Headspace Vapors from Cereal Grains

Cereal grains were found to emit vapors of complex composition. Different species and varieties of grain appeared to produce largely the same volatile components but in different, characteristic, relative amounts. The composition of the vapors might therefore be utilized for chemotaxonomic classification of the seed. Heavy insect infestation of grain samples altered the composition of the collected vapors; this may constitute a confounding effect in chemotaxonomic studies.

Complex mixtures of volatile components are known to emanate from many foods and beverages and give rise to their characteristic aromas (Schultz *et al.*, 1967). We have found cereal grains and oilseeds to emit vapor mixtures of similar complexity. Different species and varieties of grain appear to produce largely the same volatile components but in different, characteristic, relative amounts. Gas chromatography of the volatiles provides "fingerprints" which might be used for chemotaxonomy of seeds. McWilliams and Mackey (1969) have recently reported on the identification of 18 volatile flavor components from wheat.

A preliminary examination of 18 samples of grain and oilseed by gas chromatography indicated that their emanated vapors all differed from one another in quantitative composition. These samples included six varieties of maize, three of rye, two of rapeseed, and one each of wheat, triticale (Larter *et al.*, 1970), barley, oats, flax, soybean, and sunflower seed.

Four varieties of maize (*Zea mays* L.) were analyzed in more detail. Ground kernels (10 g) in a 50-ml Erlenmeyer flask sealed with a serum cap were heated in a sand bath at 120° C for 2 hr. A 2-ml sample of the headspace vapor in the flask was removed through the serum cap with a 5-ml gas tight syringe and injected for gas chromatographic analysis. A Varian Aerograph Series 1800 gas chromatograph was used, with dual flame detectors and dual columns (3.04 m $\times$ 1.83 mm. i.d., copper, packed with Porapak Q, 80- to 100-mesh). The column oven temperature was held at 75° C for 3 min after injection of a sample, then increased 10° C per min for 9 min, held at 165° C for 6 min, increased 10° C per min for 3 min, held at 195° C for 45 min (to end of analysis), reset to 75° C, and left to equilibrate for 2 min before injection of the next sample. The injection port and detector temperatures were 140° and 225° C, respectively. The flow of nitrogen carrier gas was 19 ml per min. Peak areas were measured with an electronic digital integrator (Infotronics Model CRS-108).

The headspace chromatograms of the four maize samples revealed 39 components (Figure 1); some of the smaller components were seen only in some of the samples. Thirteen of the components were tentatively identified (Figure 1) by comparing their retention times on the Porapak column with those for known compounds. Supporting evidence for the tentative identification of seven of these components (24, 26, 27, 32, 33, 38, and 39) was obtained by chromatography on a different column (3.04 m $\times$ 1.2 mm. i.d., stainless steel, packed with FFAP on Chromosorb W, acid washed, 60- to 80-mesh, 1:10 by wt). The earlier components (1 to 19) did not separate on this column; similar supporting evidence, therefore, was not obtained for the other six components (5, 9, 10, 15, 18, and 19) which had been tentatively identified on the Porapak column. Eight of these tentatively identified components from maize have recently been found in wheat by McWilliams and Mackey (1969).

The four maize varieties differed widely from one another in quantitative composition of their volatiles (Table I). Whether a wider selection of maize varieties can be distinguished from one another by the composition of their volatiles remains to be determined.

The heating of the maize samples to 120° C before collection of the headspace vapors provided a relatively high concentration of volatile components in the vapors. Headspace vapors collected at lower temperatures gave similar chromatographic patterns, but with some of the smaller components missing or undetected; samples collected at either 120°, 80°, or 25° C thus gave 39, 21, and 14 peaks, respectively. Some of the components collected at the higher temperatures could possibly be artifacts formed by the effect of heat on glucose or similar substances in the maize (Fagerson, 1969). Headspace vapors were obtained also from unbroken kernels; volatiles collected from whole kernels and from ground kernels gave nearly identical gas chromatographic patterns and peak intensities.

Using essentially the same method as for maize, some exploratory studies were made of the volatiles from wheat, three genetically related grass species, and insect-infested wheat. In these studies, the gas chromatographic components for different samples were related to each other on the basis of their retention times on the Porapak column; peaks from different samples were tentatively considered identical if they had the same retention time.

Five varieties of wheat (Can. Dept. Agr., 1969) were compared, namely, the hard red spring wheats Manitou, Selkirk, Neepawa, and Pembina (*Triticum aestivum* L.), all of similar parental background, and Mindum (*Triticum durum* Desf.). The volatiles from Manitou and Selkirk appeared similar in quantitative composition. The volatiles from Neepawa, Pembina, and Mindum differed from one another and from those of the first two varieties. The differences, however, were less pronounced than for the maize varieties.

The genetic relationship between the man-synthesized crop triticale (*Triticale hexaploide* Lart.) (Larter *et al.*, 1970) and its parents, rye (*Secale cereale* L.) and durum wheat (*Triticum durum* Desf.), appeared to be reflected in the composition of their volatiles. The compositions for the three species

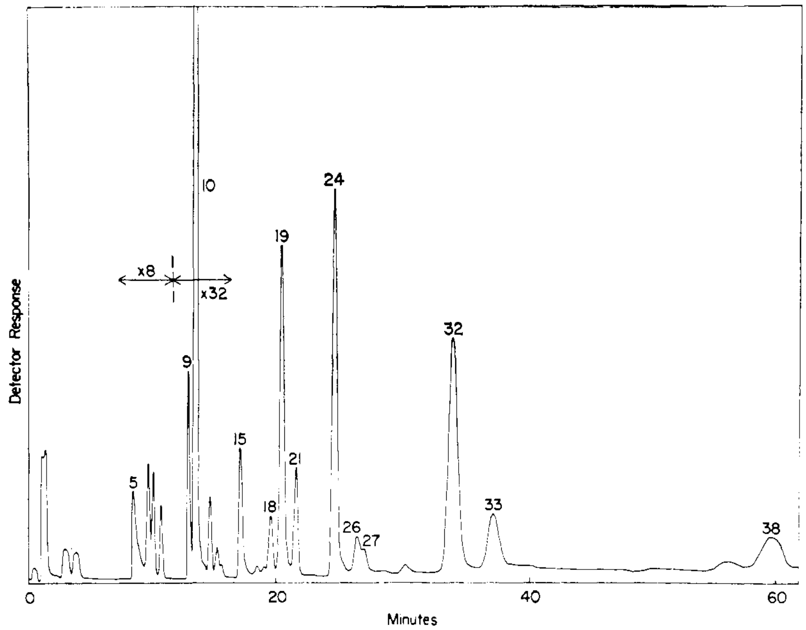

Figure 1. Gas chromatogram of headspace vapor from maize (unknown hybrid "S"). Tentative identification of peaks: water (peak 5), methanol (9), ethanal (10), ethanol (15), propanal (18), propanone (19), 2-methyl propanal (24), butanal (26), butanone (27), 3-methyl butanal or 2-methyl butanal (32), pentanal (33), hexanal (38), and heptanal (39, not shown in the figure). The chromatogram also indicates the general pattern for the headspace analyses of wheat, rye, triticale, and weevils; these gave peaks with the same retention times as for maize, but with different peak heights

Table I. Composition of Headspace Vapors for Four Varieties of Maize

	Peak Areas (%)[a]				
	Peak Number				
	10	15	19	21	32
Varieties					
CM-37[b]	22.9	*0.9*	9.2	9.0	*4.2*
K-275[b]	*17.7*	4.6	*16.7*	10.2	10.3
K-30[b]	*29.0*	3.2	8.4	*5.2*	9.6
S[c]	24.5	*10.6*	8.2	*3.6*	*17.7*
	±0.9	±1.9	±0.9	±0.3	±1.2

[a] The compositions are calculated from gas chromatographic peak areas (Figure 1), in percent of the total peak areas, without use of detector response factors. Of the 39 peaks, only five which amply discriminate among the varieties are included in the table; the percentages, therefore, do not add up to 100. The figures in italics are the most important. [b] Inbred line; single analysis. [c] Unknown hybrid; means ± standard deviations for five replicate analyses.

differed mainly in the amounts of two components (24 and 33, Figure 1); these were intermediate for triticale.

	Peak 24 (%)	Peak 33 (%)
Wheat	7.8	10.0
Triticale	9.2	5.7
Rye	16.6	3.4

Heavy insect infestation of a grain sample was found to alter the characteristic composition of its headspace vapor. The volatiles from a high quality wheat, and from the same wheat heavily damaged by granary or rice weevils [*Sitophilus granarius* (L.) and *S. oryza* (L.)] but with the weevils removed differed appreciably in the contents of components 10, 21, 24, and 32 (Figure 1). Granary weevils alone, freed from wheat particles and heated, but not crushed, produced volatiles that contained three major and at least 17 minor components, all apparently identical with components of the wheat volatiles. The three major components corresponded with peaks 10, 24, and 32 from the wheat (Figure 1). The volatile components collected from the weevils were most probably a product of the wheat they had eaten; the insects had been reared on whole Manitou wheat for over a year. Other components, peculiar to the weevils, were not found. These results indicate that a classification of grain varieties based on their headspace vapors might be confounded if insect infestation has occurred. The possible effects of mites and molds which commonly infest cereals remain to be studied.

The volatiles from the investigated varieties of maize, wheat, rye, and triticale were qualitatively similar but, except for two wheat varieties, quantitatively different. This indicates a possible use of the headspace vapors in distinguishing among seed varieties.

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