.02 ± 0.9	9.77 ± 0.82	3.51 ± 0.04	31.89 ± 2.6	1.14 ± 0.61	
TO	0.55 ± 0.07	26.23 ± 1.9	8.29 ± 0.42	3.92 ± 0.9	32.28 ± 0.9	1.92 ± 1.12	
FM	0.72 ± 0.06	27.25 ± 2.15	8.94 ± 0.64	3.56 ± 0.87	39.38 ± 2.6	3.50 ± 1.0	
SR	0.60 ± 0.06	27.72 ± 1.27	7.73 ± 0.27	4.81 ± 0.1	36.98 ± 1.2	2.81 ± 0.28	
	C18:2 (n-6)	C18:3 (n-6)	C18:3 (n-3)	C20:4 (n-6)	C20:5 (n-3)	C22:4 (n-6)	C22:6 (n-3)
TS	11.65 ± 1.3	0.10 ± 0.06	1.35 ± 0.27	0.98 ± 0.33	0.66 ± 0.6	0.32 ± 0.06	0.85 ± 0.31
MS	15.82 ± 2.6	0.10 ± 0.04	1.71 ± 0.33	1.74 ± 1.44	0.33 ± 0.22	0.41 ± 0.46	0.76 ± 0.35
TF	13.86 ± 4.4	0.06 ± 0.05	1.32 ± 0.50	2.08 ± 0.84	1.09 ± 0.71	9.71 ± 16.02	2.5 ± 1.15
TC	18.77 ± 2.3	0.14 ± 0.08	1.84 ± 0.37	1.82 ± 0.80	0.33 ± 0.06	0.27 ± 0.11	1.27 ± 0.43
LD	19.79 ± 1.2	0.10 ± 0.04	1.38 ± 0.05	2.22 ± 0.4	0.14 ± 0.09	0.76 ± 0.14	0.51 ± 0.16
MO	19.08 ± 2.9	0.07 ± 0.02	1.62 ± 0.45	3.19 ± 1.50	0.15 ± 0.06	0.47 ± 0.07	0.52 ± 0.07
TO	20.87 ± 1.0	0.11 ± 0.01	1.68 ± 0.02	2.71 ± 0.68	0.19 ± 0.65	0.63 ± 0.17	0.58 ± 0.22
FM	12.08 ± 2.0	0.08 ± 0.05	1.02 ± 0.24	2.04 ± 1.26	0.12 ± 0.05	0.52 ± 0.20	0.75 ± 0.28
SR	14.45 ± 0.5	0.07 ± 0.007	1.24 ± 0.32	1.80 ± 0.24	0.92 ± 0.38	0.55 ± 0.04	0.29 ± 0.04

RESULTS

Neutral Lipid Composition

Classes of fatty acids were aggregated, and total contents of n-3 and n-6 PUFA and n-6/n-3 ratios were calculated (Table 1). Monounsaturated fatty acids were more abundant than saturated (SFA) or polyunsatuated (PUFA) as reported by Katz et al. (1966). For SFA [30.9% corn-fed (TC) to 38.5% organic (MO) neutral lipid], palmitic (C16:0, 23.2 to 28.0%) and stearic acids (C18:0, 7.7 to 10.2%) (Table 2) were most common (Table 1), as reported by Verbeke et al. (1999). Myristic acid (C14:0) contents were 0.52% (MO) to 1.01% conventional (LD).

For the monounsaturated fatty acids [36.8% (MO) to 46.5% (chicken from farmers' market; FM) neutral lipid], C18:1 (30.6 to 39.3%) was the most common, as also reported by Katz et al. (1966); C16:1 formed 2.4 to 4.8%, and C20:1 formed 1.1 to 4.3% (Table 2).

Polyunsaturated fatty acids [15.9% (TS) to 26.8% organic (TO) neutral lipid] were primarily n-6 fatty acids (Table 1): C18:2 was 11.7% (TS) to 20.9% (TO) (24.7% in Katz et al., 1966); and C20:4 was 1.0% (TS) to 3.2% (MO) (Table 2). The frozen conventional (TF) (4.8%) had highest total n-3 PUFA content, and farmers' market free-range FM was lowest at 1.9% (Table 1). In n-3 fatty acids C18:3 (α-linolenic) formed 1.8% in TC and 1.0% in FM then C22:6 n-3 (DHA) 2.5% (TF) to 0.3% rare breed (SR). Again FM had lowest content of C20:5 (EPA) at 0.1%, and TF was highest at 1.0%. Ratios of n-6/n-3 were from 3.9% (TF) to 11.4% (LD) (Table 1).

One-way ANOVA showed significance in differences between 2 organic (MO and TO) and 2 conventional chilled chickens (TS and MS; Table 1). The former had significantly lower (P = 0.02) contents of total n-3 PUFA, C22:6 and C14:0, but significantly (P = 0.03) higher contents of total PUFA and 2 n-6 PUFA, C18:2 and C20:4. Organic MO and TO had higher n-6/n-3 ratios (~10) than conventional chicken products (~5).

The PCA of neutral lipid data yielded 2 significant (P = 0.001; P = 0.03) factors. Plotting the first two, factors 1 and 2 (Figure 1) explained 93% of the variance; the first factor (78%) clustered conventional (TS and MS) chicken with free-range chicken (FM and SR) and was polar opposite to organic products (MO and TO) linked to a budget frozen product (LD) in the product space. The second multivariate factor (15% variance), the next explaining the most residual variance, showed no clear discrimination on the basis of product categories, and for the 2 organic products MO scored positively, and TO negatively (Figure 1).

On the first factor, total PUFA, n-6 fatty acid contents, and the n-6/n-3 ratio were correlated with the organic MO and TO and budget LD chicken (Figure 1). Polar on this factor were total MUFA and n-3 fatty acid contents linked to conventional TS and MS and free-range FM and SR chicken. On the second factor, total SFA and n-6/n-3 ratio were polar to MUFA, total PUFA, total n-6, and n-3 PUFA contents correlated with the conventional chickens TF and TC.

Flavor Volatiles Data

Chromatograms for FID (Figure 2a) and NPD (Figure 2b) yielded 108 and 26 flavor components (or peaks), respectively. Considering FID (58 common components) data initially, the first 3 multivariate factors from PCA explained large proportions (87%) of variance: 45, 24, and 18%, respectively. Plotting product scores on the first 2 factors (Figure 3) showed no clustering on the basis of category but on the first factor were discriminated the majority of conventional chickens (TS, TF, TC, LD) polar

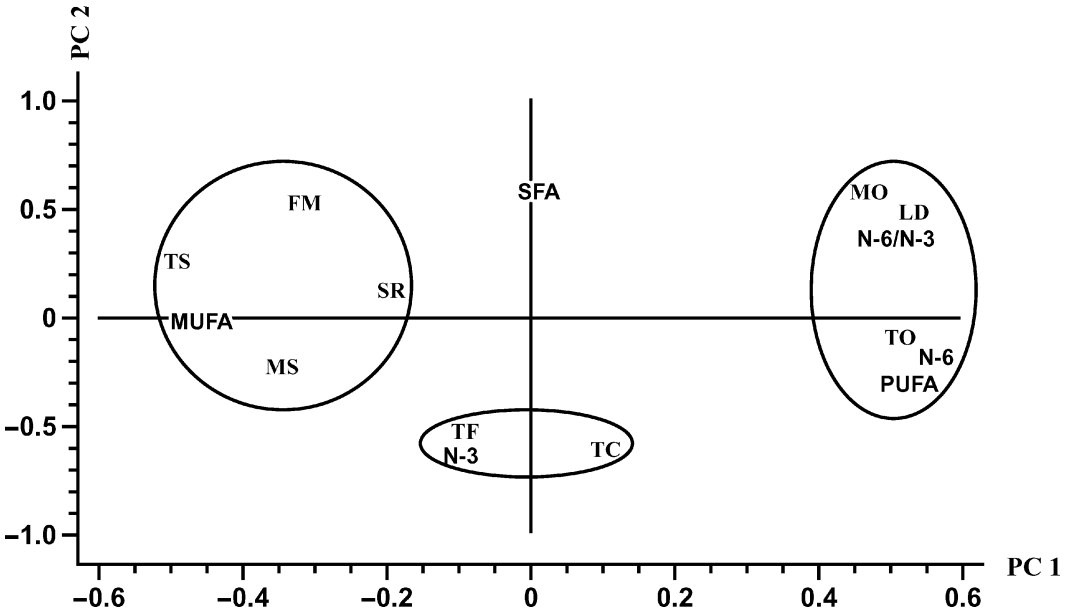

FIGURE 1. Biplot for principal component (PC) analysis product space (PC 1 vs. PC 2) of neutral lipid fatty acid composition data of chicken breasts. In this plot TS, MS, TC, LD, and TF were classified as conventional chicken breasts, TO and MO were organic products, and FM (farmers' market) and SR (rare breed) free range. TS = standard/conventional; MS = standard/conventional; TC = corn-fed; LD = conventional; TF = frozen conventional.

to a cluster of others (MO, TO, SR, FM) with MS being an outlier. Most flavor components were scored positively (39 of 58) and were correlated with conventional chicken TC and frozen TF and LD. A further 19 flavor components were scored negatively. The second multivariate factors, TC and TF, with 31 positively scored components were polarly opposed to TO and linked to 11 components, and an outlier TS was linked to 16.

Considering next the 11 common NPD flavor components, PCA explained 75% variance in 3 multivariate factors: 46, 19, and 10%, respectively. There was no clear clustering on the basis of product category. For FM, the first factor (Figure 4), TO, and TC, and MS were correlated with the majority of NPD flavor components (8) polar to conventional TS and frozen TF and LD, linked to a further 3 NPD components, and organic MO and free range SR chickens. A further 3 NPD components were correlated to the outlier MS.

Relationships Between Antioxidants and Neutral Lipid Fatty Acids

Initial PLS2 modeling, in which components of 2 matrices are extracted on the assumption of the existence of linear relationships so that information from one can be predicted from the another (Benoudjit et al., 2004), failed to show a valid relationship between data on antioxidants and neutral lipid fatty acids. Use of PLS1, in which a matrix of total antioxidant data (Table 3) was a regressor (X) and each fatty acid fraction was successively a predictor (Y), total MUFA showed $r^2 = 0.71$, and n-6/n-3 ratio $r^2 = 0.55$. The PLS1 modeling was then inverted so that fatty acid fractions became the regressor (X) and individual antioxidants were successive predictors (Y); α-tocopherol showed $r^2 = 0.67$, and glutathione showed $r^2 = 0.52$. Other antioxidants showed no valid relationship with neutral lipid fatty acid fractions (Table 3).

By using PLS1 with a matrix of n-3 fatty acid contents as a regressor (X) and individual antioxidants as successive predictors (Y), α-tocopherol had $r^2 = 0.64$. For total PUFA, n-3 and n-6 as X and individual antioxidants successively as Y, α-tocopherol yielded $r^2 = 0.59$. Thus, only α-tocopherol had a valid relationship with unsaturated fatty acids composition, notably with n-3 fatty acid contents.

Relationships Between Lipids and Flavor Components

No valid relationship was obtained between data matrices on flavor components (both FID and NPD) and fatty acids compositions (PLS2). By using PLS1, with total FID (58 components, $P < 0.05$) data as X and individual fatty acid fractions as Y, r^2 values > 0.9 were obtained, except for total SFA with $r^2 = 0.67$ (Table 4). By repeating PLS1 with the matrix of fatty acid data and single FID flavor components (58 FID components), 9 showed r^2 values > 0.5. Regressing these 9 components as X and single fatty acid fractions as Y gave r^2 values > 0.9. At $r^2 = 0.93$, the best relationship was between these 9 components as X and n-3 fatty acid content as Y (Table 4). However, (PLS 2) modeling between the matrix of these 9 FID components and that of lipid data failed to yield a valid relationship.

Again using PLS1 with the matrix of total NPD (11 components; $P < 0.05$) data as X and each fatty acid fraction as Y, total SFA showed $r^2 = 0.99$ and total MUFA $r^2 = 0.69$ (Table 4). No PUFA data showed any valid relationship. Inverting modeling with fatty acid fractions

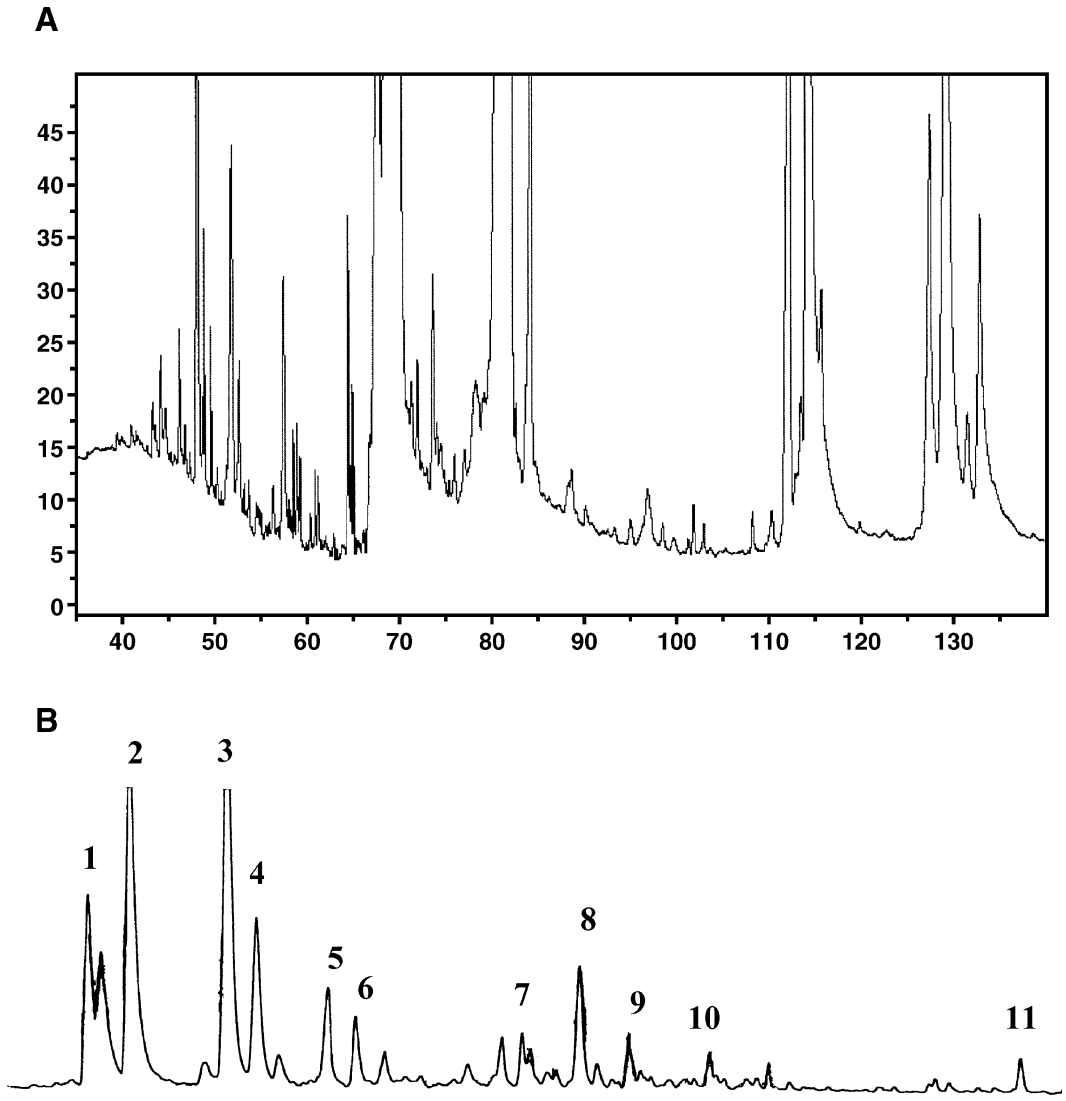

FIGURE 2. Gas chromatograms of flavor components of cooked chicken breast. A) Flame ionization detection (FID); b) nitrogen phosphorus detection.

as X and individual NPD components as successive Y only 1 flavor component (21) yielded a prediction > 0.5 at $r^2 = 0.54$ (Table 4).

Relationships Between Antioxidants and Flavor Components

No valid relationship was observed in PLS2 modeling relationships between matrices for total antioxidants and either set of flavor components (FID or NPD). Modeling with the matrix of total antioxidant data as X and each FID components (58 FID; $P > 0.05$) successively as Y, r^2 values >0.6 were obtained with a subset of 16 FID components (group I) (Table 5). A second subset (group II: 13 FID components) had $r^2 > 0.5$ and a further 9 FID components (group III) had $0.4 < r^2 < 0.5$) (Table 5). The residual 20 flavor components (group IV, not shown) showed no valid relationship with antioxidant data.

With the FID flavor component matrix as X (PLS1) and individual antioxidant as Y with flavor components, α-tocopherol gave $r^2 = 0.99$, glutathione gave $r^2 = 0.96$, catalase gave $r^2 = 0.98$, and glutathione peroxidase gave $r^2 = 0.97$.

Repeating this with the matrix of NPD flavor data as X and individual antioxidants successively as Y, only glutatione peroxidase showed $r^2 = 0.88$, and glutatione reductase $r^2 = 0.67$ (Table 5). No other antioxidants demonstrated valid relationships with NPD flavor components.

DISCUSSION

This study showed relationships between storage lipid fatty acid composition and rearing regimen and correlations between specific tissue antioxidants and flavor components of cooked chicken meat. The neutral storage lipids of the organic chickens had higher PUFA contents, notably of C18:2 n-6, as reported by Castellini et al., (2002). This result can be explained on the basis of higher wheat content of organic chicken feed, more abundant in PUFA

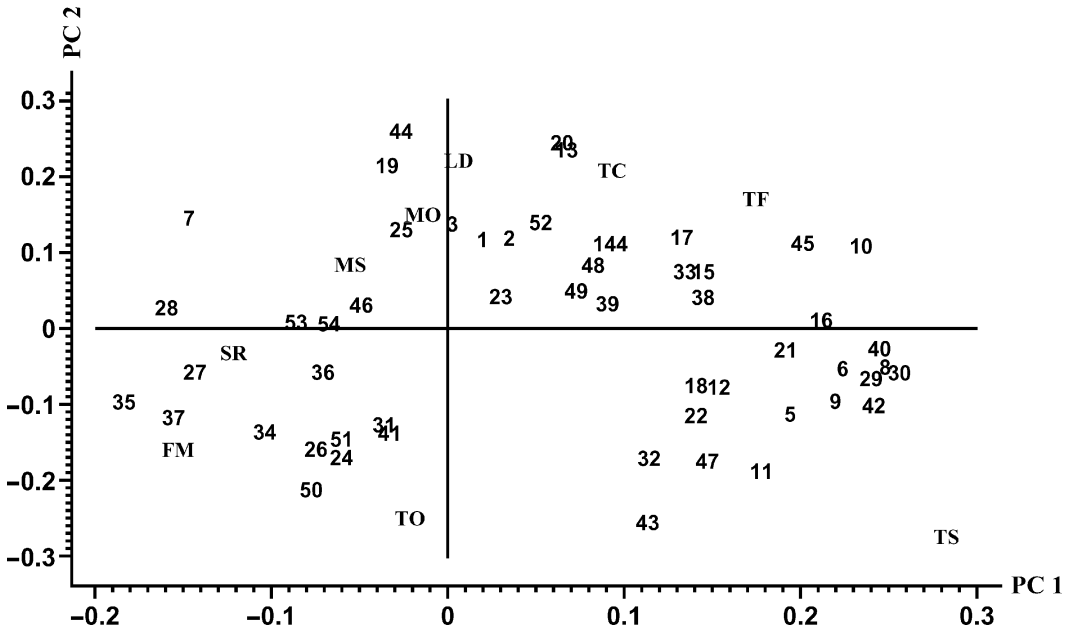

FIGURE 3. Biplot for principal component (PC) analysis product space (PC 1 vs. PC 2) of flame ionization detection (FID) of volatile components of cooked chicken breasts.Numerical representation of significant flavor components from FID. FM = free-range; LD = standard/conventional; MO = organic; MS = standard/conventional; SR = rare-breed; TC = corn-fed; TF = frozen conventional; TS = standard/conventional; TO = organic.

(32.1%) than conventional feeds (13.3 to 28.0%) (O'Keefe et al., 1995), and reflected in muscle composition (Fingenbaum and Fisher, 1959). O'Keefe et al. (1995) concluded wheat-rich feeds lead to chicken muscle accumulation of C18:2 (n-6) and a higher n-6:n-3 ratio (9.9 to 10.1) in organic chickens than in conventional chickens (4 to 5) nearer that recommended for the human diet (4 to 6; Gerster, 1998). The lower C22:6 (DHA) content of organic chicken can explained by a diet containing less (3%) n-3 rich fish meal than conventional feed (4 to 12%), which also contains vegetable oils at ~6% (O'Keefe et al., 1995; Maraschiello et al., 1998). Wood et al. (2004) concluded chicken C22:6 content was more influenced by feed components, such as fish oil, than by lipid conversions from C18:3 (n-3).

Chicken contents of myristic acid (C14:0), atherogenic with higher cholesterol-raising potential (Shand et al., 1994), at 0.5 to 1.0% neutral lipid are lower than in red

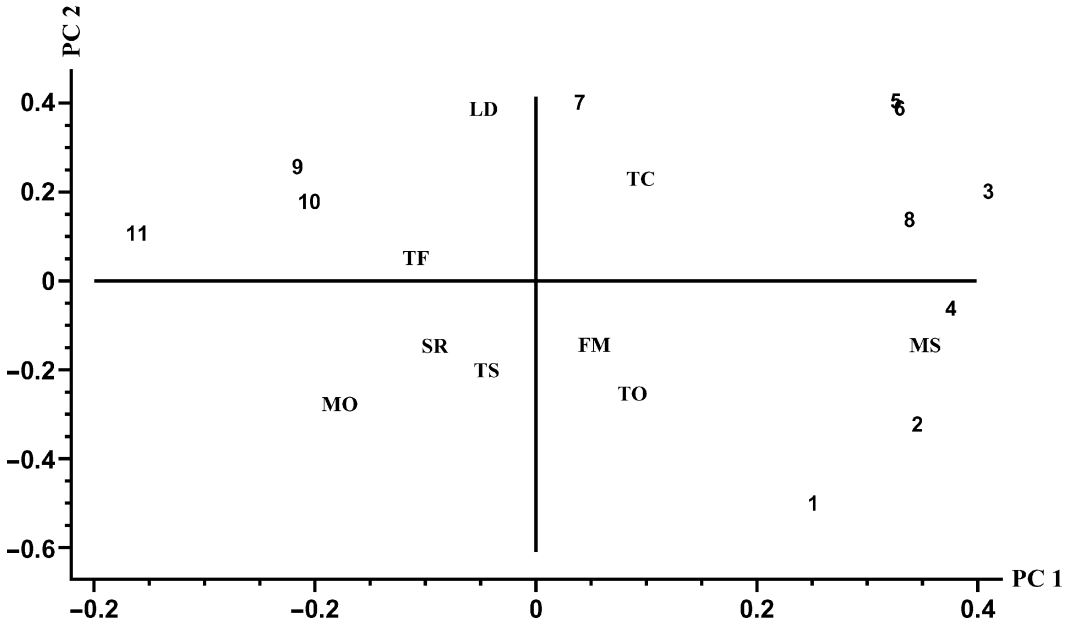

FIGURE 4. Biplot for principal component (PC) product space (PC 1vs PC 2) of nitrogen phosphorus detection (NPD) of volatile components of cooked chicken breasts. Numerical representation of significant flavor components from NPD. FM = free-range; LD = standard/conventional; MO = organic; MS = standard/conventional; SR = rare-breed; TC = corn-fed; TF = frozen conventional; TS = standard/conventional; TO = organic.

TABLE 3. Linkage (regression coefficients) of antioxidants on fatty acid fractions from partial least squares regression (PLS1) model[1]

Antioxidants (5 antioxidants)		Neutral lipid fractions (6 fractions)		n-3		Total PUFA		Total PUFA, n-3 and n-6	
SFA	NR*	α-Tocopherol	0.67	α-Tocopherol	0.64	α-Tocopherol	0.39	α-Tocopherol	0.59
MUFA	0.71	GPx	NR	GPx	NR	GPx	NR	GPx	NR
PUFA	NR	GSH	0.52	GSH	0.46	GSH	NR	GSH	0.56
n-3	0.43	GR	NR	GR	NR	GR	NR	GR	NR
n-6	NR	Catalase	NR	Catalase	0.28	Catalase	NR	Catalase	0.34
n-6/n-3	0.55								

[1]PUFA = polyunsaturated fatty acids; MUFA = monounsaturated fatty acids; NPD = nitrogen phosphorus detector; GPx = glutathione peroxidase; GR = glutathione reductase; GSH = glutathione; NR = no relationship.

meats (beef, 3.2%; lamb, 4%; and pork, 1.5%) (Verbeke et al., 1999).

In this modeling it was not possible to demonstrate valid relationships between matrices for antioxidants and neutral lipid fatty acid data using PLS 2 or between neutral lipid fatty acid composition and flavor components (either FID or NPD) and total antioxidants and matrices of either set of flavor components.

From PLS1 with a matrix as X and single Y, a small number of relationships between individual antioxidants and specific lipid fractions were valid, notably between α-tocopherol and total PUFA and total n-3 fatty acid contents. α-Tocopherol has been reported to protect tissue PUFA from oxidation (Stillwell et al., 1996) and is considered the most effective antioxidant for meat (Grau, et al., 2001; Vara-Ubol and Bowers, 2001). Valid relationships were also found between glutathione and n-3 and total PUFA (PUFA, n-3 and n-6) contents, as glutathione influences lipid oxidation, inhibiting peroxidation in rat liver microsomes (Palamanda and Kehrer, 1992). Catalase activities, as reported by Pradhan et al. (2000), did not show strong relationships with total or n-3 PUFA.

Again PLS1 showed valid relationships between certain lipid fractions and total, and subsets of FID and NPD flavor components, notably PUFA, had a very clear relationship ($r^2 = 0.96$), suggesting PUFA content was related to total FID flavor component abundance. Garnero (1982) concluded SFA contents influence development of meat flavor. Of PUFA, total n-3 had the limited influences on 9 specific FID ($r^2 > 0.5$) components. No relationships were observed between PUFA and abundance of nitrogen-rich NPD components, such as pyrazines and pyridines.

In contrast the modest relationship ($r^2 = 0.66$) between total SFA and the matrix of FID components was also as predicted by Garnero (1982). The very high correlation (r^2 of 0.98) for NPD flavor components with neutral lipid SFA content was unexpected.

α-Tocopherol had a strong ($r^2 = 0.99$) relationship with flavor (FID components) as predicted from previous research (Stillwell et al., 1996; Bou et al., 2001; Grau et al., 2001; Vara-Ubol and Bowers, 2001) as did 2 enzymic activities with the NPD components: glutathione peroxidase ($r^2 = 0.88$) and glutatione reductase ($r^2 = 0.66$).

It was tentatively possible to conclude there was clustering of products on the multivariate PCA product space for neutral lipid fatty acid data that could be related to conventional and organic production, but analysis of a larger sample set would increase confidence. However, no relationships were observed between products and rearing regimen for multivariate product spaces in either set of flavor components. It is possible that flavor components unique to specific product categories had been removed from matrices early in data processing.

Hopke (2003) has emphasized that a key role of chemometrics is identification of relationships between chemically characterized objects. In this present study specific subsets of flavor components from FID and NPD matrices were identified as related to fatty acid composition of neutral lipids and antioxidants. Such relationships would be difficult to identify using univariate analyses and facilitate flavor studies of chicken and allow targeting of flavor component identification. Sensory studies to indicate the importance of such changes in progress (Jahan et al., 2004a).

TABLE 4. Linkage (regression coefficients) of fatty acid fractions and flavor compounds [flame ionization detection (FID) and nitrogen phosphorus detection (NPD)] from partial least squares (PLS1) modeling[1]

FID (58 components) ($P < 0.05$)		FID (9 components) ($r^2 > 0.5$)		NPD (11 components) ($P < 0.05$)		All lipid fractions
SFA	(0.67)	SFA	(0.91)	SFA	(0.99)	NPD (compound 21)
MUFA	(0.93)	MUFA	(0.90)	MUFA	(0.69)	$r^2 = 0.54$
PUFA	(0.96)	PUFA	(0.90)			
n-3	(0.96)	n-3	(0.93)			
n-6	(0.96)	n-6	(0.89)			
n-6/n-3	(0.97)	n-6/n-3	(0.92)			

[1]SFA = saturated fatty acids; MUFA = monounsaturated fatty acids; PUFA = polyunsaturated fatty acids.

TABLE 5. Linkage (regression coefficients) of antioxidants on flavor compounds [flame ionization detection (FID) and nitrogen phosphorus detection (NPD)] from partial least squares (PLS1) modeling[1]

FID compounds (58 components)		Antioxidants (5)	NPD compounds (11 components)	
		Group I: ($r^2 > 0.6$)		
α-Tocopherol	0.99	(16 FID components)	GPx	0.88
		Group II: ($r^2 > 0.5$)		
GR	0.99	(13 FID components)	GR	0.67
		Group III: ($r^2 < 0.5$)		
Catalase	0.98	(9 FID components)		
GPx	0.97			
GSH	0.96			

[1]GPx = glutathione peroxidase; GR = glutathione reductase; GSH = glutathione.

Summary and Conclusions

Relationships among 3 data sets (neutral lipid fatty acids, antioxidants, and flavor components from high-resolution gas chromatography on 9 retail chicken breasts were studied using chemometrics. Organic chicken had significantly lower contents of the essential fatty acid DHA (C22:6 n-3) than conventional chicken. Examination of relationships among data with PLS revealed clear relationships among the antioxidant α-tocopherol, total PUFA, and n-3 fatty acids and also with GC flavor components from cooked chicken after FID detection. Total PUFA content and FID flavor components could be related. In contrast total SFA was related to GC flavor components from NPD detection but not FID. Two antioxidant enzymes, glutathione peroxidase and glutathione reductase had relationships with FID and NPD flavor components; glutathione had relationships with FID components only. This study demonstrates that chemometric approaches can provide important information on roles of antioxidants and lipid components in chicken flavor. Flavor components could be selected for further characterization, and relationships to sensory characteristics could be explored.

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