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Title: POROUS POLYMER TRAPPING FOR GC/MS ANALYSIS OF VOLATILE FLAVOR COMPOUNDS IN CORN

Abstract approved: _____

Dr. Max E. Morgan

Flavor profiles of canned and frozen whole kernel sweet corn were obtained by entraining the volatile compounds on Porapak Q traps and by subsequent analysis on temperature-programed, 500' by 0.03" ID capillary columns (SF-96 or Carbowax 20M). Identification was based on GC/MS data, retention indices (I_E's) and retention times. The new compounds identified in canned corn included pyridine, methional, dimethyl sulfoxide and dimethyl sulfone. Various sulfur, nitrogen and nitrogen-sulfur heterocyclic compounds were also present as previously mentioned by Libbey et al. (1). Qualitative and quantitative varietal differences were observed in both frozen and canned samples. Many of these compounds were typical of roasted foods, such as nuts or roasted meats, and were not found to any extent in samples of frozen or fresh corn. New compounds found in frozen corn included acetoin, 3-methyl-2-cyclohexenone and dimethyl sulfone. Various model systems were heated to simulate the canning process of sweet corn. Mixtures of water, sugars and sulfur-containing amino acids produced the most corn-like aromas. Systems containing glutamic acid, asparagine, proline, aspartic acid and other amino acids produced earthy, parsnip or vegetable notes. Pyrazines, furans and thiophenes were among the compounds identified. Other experiments were conducted to elucidate mechanisms of flavor formation and to simulate sweet corn flavor.

(1) Libbey, L.M., M.E. Morgan, L.A. Hansen and R.A. Scanlan. Higher-Boiling Volatiles in Canned Whole Kernel Sweet Corn. A.C.S. Meeting Atlantic City, N.J. 1975.

Porous Polymer Trapping for GC/MS Analysis of

VOLATILE FLAVOR COMPOUNDS IN CORN

by

Alayne Linda Boyko

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TABLE OF CONTENTS

POROUS POLYMER TRAPPING FOR GC/MS ANALYSIS OF
VOLATILE FLAVOR COMPOUNDS OF CORN

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Flavor profiles of canned and frozen whole kernel sweet corn were obtained by entraining the volatile compounds on Porapak Q traps and by subsequent analysis on temperature-programed, 500' x 0.03" ID capillary columns (SF-96 or Carbowax 20M). Identification was based on GC/MS data, retention indices (I_E's), and retention times. The new compounds identified in canned corn included pyridine, methional, dimethyl sulfoxide, and dimethy sulfone. Various sulfur, nitrogen, and nitrogen-sulfur hetero-cyclic compounds were also present as previously mentioned by Libbey et al. (1). Qualitative and quantitative varietal differences were observed in both frozen and canned samples. Many of these compounds were typical of roasted foods, such as nuts or roasted meats, and were not found to any extent in samples of frozen or fresh corn. New compounds found in frozen corn included acetoin, 3-methyl-2-cyclohexenone, and dimethyl sulfone. Various model systems were heated to simulate the canning process of sweet corn. Mixtures of water, sugars and sulfur-containing

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zines, furans, and thiophenes were among the compounds identified.
Other experiments were conducted to elucidate mechanisms of flavor
formation and to simulate sweet corn flavor.

I. INTRODUCTION

The analysis of vegetable flavor has been the subject of many
studies during the last 20 years. Isolation and identification of
volatile compounds present in trace quantities in vegetables has
been greatly facilitated by the advent of GC, GC/MS, and head-
space techniques. Salunkhe and Do (1) reviewed the biogenesis
of aroma constituents of fruits and vegetables and stated that
these products have genetically controlled, characteristic
flavors. The cultivar, maturity, and horticultural practices
also influence aroma. They concluded that much more research is
needed to elucidate the processes of aroma formation and degrad-
ation in vegetables in order to develop means to control the
production of flavor, to maintain the flavor produced, and to
improve the flavor of these products.

The relative quantities of low-boiling compounds present in
cooked sweet corn were measured by Self et al. (2) using GC. High
levels of dimethyl sulfide, hydrogen sulfide and acetaldehyde,
and low levels of methanethiol, ethanethiol, acetone and methanol
were found. Bills and Keenan (3), Williams and Nelson (4), and
others have emphasized the significance of dimethyl sulfide in
the top note of sweet corn flavor. More recent work by Ishii (5)
identified ethanol, butanol, pentanol, cis-3-hexene-1-ol, hexanal,
limonene, 2,3- 2,5- and 2,6-dimethylpyrazine, and α- and β-ionone
as the main flavor constituents of corn powder. Loss of low-
boiling compounds and increase of hexanal; trans, trans-3,5-
octadiene-2-one; trans, trans-2,4-heptadienal; trans, cis-2,4-

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and _trans_, _trans_-2,4-decadienal were reported to cause off-flavor
of sweet corn powder. These researchers used temperature-pro-
gramed capillary columns coated with SF-96 and headspace techniques.

In our laboratory we have used headspace sampling and porous
polymer trapping techniques. Earlier work by Libbey et al. (6)
indicated the presence of dimethyl sulfide, acetaldehyde, methyl
acetate, methanol, acetone, ethyl acetate and ethanol by on-column
trapping. Extremely volatile compounds such as hydrogen sulfide,
dimethyl sulfide or methyl mercaptan were lost during trapping. Temper-
ature-programed, 500 ft x 0.03 in ID capillary columns wall-coated with
Carbowax 20M were used to investigate canned corn aroma. A series
of alkyl pyrazines was detected and because of their low threshold
values, were thought to contribute significantly to the background
flavor of canned corn. Diacetyl was reported for the first time.
Diacetyl and other α-dicarbonyls were believed to be important
both as flavoring agents per se and as participants in Strecker degra-
dation reactions. Numerous other compounds were characterized in
several GC/MS runs, including alcohols, methyl ketones, furans, etc.
These were thought to be minor contributors to canned corn flavor.

II. EXPERIMENTAL

In our sampling procedure, 50 ml of vegetable liquor was
decanted into a screw-cap, 100 ml bottle equipped with a magnetic
stirrer (Figure 1). Corn liquor was taken directly from the can-
ned samples and saturated with Na_2SO_4. Frozen samples (375 g) were
thawed with 100 ml of hot distilled water and allowed to sit overnight
at refrigerator temperature before the liquor was removed. The
entrainment assembly was held at $60^{\circ}C$ with a water bath. Volatile
organic compounds were entrained using prepurified N_2 at 30 ml/
min for 30 min or longer. The nitrogen entrainment gas was
purified by passage through a 20 ft x 0.25 in OD firebrick trap
immersed in a Dry Ice-2-methoxyethanol slurry. The N_2 swept the
volatile compounds onto a porous polymer precolumn trap. The

Precolumn

Entrainment Gas In
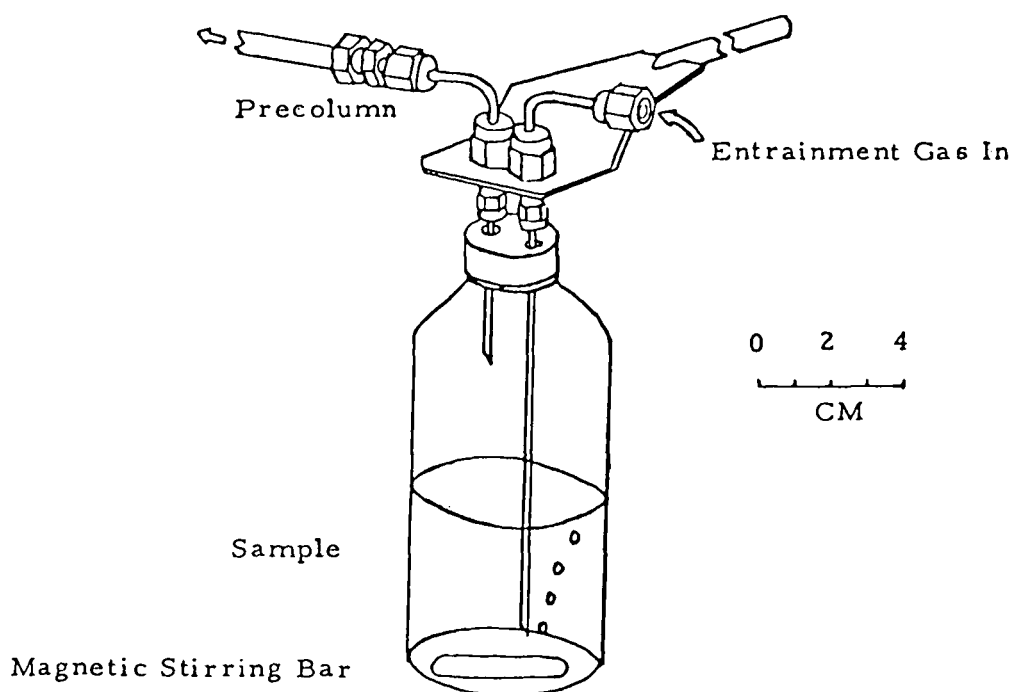
0 2 4

CM

Sample

Magnetic Stirring Bar

Fig. 1. Entrainment assembly

trap was 4 in x 0.24 in ID packed with 100/120 mesh Porapak Q, 100/120 mesh Chromosorb 102, or 60/80 mesh Tenax GC. Selection of a particular porous polymer depended on the application and will be discussed later. The precolumns were previously con- ditioned by purging with prepurified N_2 at a flow rate of 30 ml/ min--first for 4 hr at 200^OC, and finally for 12 hr at 100^OC. During the 30-min entrainment process the precolumn was main- tained at 55^OC. This prevented water condensation in the trap and subsequent water interference in the analysis. After entrain- ment the polymer trap was removed from the entrainment assembly and a solution of several ethyl esters in ethanol was applied to the upstream end of the precolumn. Ethyl esters were used in calcu- lating I_E values as discussed by Van Den Dool and Kratz (7). When working with polar compounds, ethyl esters were a more useful retention index system than the Kovats index which utilized non-

polar hydrocarbons as reference compounds. The trap was next purged with prepurified N_2, in the same direction as before, at 30 ml/min for an additional 20 min to remove any residual water. Excessive purging resulted in loss of low-boiling compounds.

The compounds on the precolumn were transferred to a capillary U-tube trap by reversing the precolumn, raising its temperature to 135°C and reducing the N_2 flow to 12 ml/min for 45 min. The 10 in X 0.03 in ID stainless steel, Dexsil-coated U-tube trap was immersed in a slurry of Dry Ice and 2-methoxyethanol during trapping. Such U-tube traps could be stored about a week in a freezer without sample loss. The volatile compounds were then flashed onto the GC and GC/MS using the inlet system described by Scanlan et al. (8) and pictured in Figure 2.
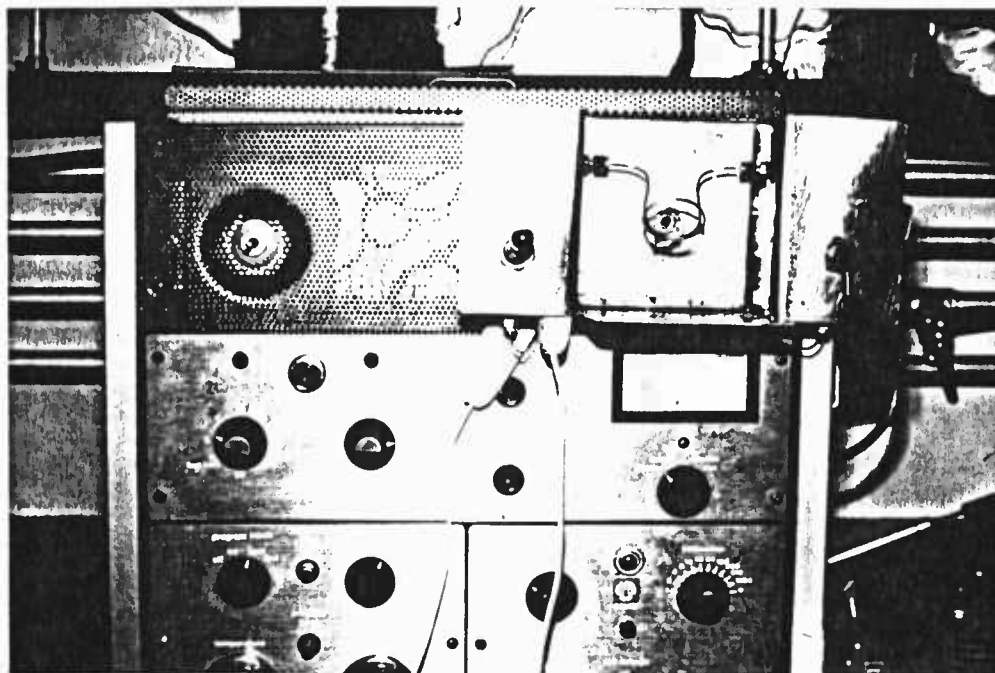

Fig. 2. GC inlet system

Volatile materials collected from vegetables in this manner were chromatographed on wall-coated, 500 ft X 0.03 in ID stainless steel capillary columns. Columns were wall-coated with 6:1 Carbowax 20M and Versamid 900 or with SF-96 and 5% Igepal 880.

The columns were held at 80°C for 5 min and then programed at 1°C/min to 145°C with He flowing at 15 ml/min. The column effluent entered the ion source of a Finnigan quadrupole electron impact MS via a glass jet separator. Electron voltage was 70 eV. Spectra were scanned from M/E 15-250, and data were collected by a System Industries Model 250 data system in the IFSS mode. The IFSS or Integration-Time-as-a-Function-of-Signal-Strength mode results in a nearly constant signal-to-noise ratio and is useful in trace analyses. Analysis of data was facilitated using this data system in conjunction with a Tektronix model 4010-1 display terminal.

III. RESULTS AND DISCUSSION

In a preliminary study the residence time of some typical flavor compounds on porous polymer precolumns was investigated. The choice of porous polymer trap was made on the basis of these retention characteristics. Table 1 shows retention times (T_R) in minutes of various compounds on Porapak Q, Chromosorb 102 and Tenax GC precolumns under simulated sampling and water removal conditions.

Retention performance on Porapak Q and Chromosorb 102 was similar, while retention times exhibited on Tenax GC were considerably shorter. Thus, during the 20-min water removal step, greater losses of low-boiling compounds would occur with use of Tenax GC traps. Porapak Q traps were used for vegetable sampling since we were interested in compounds with a wide range of boiling temperatures. Tenax GC traps would be useful in applications where high-boiling compounds were a major concern.

Recoveries of n-undecane from these porous polymers were measured. A known quantity was introduced onto a precolumn and after simulated sampling and water removal, the compound was desorbed and trapped on-column as described by Morgan and Day (9). Digital integrator response was measured and compared to a standard curve

TABLE 1

Retention Times on Precolumns Under Simulated Loading and
Water Removal Conditions[a]

Compound	BP °C[b]	Porapak Q			Chromosorb 102			Tenax GC		
		First Det[c]	TR	Last Det	First Det	TR	Last Det	First Det	TR	Last Det
Water	100	0.63	1.44	6.0	0.63	1.38	6.0	0.25	1.0	5.5
Methanol	64.6	2.13	3.36		1.25	2.13		0.44	0.75	
Ethanol	78.5	8.5	11.63[d]		5.25	7.0[d]		1.12	1.5[d]	
Formic acid	100.7	14.63	20.0[e]		12.0	15.75[e]		2.0	3.25[d]	
Acetic acid	118.1		>34					8.25	10.0[e]	
Acetaldehyde	21	3.63	5.0[d]		2.13	3.0[d]		0.5	0.75	
Propanal	48.8	18.0	22.75[e]		12.0	15.0[e]		2.0	2.63[d]	
n-Butanal	75.7							5.5	6.5[e]	
Isobutanal	61.5							4.5	6.0[e]	
Methyl mercaptan	7.6	3.0	3.75[d]		5.13	6.75[d]		1.25	1.88	
Ethyl mercaptan	34.7	23.5	29.13[e]		10.75	13.75[d]		1.75	2.5[d]	
Isobutyl mercaptan	98							8.5	12.5[e]	
Dimethyl sulfide	37.5	23.63	28.5[e]		17.0	21.0[e]		1.69	2.13[d]	
Diethyl sulfide	92							14.38	17.38[e]	
Methyl formate	31.5	6.5	8.63[d]		3.5	4.5[d]		0.81	1.25	
Ethyl formate	54	33.0	37.0[e]		16.5	19.25[e]		2.0	3.38[d]	
Methyl acetate	57.5				17.0	20.5[e]		2.5	3.38[d]	
Ethyl acetate	77.2							7.38	9.0[e]	

[a] Precolumn conditions:

Column temperature	55° C	He flow rate	12 ml/min
Injection port temperature	120° C		
Detector temperature	160° C		

[b] From <u>Handbook of Chemistry and Physics</u>. Cleveland: Chemical Rubber Publishing Co. 1960.

[c] Det = Detected

[d] Moderate tailing

[e] Extreme tailing

AMPLITUDE

2. $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$ 9. (pyridine)   17. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-CH_3$ 24. $CH_3-S-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$ 33. (pyrazine) and (pyrazine)   38. (thiazole)$-\overset{O}{\overset{\|}{C}}-CH_3$

4. $CH_3-CH-CH_2-OH$ 8. (pyrazine)   11. $CH_3-CH_2-\underset{CH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H$ 19. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-OH$ 30. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

$\overset{|}{CH_3}$ $\overset{|}{CH_3}$ 16. (furan)$-\overset{O}{\overset{\|}{C}}-CH$ 22 23   25. (furan)$-\overset{O}{\overset{\|}{C}}-CH_3$ 28. (furan)$-CH_2-OH$ 39. (cyclohexenone)

5. $CH_3-O-CH_2-CH_2-OH$ 14. (pyrazine)   22. (pyrazine)   26. $CH-S-CH_3$?   29. $CH_3-S-S-S-CH_3$ 41. (pyrazine)

6. $CH_3-O-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$ 23. (pyrazine)   27. (furanone) ?   31. (thiolane) ?   43. $CH_3-\overset{O}{\overset{\|}{S}}-CH_3$

7. $CH_3-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{CH}}-CH_3$ 46. (furan)$-\overset{O}{\overset{\|}{C}}-CH$ 47. (thiazole)$-\overset{O}{\overset{\|}{C}}-CH_3$?

100   80   60   40   20

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47

|91° |101° |115° |127°

0   10   20   30

48. (pyrazine)   50. (thiophene)$-CH_2-OH$?   55. (dithiolanone) ?   65. (pyrazine) ?

49. 1,8-cineole ?   51. (benzene)$-C_4$ 57. (dithiolanone) ?

60   40   20

48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71

|141° |160° |176°

40   50   60   70
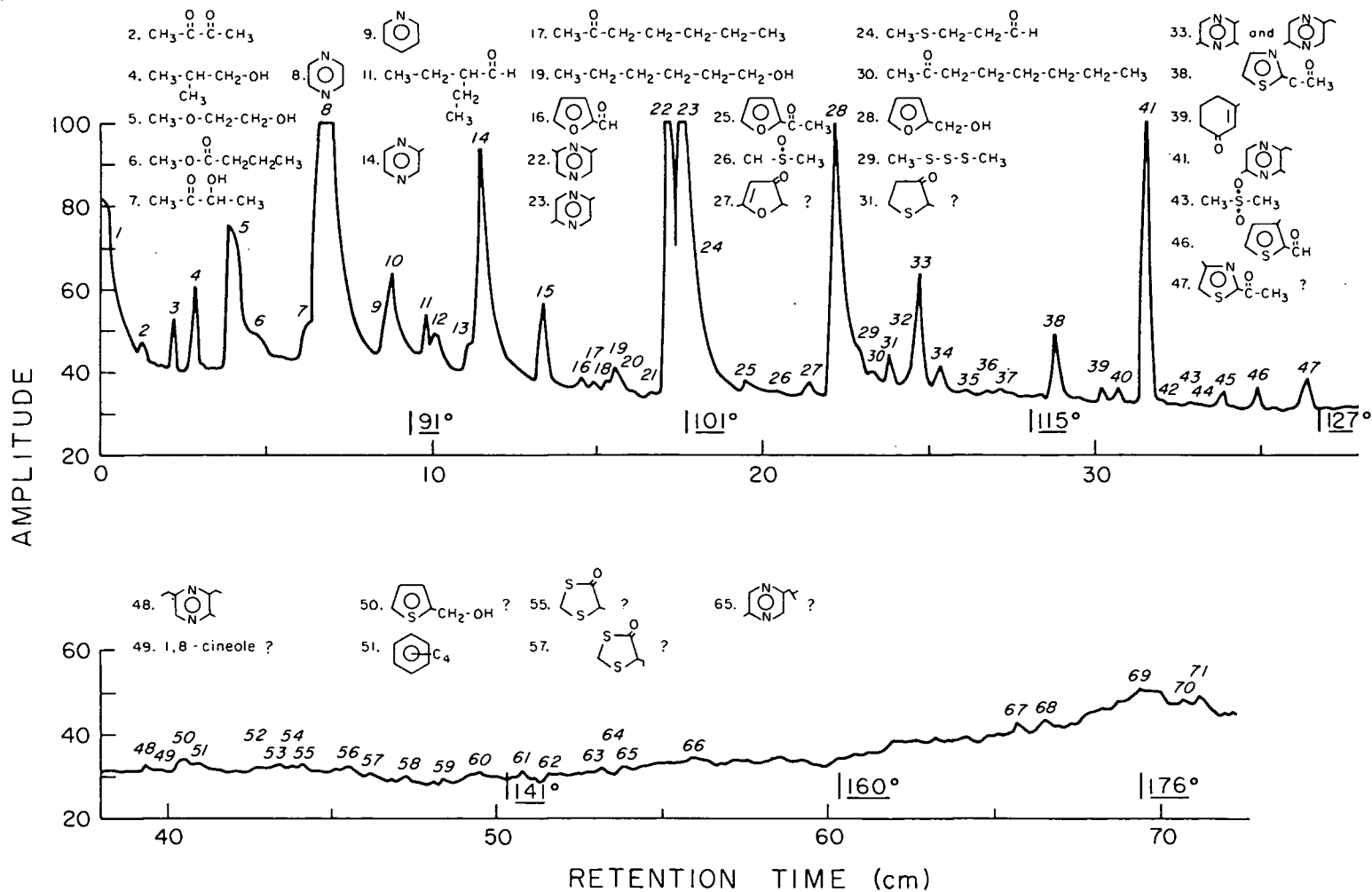
RETENTION TIME (cm)

8

Fig. 3.   Total ionization chromatogram of canned Jubilee sweet corn (SF-96)

nedubaprepared by direct injection. Recoveries of n-undecane were
nearly 100% from these three porous polymers; however, recoveries
of other compounds may not be as complete. Particular care must
by exercised when using porous polymer trapping in quantitative
studies.

We investigated four varieties of canned corn: Jubilee,
Fanfare, Stylepak and No. 70-2367. Figure 3 shows a typical
total ionization chromatogram of the volatile compounds entrained
from Jubilee. Table 2 lists the compounds we identified, their
I_E values and odor descriptions. Odor assessments were made by
sniffing GC effluent from an effluent splitter. Pyrazine and a
series of alkyl pyrazines were detected. These compounds have been

TABLE 2

Compounds Detected in Canned Jubilee Sweet Corn

| Compounds Detected | Retention Index[a] | | Odor Description |
	GC-MS	Literature[b]	
1. water	d		
2. diacetyl	d	1.69	butter
3. unidentified			
4. 2-methylpropanol	d		
5. 2-methoxyethanol			(artifact)
6. methyl butyrate	d		
7. acetoin	d	3.08	
8. pyrazine	d		corn-like with bitter note
9. pyridine	d		
10. C 4 ethyl ester	4.00	4.00	
11. 2-ethylbutanal	d		
12. unidentified			
13. unidentified			
14. methylpyrazine	4.32	4.38	grassy
15. unidentified			
16. furfural	4.70	4.62	
17. unidentified			
18. 2-heptanone	4.89	4.95	
19. 1-hexanol	4.90	4.87	
20. C 5 ethyl ester	5.00	5.00	
21. unidentifed			
22. 2,6-dimethylpyrazine	5.14	5.12	ether-like with corn note
23. 2,5-dimethylpyrazine	5.19	5.17	grassy, "corn nuts"
24. methional	5.21	5.21	
25. 2-acetylfuran	5.37	5.29	
26. dimethyl sulfoxide	5.49	5.41	burned egg shell
27. 2,5-dimethyldihydro-2H-furan-3-one	5.60[d]		corn-like
28. 2-furfuryl alcohol	5.70	5.33	sweet mild odor
29. dimethyl trisulfide	5.76	5.90	corn-like, musty
30. 2-octanone	5.90[d]		fruity
31. 2-methyltetrahydrothiophen-3-one	5.94[d]		
32. C 6 ethyl ester	6.00	6.00	
33. trimethyl- and 2-ethyl-5-methylpyrazine	6.06(6.06)	6.07(6.07)	grassy
34. unidentified			
35. unidentified			
36. unidentified			
37. unidentified			

(Continued)

TABLE 2 (Continued)

Compounds Detected in Canned Jubilee Sweet Corn

	Retention Index[a]		
Compounds Detected	GC-MS	Literature[b]	Odor Description
38. 2-acetylthiazole	6.51	6.30	taco, grassy
39. 3-methyl-2-cyclohexenone	6.69	6.64	pleasant, corn-like
40. unidentified			
41. 2-ethyl-3,6-dimethylpyrazine	6.84	6.83	roasted, pungent
42. unidentified			
43. dimethyl sulfone	6.98	7.06[c]	sulfury, taco
44. C 7 ethyl ester	7.00	7.00	
45. unidentified	7.07		old socks
46. 2-methylfurfural	7.19[d]	7.48	corn note
47. 2-acetyl-4-methylthiazole	7.35		
48. 2,6-diethyl-3-methylpyrazine	7.66[d]	7.64	grassy
49. 1,8-cineole	7.71[d]		fruity
50. 2-thienyl alcohol	7.79[d]		
51. butyl benzene	7.84[d]		(artifact)
52. C 8 ethyl ester	8.00	8.00	
53. unidentified			
54. unidentified			
55. 5-methyl-4-one-1,3-dithialane	8.14[d]		corn-like
56. unidentified			
57. 5-ethyl-4-one-1,3-dithialane	8.34[d]		
58. unidentified			
59. unidentified			
60. unidentified			
61. unidentified			
62. unidentified			
63. unidentified			
64. C 9 ethyl ester	9.00[d]	9.00	
65. C 6 substituted pyrazine	9.11[d]		

[a]I_E values were for a 500 ft x 0.03 in IO SF-96 stainless steel open-tubular column.

[b]Literature I_E values were taken from Katz et al. (28), Kinlin et al. (29), Walradt et al. (30) or Mussinan et al. (31).

[c]I_E was measured with authentic compound.

[d]Tentative identification. MS only, retention index not used or not available

characterized by Maga and Sizer (10) as contributing significant-ly to the unique flavor and aroma associated with roasting or toasting of numerous foods. Because of their low odor thresholds, characteristic odors and the relatively large amounts present, we believe the pyrazines are important contributors to the odor of canned corn. When using the odor unit concept of Guadagni et al. (11), the major flavor contributors were calculated to be 2,5- and 2,6-dimethyl-, 2-ethyl-5-methyl- and 2-ethyl-3,6-dimethylprazine. 2-Acetylthiazole and 2-acetyl-4-methylthiazole were also present. Pittet and Hruza (12) described the sensory properties of thia-zoles as being green, roasted, or nutty, with some vegetable notes. Libbey et al. (6) suggested these compounds may add to the flavor of canned corn. Furan derivatives, including 2-fur-fural, 2-furfuryl alcohol, 2-acetylfuran and 2,5-dimethyldihydro-

2H-furan-3-one, were also detected. According to Stahl (13), flavor thresholds in water range from 30 ppm for 2-furfural to 410 ppm for 2-acetylfuran. Thus these compounds are thought to play relatively minor roles in corn flavor. Maga (14) noted that, except in raw onion, thiophenes have been reported only in heated products. Canned corn contained 2-methyltetrahydro-thiophen-3-one, 5-methyl-2-thiophene-carboxaldehyde, 4- or 5-methylthiophen-3-one and 2-thienyl alcohol. More work needs to be done on the sensory properties and thresholds of thiophenes before their importance to corn flavor can be assessed.

The following compounds were identified for the first time in canned sweet corn: pyridine, methional, dimethyl sulfone, di-methyl sulfoxide (DMSO), acetoin, and 3-methyl-2-cyclohexenone (MCH). Pyridine has an odor threshold in water of 82 ppm and was found to be an important constituent of canned snap bean aroma by Stevens et al. (15). Pyridine and related compounds were also found in roasted pecans by Wang (16) and in cocoa by Vitzthum (17). Methional has been identified in tomato by Buttery et al. (18), chocolate by van Pragg (19), beef by Watanabe (20), and in other products. Guadagni (21) identified methional as the character-istic flavor in potatoes. Strecker degradation of methionine is the generally accepted mechanism of formation. Because of its low taste threshold[50 ppb in skim milk (Stahl, (13))]methional may contribute to canned corn flavor. However, it is present only in trace quantities. Dimethyl sulfoxide is formed from the oxi-dation of dimethyl sulfide. It was found by Ralls et al. (22) in the volatile compounds from a commercial pea blancher and by Liebich et al. (23) in roast beef. Dimethyl sulfone, an oxidation product of DMSO, was also found in roast beef as well as in stale non-fat dry milk by Ferretti and Flanagan (24). Dimethyl sulfone, DMSO, acetoin and 3-methyl-2-cyclohexenone are not flavorful compounds and probably contribute little to canned corn flavor. A single peak with characteristic "canned-corn" odor has not been

identified. Instead, corn aroma appears to be a blend of many compounds peculiar to corn with dimethyl sulfide as the sweet top note.

In the four varieties we investigated, a total of 76 components was detected (Table 3). However, all were not present in each variety. Of the 38 identified compounds only two were missing from certain varieties. 5-Ethyl-4-one-1,3-dithialane was not detected in Stylepak or 70-2367, and 2-furfuryl alcohol was

TABLE 3

Varietal Differences in Canned Sweet Corn

Peak Number	Fanfare	Jubilee	Stylepak	70-2367	I_E [a]	Compound
1	VL[b]	VL	L ·	L		diacetyl
2	VL	M	L	L		2-methyl-1-propanol
3	VL	VL	VL	VL		ethanol
4	VL	M	VL	T		
5	VL	VL	L	VL		
6	?	L	S,Sh	L,Sh		
7	?	L	L	L,Sh		
8	VL	VL	VL	L		
9	VL	VL	L	VL		
10	?	VL	L	L,Sh		
11	?	T	L	?		
12	VL	VL	VL	VL		2-methoxyethanol (artifact)
13	?	VL	?	L,Sh		
14	?	?	?	L,Sh		
15	M	S	L,Sh	L,Sh		
16	M	S	L,Sh	L,Sh		
17	L	M	L,Sh	N		
18	S	S	L,Sh	M		
19	VL	VL	VL	VL		pyrazine
20	L,Sh	?	L,Sh	M,Sh		pyridine (?)
21	VL	L	L,Sh	M		
22	VL	L	L,Sh	L		
23	L,Sh	L	M,Sh	M,Sh		
24	VL	VL	T,Sh	M		
25	T	T,Sh	T	T		
26	S	T	T	T		
27	VL	VL	L	L		methylpyrazine
28	S,Sh	S,Sh	T,Sh	M		
29	T	T	N	T		
30	S	S	T	S		
31	T	T	N	N		
32	L	L	T	M		2-heptanone
33	T	S	T	S		
34	S,Sh	T	S	T	S.10	2,6-dimethylpyrazine
35	VL	VL	VL	VL	S.18	2,S-dimethylpyrazine
36	S,Sh	S,Sh	S,Sh	S,Sh	5.26	methional
37	N	N	L,Sh	L	S.36	
38	M,Sh	M,Sh	S,Sh	M	S.43	dimethyl sulfoxide .
39	S	T	T	M	5.57	2,S-dimethyldihydro-2H-furan-3-one
40	N	N	N	T	5.66	
41	T	T	M	N	S.70	2-furfuryl alcohol
42	M	VL	L	M	S.77	dimethyl trisulfide
43	L	S	S	S	S.88	2-octanone
44	T	S	T	T	S.92	2-methyltetrahydrothiopen-3-one
4S	M	T	T	T	6.04	
46	L	L	VL	L	6.09	trimethyl-and 2-ethyl-S-methylpyrazine

(Continued)

TABLE 3 (Continued)

Varietal Differences in Canned Sweet Corn

Peak Number	Fanfare	Jubilee	Stylepak	70-2367	$I_E{}^a$	Compound
47	T	S	T	T	6.18	
48	T	T	T	T	6.24	
49	T	T	T	T	6.33	
50	N	T	N	T	6.40	
51	L	M	L	M	6.53	2-acetylthiazole
52	S	S	S	S	6.70	3-methyl-2-cyclohexenone
53	VL	VL	VL	VL	6.82	2-ethyl-3,6-dimethylpyrazine
54	L	T	L	L	6.94	dimethyl sulfone
55	L	T	T	M	7.07	
56	T	N	N	N	7.15	
57	S	S	S	T	7.20	3-methyl-2-thiophene-carboxaldehyde (?)
58	T	T	N	T	7.27	
59	M	S	L	S	7.34	4-methyl-2-acetylthiazole
60	T	T	T	T	7.41	
61	T	T	N	N	7.53	
62	N	N	T	N	7.57	
63	S	T	L	S	7.63	2,6-diethyl-3-methylpyrazine
64	L	T	S	M	7.83	C 4 -benzene (artifact)
65	S	S	N	N	8.06	
66	S	T,Sh	M	S	8.09	
67	T	T	L	T	8.17	5-methyl-4-one-1,3-dithiolane (?)
68	T	T	N	N	8.44	5-ethyl-4-one-1,3-dithiolane (?)
69	T	N	N	N	8.67	
70	T	N	L	T	8.80	
71	T	N	T	N	8.85	
72	T	T	T	T	9.11	C 6 -pyrazine
73	T	T	T	T	9.18	
74	N	T	M	N	9.28	
75	N	T	N	N	9.73	
76	T	N	T	?		

a I_E on SF-96 500 ft capillary column

b Relative Peak Heights
    N = Not detected
    T = Trace, less than 1 cm
    S = Small, greater than or equal to 1 cm and less than or equal to 2 cm
    M = Medium, greater than 2 cm and less than 5 cm
    L = Large, greater than or equal to 5 cm and less than 20 cm
    VL = Very Large, greater than or equal to 20 cm
    Sh = Shoulder peak

not detected in 70-2367. Eleven unidentified peaks were missing from various varieties. When using ethyl octanoate as an internal standard, relative peak heights were measured and assigned various letter designations. "Trace" designated a peak height of less than one cm. Criteria for small, medium, large and very large were also established (see Table 3). The peaks for 13 of the components, were in the same size designation for all varieties. For 24 components three out of four designations were the same. One component had different peak sizes for each variety and, in the remaining 38 components, two of the four

varieties had similar peak size designations. These qualitative
and quantitative similarities for the four varieties were ex-
pected, since these varieties all had good canned corn flavor. The
qualitative variations present and quantities found would account
for the subtle flavor differences.

Nine varieties of frozen blanched corn were investigated.
In frozen Jubilee a total of 38 compounds was detected, and 14 of
these were subsequently identified (Table 4). Figure 4 shows a
typical total ionization chromatogram of frozen Jubilee. Rela-
tively large amounts of alcohols, diacetyl, acetoin, and dimethyl
sulfone were detected. Other compounds including pyridine,
pyrazines, a furan and a thiazole were present only in trace
quantities. New compounds found in frozen corn included acetoin,
pyridine, 3-methyl-2-cyclohexenone and dimethyl sulfone. The
flavor of frozen corn is much less developed than that of canned
corn and can be described as rather bland. Important flavor con-
tributors to frozen corn were the low-boiling compounds such as
alcohols, diacetyl, and certainly dimethyl sulfide. Forty
eight peaks were detected with I_E values of 5.00 or greater
(Table 5). The several varieties had from 16 to 38 peaks present in
their respective chromatograms; 89% of these peaks were present
only in trace quantities. Two of the varieties, NC04 and white
field corn, had poor texture and flavor was characterized as chalky,
grassy or straw-like. Little difference in higher-boiling
compounds was observed between those frozen samples with good
or poor flavor. 2-Ethyl-3,6-dimethylpyrazine, trimethylpyrazine
and 3-methyl-2-cyclohexenone were not detected in those
samples with poor flavor. Presumably,lower-boiling compounds
and bitter non-volatile compounds present in the raw corn were
mainly responsible for the poor flavors.

Major qualitative and quantitative differences occurred in
the compounds present in canned and frozen corn and were
responsible for the different flavors of these products. Frozen
Jubilee with 38 compounds had one furan, one thiazole and no

TABLE 4

Compounds Detected in Frozen Jubilee Sweet Corn

Compounds Detected	Retention Index[a]	
	GC-MS	Literature[b]
1. water	d	
2. diacetyl	d	1.69
3. 2-methylpropanol	d	
4. 2-methyoxyethanol		
5. acetoin	d	3.08
6. 1-pentanol	d	3.88
7. unidentified		
8. unidentified		
9. pyridine	4.02	
10. furfural	d	4.62
11. unidentified		
12. unidentified		
13. unidentified		
14. unidentified		
15. 2,5-dimethylpyrazine	5.18	5.17
16. unidentified		
17. unidentified		
18. unidentified		
19. unidentified		
20. unidentified		
21. trimethylpyrazine	6.09	6.07
22. unidentified		
23. 2-acetylthiazole	6.51	6.30
24. 3-methyl-2-cyclohexenone	6.70	6.64
25. unidentified		
26. 2-ethyl-3,6-dimethylpyrazine	6.83	6.83
27. dimethyl sulfone	6.92	7.06[c]
28. unidentified		
29. unidentified		
30. unidentified		
31. unidentified		
32. unidentified		
33. unidentified		
34. unidentified		
35. unidentified		
36. unidentified		
37. unidentified		
38. unidentified		

a I_E values were for a 500 ft x 0.03 in SF-96 stainless steel open-tubular column.
b Literature I_E values were taken from Katz et al. (28), Kinlin et al. (29), Walradt et al. (30) or Mussinan et al. (31).
c I_E was measured with authentic compound.
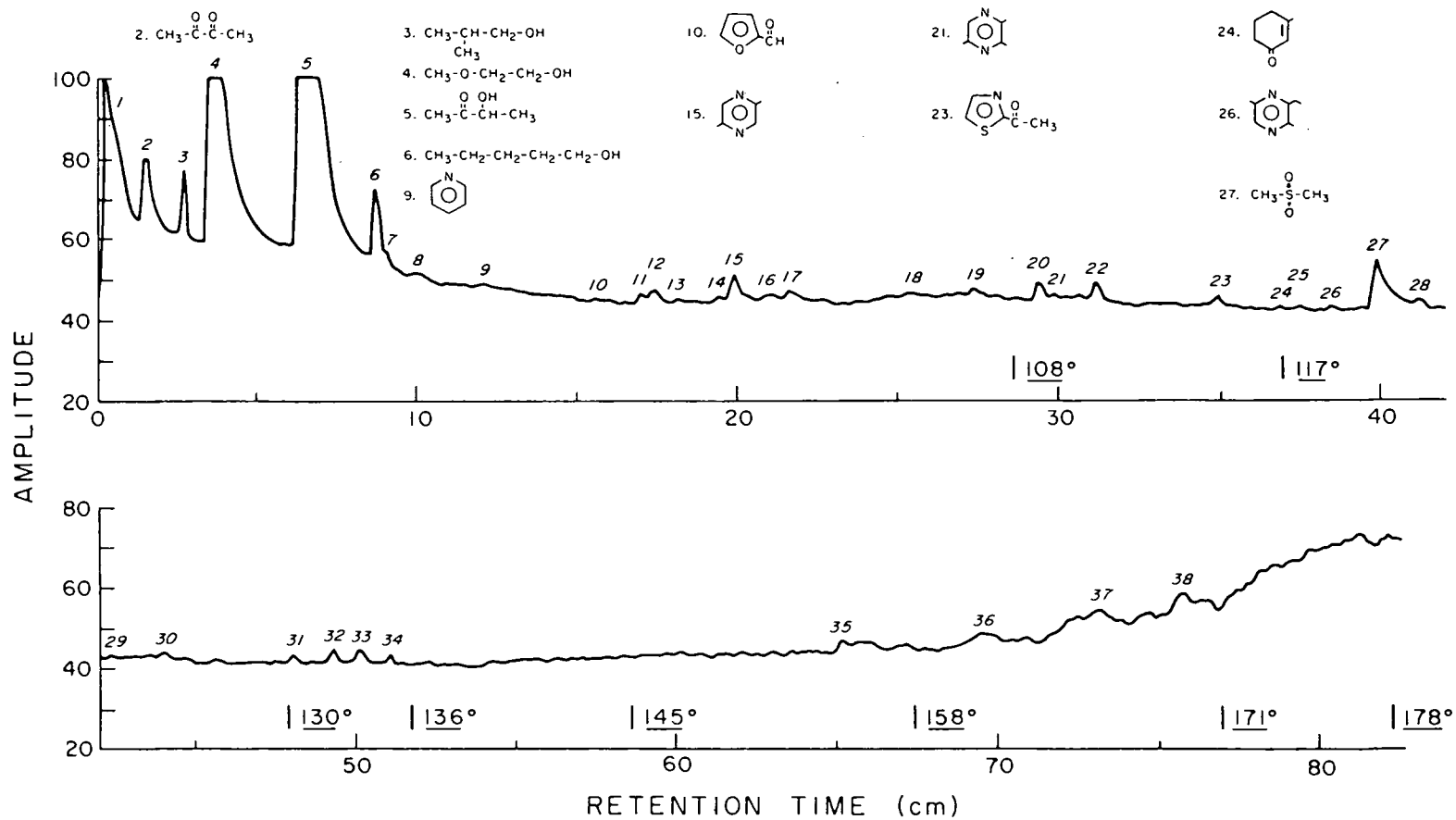d Tentative identification, MS data only

Fig. 4. Total ionization chromatogram of frozen Jubilee sweet corn (SF-96)

thiophenes while canned Jubilee with 65 compounds had four, two and five, respectively. Thiophenes, furans and thiazoles result from chemical interactions during the thermal exposure of amino acids and carbohydrates and thus greater numbers and/or amounts of these compounds were expected in canned corn. The most outstanding difference between the two Jubilee corns was in the pyrazines. In canned corn nine pyrazines were present with relatively large peaks, in frozen only trace amounts of 2,5-dimethyl-, trimethyl- and 2-ethyl-3,6-dimethylpyrazine were present. These trace amounts may have been formed during blanching or sampling. As mentioned previously, pyrazines were thought to play a major role in canned corn flavor.

TABLE 5

Varietal Differences in Frozen 5weet Corn

I_E^a	5tylepak	Goldie	Commander	70-1631	Illan Chief	FM Cross	Jubilee	White Field Corn	NCO4	Compound
5.05	T[b]	M,5h	T	T,5h	M	T	T	5,5h	S	
5.08	N	N	N	T	N	5	N	T	N	
5.12	T	T	M	T	5	5	T	T	T	
5.18	5	T	S	T	T	T	5	T	T	2,5-dimethyl-pyrazine
5.22	T	5	5	N	5	N	T	N	N	
5.28	N	N	T	N	N	N	T	N	N	
5.33	T	N	N	T	N	T	T	T	N	
5.36	N	L	N	N	T	N	N	N	N	
5.39	T	N	T	T	N	T	T	T	T	
5.44	N	N	N	N	N	T	N	N	T	
5.51	N	N	T	T	N	T	T	T	N	
5.58	T	T	T	N	T	T	N	N	T	
5.68	T	N	T	T	N	T	T	T	T	
5.75	N	N	T	T	T	T	N	T	N	
5.82	N	N	N	N	N	T	T	T	N	
5.89	T	T	T	N	T	N	T	N	T	
5.93	N	N	T	T	T,Sh	T	T	T	N	
6.05	T	M	N	T	M	T	5	5	5	
6.09	T	N	T	N	N	T	T	N	N	trimethyl-pyrazine
6.14	N	T	T	N	T	N	T	N	T	
6.19	N	T	T	T	N	T	T	T	N	
6.26	N	N	N	T	T	T	T	T	T	
6.30	T	N	T	N	N	T	T	N	N	
6.35	N	N	N	N	N	T	N	T	N	
6.40	T	N	T	N	T	N	T	T	T	
6.47	N	N	N	N	N	T	N	N	N	
6.51	T	T	T	N	T	T	T	T	T	2-acetyl-thiazole
6.61	N	T	T	T	T	T	T	T	T	
6.70	N	N	T	T	T	N	T	N	N	3-methyl-2-cyclo-hexenone
6.79	N	N	N	T	T	T	T	T	N	
6.84	T	N	T	T	T	T	T	N	N	2-ethyl-3,6 di-methyl-pyrazine

TABLE 5 (Continued)

Varietal Differences in Sweet Corn

I_E^a	Stylepak	Goldie	Commander	70-1631	Illan Chief	FM Cross	Jubilee	White Field Corn	NCO4	Compound
6.92	T	N	T	N	N	T	S	T	N	dimethyl sulfone
7.06	T	S	S	T	S	T	T	S	M	
7.21	N	N	N	N	N	T	N	N	N	
7.27	T	N	T	T	T	T	T	T	T	
7.34	T	T	N	N	N	N	T	N	N	
7.41	T	N	T	T	T	N	T	T	N	
7.58	N	N	T	T	N	T	T	N	N	
7.65	T	T	T	N	T	N	T	T	T	
7.73	N	N	N	N	N	N	T	T	N	
7.82	T	N	T	N	T	T	T	N	T	
7.95	N	N	T	N	N	N	T	N	T	
8.09	T	T	T	N	T	T	T	T	T	
8.17	T	N	N	N	T	N	T	T	N	
8.28	N	N	N	N	T	N	T	T	N	
8.80	N	N	N	N	T	N	T	N	N	
Flavor	Good	Good	Good	Good	Good	Good	Good	Straw-like	Grassy Chalky	
Texture	Good	Good	Good	Good	Good	Good	Good	Tough	Tough	

$^a I_E$ on SF-96 500 ft capillary column

^{b}Relative Peak Heights:
    N = Not detected
    T = Trace, less than 1 cm
    S = Small, greater than or equal to 1 cm and less than or equal to 2 cm
    M = Medium, greater than 2 cm and less than 5 cm
    L = Large, greater than or equal to 5 cm and less than 20 cm
    VL= Very Large, greater than or equal to 20 cm
    Sh= Shoulder peak

To investigate the source of flavor compounds in canned corn, 17 model systems were prepared and examined. In model systems containing corn starch (Merck) and amino acids, we found that most of the peaks were coming from the corn starch alone. We then abandoned the use of corn starch and used sucrose, fructose and glucose as the carbohydrate sources. These were found to be the primary sugars in corn by thin layer chromatography. A typical model system consisted of 100 ml of distilled water buffered to pH 7.0, 0.1 moles of sugar and 0.1 moles of amino acids. The model systems were autoclaved in sealed bottles at 120^OC at 20 psi for 0.5 to 2.5 h. The amino acids chosen for the model systems were listed by Sodek and Wilson (25) as the free amino acids present in normal and opaque-2 corn.

Model system 13 which had a slight corn-like aroma contained the following compounds in 100 mls of buffer solution (pH 7.0):

d-glucose (0.022 mole), d-fructose (0.022 mole), sucrose (0.058 mole), L-proline (0.038 mole), L-cystine (0.012 mole), L-alanine (0.014 mole) and L-glutamic acid (0.038 mole). The resulting pH was 6.2; the pH of canned Jubilee liquor was 6.3. After autoclaving for 1.5 h, the model system was subjected to headspace analysis. Some of the major peaks identified by MS and confirmed by comparing I_E values were: 2-furfural, 2,5-dimethylpyrazine, furfuryl alcohol (slight amount), 2-ethyl-?-methylpyrazine, 2-acetylthiazole, 2-ethyl-?,?-dimethylpyrazine and 2,5-dimethyl-3-thiophene carboxaldehyde. Acetoin and 2-acetyl-4-methylthiazole were tentatively identified. A sulfur-containing compound (I_E = 6.84) and a large peak (I_E = 6.37) which contained oxygen and had a MW 98 were not identified. All of these identified compounds were detected in canned corn except for 2,5-dimethyl-3-thiophene carboxaldehyde. Although the compounds in the model system were not formed in the same proportions as those in canned corn, a corn-like aroma was still present and the importance of amino acid-carbohydrate interactions to corn flavor was demonstrated.

Odors of some of the other model systems were described as burned popcorn, toasted nut, cold cauliflower, butter-like, musty, sulfury vegetable and meaty. Pyrazines, furans, thiazoles, thiophenes and other compounds were tentatively identified. The precursors and their relative proportions in the model systems of course determined the flavors formed upon heating.

Using the same porous polymer sampling techniques, the flavor of fresh parsnip roots was investigated in our laboratory by Grieco et al. (26). Previous work was done by Self (2), Johnson et al. (27) and Cronin (28). Cronin stated that parsnip-like aroma was only associated with the largest peak, terpinolene. We,however, noted that pure terpinolene does not have a parsnip-like odor, and that Cronin had concluded that the terpinolene peak was masking an unknown parsnip-like compound. Table 6 shows some volatile compounds we identified in parsnips. There was a

TABLE 6

Compounds Identified in Parsnips

Compound	GC-MS Identification	Flavor Contribution
1-pentanol	a	no
methional	a	yes
3-methylthiopropanal	a,b	yes
dimethyltrisulfide	a	yes
dimethylsulfide	a	yes
dimethyl sulfoxide	a	no
limonene	a	yes
α-phellandrene	a	yes
terpinolene	a,b	yes
α-terpineol	a	yes
p-cymen-8-ol	a	yes
biphenyl	a	no
methyl eugenol	a	yes
butylated hydroxy toluene	a	no
myristicin	a,b	yes

a = Compound identified by data system flavor file.

b = Spectrum matches that of authentic compound.

pungent note to **parsnip aroma which resembled myristicin more than**
terpinolene. However, the background was terpenoid and was
similar in some respects to the flavor of raw carrots. The
spiciness of methyl eugenol also contributed to the unique
pungency of parsnip, but myristicin was the most characteristic
and strongest component of parsnip odor. Through olfactory analy-
sis of the split GC effluent, we concluded that myristicin was
the chracteristic parsnip aroma.

The previous inability to identify myristicin as the

parsnip compound may have been due to the method of isolation. Porous polymer trapping has several advantages over steam distillation, extraction, etc. An isolate is produced which more closely resembles the aroma that the nose perceives, and artifact formation is minimized. Other advantages include preliminary separation of water from organic compounds, ease of sample handling, relatively short analysis times, lack of water vapor interference, reproducibility and sensitivity. Of course, porous polymers are not without problems. Oxidizing atmospheres, high MW compounds, deposition of salts and excessive temperature are detrimental to porous polymers. Other problems include artifacts, irreversible adsorption, tailing, peak broadening and reactions with the polymer. However, we have found porous polymer trapping a very useful technique for investigating vegetable flavors.

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