Gas Chromatographic and Mass Spectral Analyses of Cooked Chicken Meat Volatiles

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An odorous fraction isolated from boiling chicken meat was fractionated by capillary gas chromatography and the effluent analyzed directly by mass spectrometry. Sixty two of the approximately 227 compounds evident on the chromatogram were identified. They include sulfur compounds, aldehydes, ketones, aromatic compounds, furans, esters, hydrocarbons, alcohols, and terpenes. Only 13 of the 62 compounds have been previously reported in cooked chicken volatiles. Hence, to a major extent, the results provide new and unusual information about the number and variety of compounds that occur in cooked chicken volatiles.

Older studies carried out on the isolation and identification of volatile components of cooked chicken revealed the identity of about 20 compounds, most of them carbonyls (Pippen, 1967), but recent applications of gas chromatography in this area have revealed an ever-increasing number and variety of volatile compounds. Thus, Shrimpton and Grey (1965) found 23 volatile components and tentatively identified 15, including the sulfide, thiol, aldehyde, and ketone classes. Recent gas chromatograms by Minor *et al.* (1965b) show 25 and 30 peaks in volatiles of cooked chicken breast and leg muscles, respectively, and further characterization led to tentative identification of a variety of compounds not previously detected in cooked chicken volatiles. This suggests there is still much to be learned about the number, variety, and identity of compounds that make up the volatile or aroma fraction of cooked chicken.

Since volatile material is obtained from cooked chicken in very low yield and is chemically complex, its analysis presents unusual difficulties. One of the most successful ways to overcome some of these difficulties is to elute fractions from the gas chromatograph directly into a mass spectrometer where their mass spectra can be determined (Day and Anderson, 1965; McFadden and Teranishi, 1963; McFadden *et al.*, 1963). This report describes results of an approach of this type to the analysis of a volatile fraction isolated from cooked chicken meat.

Materials and Methods

Chickens. Ice-packed ready-to-cook fryers weighing 3 to 5 pounds were obtained from a commercial source on the day they were processed. They were then promptly bagged in polyethylene, frozen in a blast freezer at −30° F., and stored at −10° F. until used.

Isolation of Meat Volatiles. Volatiles were isolated in a batch-type operation from the meat of three fryers. The meat was separated from skin and bone of partially thawed fryers and then ground through a plate having about 3/16-inch holes. Three fryers provided about 1400 grams of ground meat. Details regarding cooking, distillation, isopentane extraction of volatiles from the distillate, and concentration of the isopentane extract have been described (Pippen and Nonaka, 1963). The odorous concentrate isolated from 1400 grams of ground meat weighed about 25 to 30 mg.

Gas Chromatography. Separations were carried out on a Perkin-Elmer Model 226 gas chromatograph. Hydrogen flame detector and injector housings were kept at 200° C. The 300-foot × 0.01-inch i.d. stainless steel column, coated with Apiezon L, was programmed from 75° to 200° C. at a rate of 2° C. per minute. Helium carrier gas inlet pressure was 30 p.s.i. At a column temperature of 75° C., laboratory fuel gas had a front time of 453 seconds and the helium flow rate was calculated to be 7.8 ml. per minute. An injector splitter ratio was used which applied about 1% of the material injected to the column. The above conditions were used to separate components in the isolated concentrate of meat volatiles and to determine the retention time of authentic compounds. When the hydrogen flame was used to detect fractions in the effluent, only 1 μl. of the isolated concentrate was injected into the gas chromatograph, but 15 μl. were injected when the gas chromatograph was coupled to the mass spectrometer.

Mass Spectrometry. Mass spectra were obtained on a Bendix Model 12 time-of-flight mass spectrometer. The conditions for operating the combined gas chromatograph and mass spectrometer were described [McFadden *et al.* (1963) and Day and Anderson (1965)]. In addition to the oscilloscopic monitoring of the gas chromatographic effluent, the positive ion at *m/e* 41 was also monitored to provide a concurrent strip chart recording (McFadden and Teranishi, 1963). Whenever a mass spectral output appeared, the time and mass spectrum were recorded on a Minneapolis-Honeywell Visicorder at a scan rate of *m/e* 24 to 200 in 2 to 4 seconds. A check on the identity of the compound indicated by the spectrum was made by comparing the component gas chromatographic retention time with that of the authentic compound when available. Not all spectra gave positive identification and in these situations the mass spectra of likely known compounds were obtained to determine their compatibility with the spectra of the component peaks. When mass spectral

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compatibility was assured, the retention time of the authentic compound had to agree with that of the peak component before it was considered identified.

Results and Discussion

Repeated isopentane extraction of the aqueous distillate of cooked chicken meat did not remove all odor from it. Furthermore, during concentration of the isopentane extract, loss of low boiling components was substantial. Therefore, the quantitative composition of the concentrate isolated must have differed substantially from that of the volatile material that distilled from the cooking chicken meat. Hence, it is not surprising that the odor of the concentrate differed from the aroma of boiling chicken meat. For similar reasons, peak sizes on the chromatograms (Figures 1 and 2), although they bear some relationship to the relative quantities of components in the concentrate isolated, do not necessarily reflect the relative quantities of components in the blend responsible for the aroma of boiling chicken meat.

Approximately 227 peaks can be counted on the 150-minute gas chromatogram (Figure 1). The peaks identified (Figure 2, numbered peaks) all fall within the first 65-minute portion of the chromatogram. There are many peaks, both large and small in this region, that could not be identified (Figure 2). This situation resulted from difficulties encountered in interpreting the mass spectrum of many of the fractions as they eluted from the gas chromatograph, such as incomplete separation of components during chromatography and a high level of interfering spectral background. A possible source of this interference was suggested by distillation of the chicken volatile concentrate. Distillation (for 30 minutes at 40° C. and 0.04 torr) removed odorous constituents without distilling the bulk of the concentrate. Conceivably, the continuous bleeding of this high boiling material from the chromatographic column was responsible for the spectral background which progressively increased during the chromatogram until, after about 65 minutes, the spectra could no longer be interpreted.

In spite of these difficulties, approximately 62 compounds were identified (Table I). In 31 instances, interpretation of the mass spectra left little, if any, doubt about the identity of the compound ["positive" spectral identifications (Table I)]. In all of these cases, the retention times of the compounds identified by mass spectrometry agree reasonably well with the retention times of the corresponding authentic compounds (Table I). In the remaining 31 instances, interpretation of the mass spectra involved left some doubt about the identity of the compound ["tentative" spectral identifications (Table I)]. But even in this tentative category, the retention time of the compound identified agrees reasonably well with the retention times of the corresponding authentic compounds in the 23 instances out of 31 in which the authentic compounds were available (Table I). This leaves only eight compounds out of 62 whose identity is supported solely by mass spectral data.

The sulfur compounds (Table I) are of particular interest, because their importance to cooked chicken

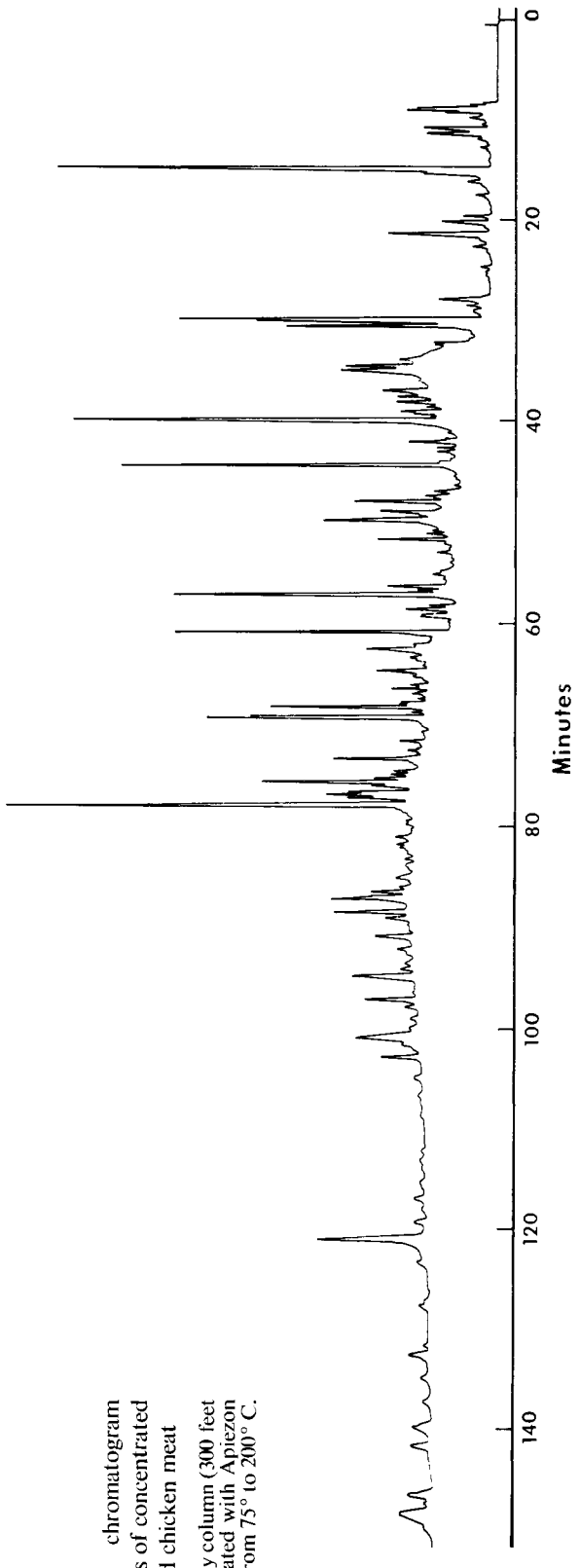

Figure 1. Gas chromatogram through 150 minutes of concentrated volatiles from boiled chicken meat

Stainless steel capillary column (300 feet × 0.01 inch) was coated with Apiezon L, and programmed from 75° to 200° C. at 2° C. per minute

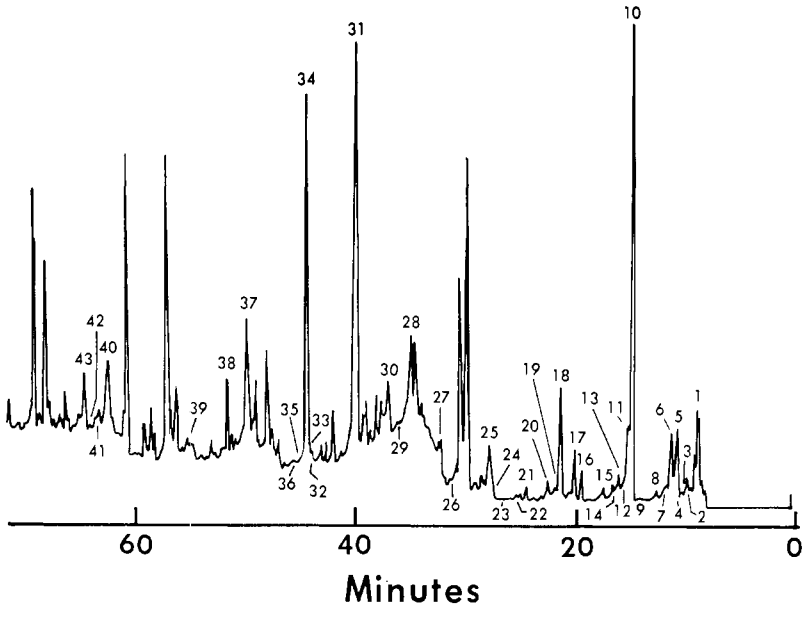

Figure 2. Enlarged portion of gas chromatogram showing numbered peaks identified

Table I indicates relationship between numbered peaks and compounds identified

flavor has been emphasized recently by Minor *et al.* (1965b). In this study only three (methyl and ethyl mercaptan and methyl disulfide) of the 13 sulfur compounds reported by Minor *et al.* (1965b) were identified; also, the four others listed in Table I were found.

Only 9 of the 23 carbonyl compounds identified (Table I) were previously reported in cooked chicken volatiles and a tenth, 2-methyl-1-butanal, was reported in turkey volatiles by Hrdlička and Kuča (1965). It is not surprising to find saturated and unsaturated aliphatic aldehydes and 2-alkanones, because compounds like them have been previously reported in cooked chicken volatiles (Minor *et al.*, 1965b; Pippen *et al.*, 1958; Pippen and Nonaka, 1960). But there seems to be no precedent for carbonyl compounds like methyl vinyl ketone, ethyl vinyl ketone, 3-octanone, 5-undecanone, phenyl propionaldehyde, and *n*-propyl benzaldehyde in cooked chicken volatiles.

With a few exceptions, the aromatic and furan compounds are *n*-alkyl homologs (Table I). The aromaticity of the alkyl benzenes was readily determined on the mass spectrometer. But positive mass spectral identification of the furans presented difficulty because their spectral patterns were much like those of the 2,4-dienals (Black *et al.*, 1967).

Finally, the alcohols, esters, and aliphatic hydrocarbons identified (Table I) are unlike any previously reported in cooked chicken (Minor *et al.*, 1965b). Furthermore, no member of the terpene class has previously been reported in cooked chicken volatiles.

On the chromatogram (Figure 1, at about 70 minutes), there is a fairly large peak whose retention time is nearly identical with that of authentic 2-*trans*-4-*trans*-decadienal. The dienal could not be identified by mass spectrometry because its retention time fell in an area where the spectra could not be interpreted. Studies on the oxidation products of this aldehyde have revealed the presence of *p*-xylene, *n*-propyl- and *n*-butylbenzene, and *n*-butyl and *n*-pentyl furan (Nonaka and Black, unpublished data). Hence, it is possible that 2,4-decadienal and compounds similar in structure are precursors of the aromatics and furans we detected in chicken volatiles.

Heyns *et al.* (1966) have shown that 100 compounds, including a variety of aromatic, furan, and carbonyl compounds, are formed when pure glucose decomposes at 300° C. Hence, it is conceivable that glucose in chicken muscle decomposes during cooking to form some of these compounds. Of course, it seems unlikely that glucose in chicken muscle boiled at 100° C. would decompose at the same rate or extent as pure glucose when heated to 300° C. On the other hand, thermal degradation of glucose might proceed to a considerable extent at the higher temperatures (163° C. and up) and drier conditions that prevail during roasting and frying.

There is no particular reason to suspect that some of the compounds identified represent artifacts of contaminants, but neither can one exclude these possibilities. Artifact formation during concentration of the isopentane extract and during chromatography is a possibility. Conceivably, the chicken could have become contaminated with trace compounds before it reached our laboratory. Hence, further information will be needed to determine whether any of the compounds identified represents artifacts or contaminants.

The isopentane used for extraction would seem the most likely source of contamination in the laboratory, but it was excluded because no contaminants were seen in it when an amount of isopentane equivalent to that used in the extraction of chicken volatiles was evaporated to about 100 μl. and chromatographed. Similarly treated isopentane was not analyzed mass spectrally because there seemed little chance that the less sensitive mass spectral detector would find contaminants where the more sensitive hydrogen flame had failed.

Table I. Volatile Compounds of Boiled Chicken Meat Identified by Gas Chromatography and Mass Spectrometry

Compounds	Peak No. (Figure 2)	Retention Time, Minutes: Of peak (Figure 2)	Retention Time, Minutes: Of authentic compound	Mass Spectral Identification	References to Prior Detection in Poultry
Sulfur compounds					
Carbonyl sulfide	1	8.8	8.9	Positive	
Methyl mercaptan	2	9.3	9.1	Positive	Minor *et al.*, 1965a
Ethyl mercaptan	3	9.8	9.6	Tentative	Minor *et al.*, 1965a
1,2-Ethane dithiol	4	10.0	10.0	Tentative	
Carbon disulfide	5	10.2	10.0	Positive	
Methyl disulfide	9	13.7	13.5	Positive	Minor *et al.*, 1965a
2-Methyl thiophene	13	15.5	15.5	Positive	
Aldehydes					
Acetaldehyde	1	8.9	8.8	Positive	Minor *et al.*, 1965a, b; Pippen, 1967; Pippen and Nonaka, 1960
1-Butanal	2	9.4	9.3	Tentative	Pippen, 1967; Pippen and Nonaka, 1960
2-Methyl-1-butanal	6	10.4	10.3	Positive	
1-Pentanal	7	11.5	11.2	Positive	Minor *et al.*, 1965a, b; Pippen, 1967; Pippen and Nonaka, 1960
1-Hexanal	10	14.5	14.5	Positive	Minor *et al.*, 1965a, b; Pippen, 1967; Pippen and Nonaka, 1960
Branched heptanal (?)	12	15.2	Not available	Tentative	
1-Heptanal	18	20.3	20.1	Positive	Pippen and Nonaka, 1960
2-Hepten-1-al	21	24.6	Not available	Tentative	Pippen, 1967; Pippen and Nonaka, 1960
1-Octanal	25	27.2	27.8	Positive	Minor *et al.*, 1965b; Pippen, 1967; Pippen and Nonaka, 1960
Phenyl propionaldehyde	31	39.5	38.6	Tentative	
n-Propyl benzaldehyde	35	45.4	Not available	Tentative	
1-Tridecanal	41	63.1	64.5	Tentative	
Ketones					
Methyl vinyl ketone	2	9.4	9.6	Tentative	
2-Butanone	2	9.4	9.4	Tentative	Minor *et al.*, 1965b; Pippen, 1967
2-Pentanone	7	11.5	11.5	Tentative	Pippen and Nonaka, 1960
Ethyl vinyl ketone	7	11.5	11.5	Tentative	
2-Heptanone	16	19.0	19.3	Positive	Pippen and Nonaka, 1960
2-Methyl-6-heptanone	21	23.2	23.0	Positive	
3-Octanone	22	25.2	25.2	Positive	
2-Octanone	23	25.7	24.9	Positive	
2-Nonanone	28	34.3	34.3	Positive	
2-Decanone	32	43.2	42.5	Positive	
5-Undecanone	37	51.6	51.1	Tentative	
Aromatic compounds					
Benzene	7	11.6	11.4	Positive	
Toluene	11	15.0	15.0	Positive	
m-Xylene	17	19.5	19.5	Positive	
p-Xylene	19	20.6	20.0	Positive	
o-Xylene	20	22.4	21.7	Positive	
n-Propylbenzene	23	25.9	27.0	Positive	
1,2,4-Trimethylbenzene	26	31.0	30.8	Positive	
n-Butylbenzene	28	34.7	35.3	Positive	
n-Amylbenzene	33	43.7	44.0	Positive	
n-Hexylbenzene	38	53.0	52.7	Positive	

Table I. Continued

Compounds	Peak No. (Figure 2)	Retention Time, Minutes: Of peak (Figure 2)	Retention Time, Minutes: Of authentic compound	Mass Spectral Identification	References to Prior Detection in Poultry
n-Heptylbenzene	40	62.0	63.0	Tentative	
2-Methyl naphthalene	42	63.6	64.9	Tentative	
Furans					
2-Methyl furan	5	10.2	9.9	Tentative	
2-Ethyl furan	7	11.6	11.3	Tentative	
2-*n*-Propyl furan	14	16.6	15.5	Tentative	
2-*n*-Butyl furan	17	19.5	19.6	Positive	
2-*n*-Pentyl furan	24	26.2	26.2	Positive	
2-*n*-Hexyl furan	29	36.0	35.8	Tentative	
2-*n*-Heptyl furan	34	44.2	44.3	Tentative	
Esters					
Methyl acetate (or ethyl formate)	2	9.3	9.1	Tentative	
Methyl-2,4-pentadienoate	13	15.5	Not available	Tentative	
Hydrocarbons					
3-Pentene-1-yne	3	9.8	Not available	Tentative	
n-Heptane	8	12.0	11.3	Positive	
4-Octyne	15	16.3	16.3	Tentative	
n-Undecane	30	37.0	36.0	Tentative	
n-Tridecane	39	54.7	53.5	Tentative	
n-Tetradecane	40	62.0	62.0	Tentative	
Alcohols					
2-Propyn-1-ol (propargyl alcohol)	1	8.9	8.9	Tentative	
1-Methyl-2,3-dihydroxyindane[a]	36	45.6	Not available	Tentative	
Terpenes					
d-Limonene	27	32.6	32.5	Positive	
Terpene (mass 152)	37	51.6	Not available	Tentative	
Oxygenated terpene (mass 194)	43	63.8	Not available	Tentative	

[a] Or 4-methyl-2,3-dihydroxyindane.

Conclusions

The volatile compounds of cooked chicken are evidently greater in number and more varied in type than previously supposed. Furthermore, a vast majority of them are apparently still unidentified. Hence, the extremely complex nature of the gross volatile fraction indicated by this study suggests that it may be impractical to try to identify all the volatile compounds of cooked chicken and determine the contribution of each to aroma on a nondiscriminatory basis. Additional studies, more selective in nature, are needed to confirm, consolidate, and extend our knowledge in this area.

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