Cereal Volatiles, A Review

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Although cereal grains constitute an important portion of worldwide diet, little is known of their volatile composition, especially in the raw state. This review summarizes volatile compounds identified to date in corn, oats, rye, wheat, triticale, barley, and rice and points out potential areas for further investigation for the flavor chemist.

Cereal grains represent the most important food staple for the world's population and in some cultures can represent up to 80% of the diet. Not only are cereals consumed alone but they are primary ingredients for many food products throughout the world.

Since sensory properties can significantly influence consumption patterns, one would assume that the flavor composition and chemistry of cereal grains would be thoroughly investigated and documented. Surprisingly this is not the case since published investigations relative to the volatile composition of the three primary cereals in the raw state (rice, corn, and wheat) number less than a dozen. Some investigators have reported on the volatiles associated with the roasting of cereals and the development of off flavors during their storage, yet extensive evaluation of the volatiles associated with unprocessed cereals has been noticeably neglected. Information of this type would be useful to the flavor chemist to better understand the origin and formation of volatiles in such products.

Therefore, this brief review was undertaken to summarize the data to date and hopefully act as a stimulus to flavor chemists who have neglected this interesting and important area of investigation.

CORN

Hougen et al. (1971) reported on the headspace volatile composition of numerous raw cereal grains, including corn, and as seen in Table I, simple alcohols and carbonyls were identified. Four varieties of corn kernels were ground and heated in a container maintained at 120 °C for 2 h, and aliquots of headspace vapor were analyzed by gas chromatography. Using this technique, a total of 39 peaks were detected with 12 being assigned the identifications listed in Table I.

The authors acknowledged that heating at 120 °C for 2 h could induce artifact formation since preliminary studies demonstrated that heating at lower temperatures resulted in missing or undetected peaks.

Headspace analyses were also performed on whole kernels, presumably using the same isolation technique, and it was reported that whole and ground kernels gave essentially similar chromatographic patterns and intensities. One would have postulated that perhaps certain enzymatic reactions, activated by the grinding process, could have produced significantly different volatile profiles.

This headspace technique was used by Hougen et al. (1971) to demonstrate that varietal volatile differences existed with corn. As seen in Table II, certain compounds among the 39 detected varied widely among varieties and thus potentially could result in differences among their sensory properties.

To the author's knowledge, this brief study by Hougen et al. (1971) represents the current published information available relative to raw corn volatiles. Interestingly, the pleasing aroma associated with heated corn has not even been publically reported.

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Table I. Volatiles Associated with Corn[a]

Methanol	Butanal
Ethanol	Butanone
Ethanal	3-Methylbutanal or 2-methylbutanal
Propanal	Pentanal
Propanone	Hexanal
2-Methylpropanal	Heptanal

[a] Hougen et al. (1971).

Table II. Influence of Corn Variety on Headspace Volatile Composition[a]

Variety	Peak area, % Ethanal	Ethanol	Propanone	Unknown	3-Methylbutanal or 2-methylbutanal
1	22.9	0.9	9.2	9.0	4.2
2	17.7	4.6	16.7	10.2	10.3
3	29.0	3.2	8.4	5.2	9.6
4	24.5	10.6	8.2	3.6	17.7

[a] Hougen et al. (1971).

Table III. Volatiles Associated with Oat Flakes[a]

Steamed	Toasted
Furfural	Furfural
Formaldehyde	Hydroxymethylfurfural
Propanal	Formaldehyde
Acetone	Diacetyl
Two unidentified carbonyls	Acetaldehyde
	2-Butanal
	Propanal
	Acetone
	n-Butanal
	2-Methylpropanal
	3-Methylbutanal
	2-Pentanone
	n-Hexanal
	2-Methylbutanal
	2-Hexanone
	n-Octanal
	2-Octanone

[a] Hrdlicka and Janicek (1964).

Dravnieks (1973) and Dravnieks et al. (1973) attempted to use gas chromatographic analysis of corn headspace volatiles as a means of distinguishing corn with musty and sour aromas from normal corn. Extensive statistical evaluation was involved and in one study only 3 of 20 samples were misclassified using their technique when compared to sensory judgement by grain inspectors. However, no identification was attempted on the volatiles detected.

OATS

Oat represents another cereal grain that has unique and characteristic flavor properties, especially in its toasted

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Table IV. Volatiles Associated with Rye

Methanol[a]	Butanone[b]
Ethanol[a]	3-Methylbutanal or 2-methylbutanal[a]
Acetaldehyde[b]	Pentanal[a]
Ethanal[a,b]	2-Pentanone[b]
Propanal[a]	Hexanal[a,b]
Propanone[a]	Heptanal[a]
2-Methylpropanal[a]	2-Heptenal[b]
Butanal[a,b]	2-Octenal[b]

[a] Hougen et al. (1971). [b] Prince and Mackey (1972).

Table V. Volatile Compositional Differences among Wheat, Rye, and Triticale Grain[a]

Grain	Peak % 2-Methylpropanal	Peak % Pentanal
Wheat	7.8	10.0
Triticale	9.2	5.7
Rye	16.6	3.4

[a] Hougen et al. (1971).

form. An earlier study by Hrdlicka and Janicek (1964) reported on the presence of mainly carbonyls in toasted oat flakes. These are summarized in Table III. Paper chromatography of 2,4-dinitrophenylhydrazone derivatives was used for separation. As expected, toasting significantly influenced the number of compounds detected.

From this very brief study the authors concluded that carbonyls could not be regarded as the only source of tasted oat flavor. Thus although oats represent the major ingredient in certain food systems, especially certain breakfast cereals, its volatile composition has not been reported.

RYE

The volatiles associated with raw rye were briefly mentioned by Hougen et al. (1971) as being qualitatively similar to those formed in corn. Quantitative differences were noted but actual data were not presented. Prince and Mackey (1972) reported on the volatiles associated with rye flour. The volatiles reported in these studies are summarized in Table IV.

TRITICALE

Triticale represents a genetic cross between durum wheat and rye. Thus Hougen et al. (1971) predicted that this would be reflected in its volatile composition. Triticale is said to have a mild rye flavor, and as shown in Table V, Hougen et al. (1971) apparently choose two compounds among the 39 detected to stress this point. However, it is highly unlikely that only these two compounds are the key differences in sensory differentiation among the three grains.

In investigating compositional differences among wheat and triticale flours, the volatile carbonyl composition of several varietal spring and winter triticale flours was briefly surveyed by Lorenz and Maga (1972). As seen in Table VI, no qualitative differences were noted but apparent quantitative differences were obvious with acetaldehyde, pentanal, hexanal, and heptanal being the compounds most susceptible to change as influenced by variety. Volatile compounds identified to date in triticale are summarized in Table VII.

WHEAT

Wheat represents the cereal grain most commonly used for human consumption in the United States. However, a survey of the flavor literature revealed that only three published studies have dealt with the volatiles associated with the grain or flour form of this commodity. Volatiles

Table VI. Carbonyl Composition (%) as Influenced by Triticale Variety[a]

Compound	Spring varieties 6TA204	Spring varieties 6TA206	Winter varieties TR385	Winter varieties TR386
Acetaldehyde	6.9	16.2	7.3	15.0
Propanal	2.1	7.5	2.3	9.0
Acetone	22.4	16.0	19.8	12.0
Butanal	5.2	8.7	11.4	13.8
2-Butanone	15.6	12.7	19.4	17.0
Pentanal	32.0	23.6	5.1	15.1
2-Pentanone	10.0	3.4	6.8	6.6
Hexanal	3.8	8.0	10.3	7.6
Heptanal	2.0	3.9	17.6	3.9

[a] Lorenz and Maga (1972).

Table VII. Volatiles Associated with Triticale

Methanol[a]	Propanal[a,b]
Ethanol[a]	Propanone[a]
Acetaldehyde[a,b]	2-Methylpropanal[a]
Butanal[a,b]	Pentanal[a,b]
Butanone[a,b]	Pentanone[b]
3-Methylbutanal or 2-methylbutanal[a]	Hexanal[a,b]
Acetone[b]	Heptanal[a,b]

[a] Hougen et al. (1971). [b] Lorenz and Maga (1972).

Table VIII. Volatiles Associated with Wheat

Methanol[a]	Pentanal[a-c]
Ethanol[a]	Isopentanal[c]
Acetaldehyde[a-c]	Pentanone[b]
Acetone[b]	2,3-Dimethyl-3-pentanone[c]
Butanal[a-c]	Hexanal[a-c]
Isobutanal[a,c]	Heptanal[a-c]
Butanone[b,c]	Octanal[c]
3-Methyl-2-butanone[c]	Ethyl acetate[c]
Butenal[c]	Isoamyl alcohol[c]
Diacetyl[c]	Cyclopentanone[c]
Propanal[a,b]	Phenylacetaldehyde[c,d]
Propanone[a]	Amyl alcohol[c]

[a] Hougen et al. (1971). [b] Lorenz and Maga (1972). [c] McWilliams and Mackey (1969). [d] LaVoie et al. (1970).

identified in these studies are summarized in Table VIII. It is granted that intensive investigations have been conducted on bread systems where wheat is the most prominent ingredient but undoubtedly flavor formation during the complex baking process would be better understood if more detailed information on the volatile composition of wheat were available.

The volatile headspace composition of five wheat varieties was investigated by Hougen et al. (1971). Four of the varieties had similar parental backgrounds; however, only two of these had similar quantitative compositions whereas the other two, along with the fifth variety evaluated, differed quantitatively from one another.

An interesting sidelight to the Hougen et al. (1971) study included insect infestation of wheat. The three major volatiles associated with isolated weevils were found to be also among the predominant volatiles associated with wheat.

Lorenz and Maga (1972) also evaluated the short-chain carbonyl composition of several winter and spring wheat flour varieties. No qualitative differences were apparent and only small quantitative differences were detected. Thus from a varietal standpoint this brief study pointed out that wheat varieties are apparently more uniform in carbonyl composition than triticale varieties.

A total of 18 volatiles associated with steam distillation of lightly milled whole grain wheat flour was reported by

Table IX. Volatiles Associated with Barley

Ethanol[a,b]	Pentanal[a]	Acetylfuran[c]
Propanol[a,b]	Isopentanal[h]	Vanillin[f]
Butanol[b]	Hexanal[a,h,i]	Protocatechuic aldehyde[f]
Isobutanol[b]	2-Hexenal[i]	2-Pyrrolealdehyde[f]
Pentanol[b]	Furfural[a,d]	Syringaldehyde[f]
Hexanol[b]	Propanone[a]	*p*-Hydroxybenzaldehyde[f]
Furfuryl alcohol[b,c]	Pentanone[i]	Pyridine[a,g]
Hydrogen sulfide[b]	Butanone[a,i]	3-Hydroxypyridine[c]
Dimethyl disulfide[b]	2-Hexanone[h]	Pyrazine[a]
Acetic acid[b]	2,3-Butanedione[a]	2-Methylpyrazine[a,g]
Propionic acid[b]	2,3-Pentanedione[a,d]	2,3-Dimethylpyrazine[a]
Butyric acid[b]	γ-Octalactone[b]	2,5-Dimethylpyrazine[a,g]
Valeric acid[b]	γ-Nonalactone[b]	2,3,5-Trimethylpyrazine[a,g]
Isovaleric acid[b]	γ-Decalactone[b]	2-Ethyl-3-methylpyrazine[a]
Caproic acid[b]	5-Hydroxymaltol[e]	2-Ethyl-5-methylpyrazine[a,g]
Isocaproic acid[b]	Maltol[e]	Ethyldimethylpyrazine[g]
Ethanal[a,d]	Phenol[e]	3-Ethyl-2,5-dimethylpyrazine[a]
Propanal[a]	*m*-Cresol[e]	2-Ethyl-3,5-dimethylpyrazine[a]
Butanal[i]	Pyrocatechol[e]	Ammonia[g]
2-Methylpropanal[a,d]	Resorcinol[e]	Acetaldehyde[h]
2-Methylbutanal[a,d,i]	5-Methylcyclopent-2-en-ol-1-one[e]	Acetone[h,i]
3-Methylbutanal[a,d]		

[a] Collins (1971). [b] Wang et al. (1970). [c] Shimizu et al. (1970a). [d] Wang et al. (1968). [e] Shimizu et al. (1970b). [f] Shimizu et al. (1970c). [g] Wang et al. (1969). [h] Hrdlicka et al. (1970). [i] Wagner (1971).

Table X. Volatiles Associated with Rice Products

Acetaldehyde[a,f,h]	2-Octanone[a]	Benzaldehyde[a]
Acetone[a,b,e,f]	Octanal[a]	*p*-Methylbenzaldehyde[a]
Methanol[b]	2-Octenal[a]	*o*-Xylene[a]
Ethanol[a,b]	2-Nonanone[a]	*m*-Xylene[a]
Ethanal[b]	Nonal[a]	*p*-Xylene[a]
Butanone[a,c,e]	2-Nonenal[a]	Benzene[a]
Butanol[b]	2-Decanone[a]	Ethylbenzene[a]
sec-Butanol[b]	Decanal[a]	*N*-Propylbenzene[a]
Isobutanol[b]	2-Decenal[a]	1-Ethyl-4-methylbenzene[a]
Butanal[a-c,g,h]	2-Undecanone[a]	1,2,3-Trimethylbenzene[a]
Isobutanal[a-c]	2-Dodecanone[a]	1,2,4-Trimethylbenzene[a]
Propanol[a,b]	2-Dodecenal[a]	1,3,5-Trimethylbenzene[a]
Propanal[a,h]	Hydrogen sulfide[h]	o-Diethylbenzene[a]
Pentanal[a-c,e-h]	Toluene[a]	*m*-Diethylbenzene[a]
Isopentanal[a-c,h]	2,5-Dimethylfuran[a]	*p*-Diethylbenzene[a]
Pentanone[a-c,f]	2-Butylfuran[a]	1,4-Dimethyl-2-ethylbenzene[a]
Pentanol[b]	2-Acetylfuran[a]	1,3-Dimethyl-4-ethylbenzene[a]
Isopentanol[b]	2-*N*-Pentylfuran[a]	1,3-Dimethyl-5-ethylbenzene[a]
2-Methylbutanal[a]	2,4-Hexadienal[a]	1,2-Dimethyl-3-ethylbenzene[a]
2-Methylpentanal[a]	2,4-Heptadienal[a]	1,2,3,4-Tetramethylbenzene[a]
3-Penten-2-one[a]	2,4-Octadienal[a]	1,2,3,5-Tetramethylbenzene[a]
2-Hexanone[a]	2,4-Nonadienal[a]	1,2,4,5-Tetramethylbenzene[a]
Hexanal[a-c,e-h]	2,4-Decadienal[a]	Naphthalene[a]
Hexanol[b]	6-Methyl-5-hepten-2-one[a]	1-Methylnaphthalene[a]
2-Hexenal[a]	α-Pinene[a]	2-Methylnaphthalene[a]
2-Heptanone[a]	Δ^3-Carene[a]	2-Ethylnaphthalene[a]
Heptanal[a]	*p*-Cymene[a]	Phenylacetaldehyde[a]
2-Heptenal[a]	*trans*-β-Methylstyrene[a]	

[a] Bullard and Holguin (1977). [b] Mitsuda et al. (1968). [c] Chikubu (1970). [d] Obata and Tanaka (1965). [e] Yasumatsu et al. (1966a). [f] Yasumatsu et al. (1966b). [g] Tanaka (1972). [h] Ayano and Furuhashi (1970).

McWilliams and Mackey (1969). To date this represents the largest number of volatiles associated with wheat. This is quite interesting in light of the vast numbers and various classes of volatile compounds isolated, detected, and identified in other food systems. As noted by McWilliams and Mackey (1969), the vast majority of the compounds found in their study had previously been identified as components of bread in various stages of preparation and thus they postulated that the flavor of baked bread may have a significant correlation to volatiles associated with wheat. However, it should be noted that wheat is only one of many potential flavor compound sources relative to bread.

BARLEY

Aside from rice, barley is the cereal grain most widely investigated from a volatile composition standpoint. As seen from Table IX, a wide range of interesting flavor associated volatile compounds have been identified which because of their low thresholds and unique properties have the potential to contribute significantly to the sensory properties of roasted barley. However, somewhat surprisingly, none of the investigators have considered evaluating raw barley.

Wang et al. (1968) trapped volatiles from ground roasted barley along with those formed during the roasting of barley. The same six carbonyls were identified from both systems. They postulated that the compounds resulted from carbohydrate and amino acid degradation during roasting. Removal of the volatile carbonyls from roasted barley resulted in a barley product that did not have characteristic barley aroma and thus the authors concluded that carbonyls play an important role in the flavor of roasted barley.

In a later study Wang et al. (1969) investigated the volatile basic fraction of roasted barley and reported on the presence of five pyrazine compounds, pyridine, and ammonia.

In still a later study Wang et al. (1970) identified two sulfur compounds, seven short-chain volatile fatty acids, seven alcohols, and three lactones from roasted barley. They postulated that the fatty acids could lead to undesirable flavors or be precursors for esters; however, no esters were detected. Although numerous alcohols were detected they concluded that alcohols do not contribute significantly to roasted barley aroma since a specific alcohollike odor was not detected in the trapped neutral noncarbonyl oxygenated fraction. However, they felt that the lactones detected, because of their unique aroma, could significantly be important to roasted barley aroma.

Another group of Japanese workers have investigated the volatiles associated with the neutral fraction of roasted barley. Shimizu et al. (1970a) identified three major compounds including two furan derivatives which had characteristic flavor significantly related to the flavor of roasted barley and a pyridine derivative that had no characteristic odor but did possess a bitter taste.

Shimizu et al. (1970b,c) also reported on the volatiles associated with the acidic fraction of roasted barley. A total of 13 phenolic related compounds were identified. They concluded that among these 5-methylcyclopent-2-en-2-ol-1-one, maltol, and vanillin contributed to the fragrant flavor of roasted barley while phenol, *m*-cresol, pyrocatechol, and resorcinol were associated with the smoky flavor of roasted barley.

Collins (1971) also investigated the volatile composition of roasted barley. He identified eight aldehydes, four ketones, and two alcohols in the headspace from the steam volatile fraction and nine pyrazines along with pyridine in the basic fraction.

RICE

Rice represents the major cereal grain which is grown and consumed throughout the world and yet until only recently approximately 20 volatile compounds had been reportedly identified relative to rice products. The recent study by Bullard and Holguin (1977) reported on the identity of 73 volatiles in unprocessed rice with 54 of these never having been previously reported in any unprocessed cereal grain. The volatiles identified in rice products to date are summarized in Table X.

Several types of rice products are represented in Table X. For example, Mitsuda et al. (1968) were primarily concerned with rice bran and identified nine simple alcohols along with eight carbonyls. In addition, Japanese workers have been especially interested in the volatiles associated with stale rice, and both Ayano and Furuhashi (1970) and Tanaka (1972) reported that stored rice, which had been judged to be stale, had higher levels of pentanal and hexanal than fresh rice. An earlier review by Chikubu (1970) dealt specifically with the stale flavor of stored rice and due to the types of carbonyl compounds reported at that time, both Strecker degradation of amino acids and lipid autoxidation were believed to be the primary pathways for stale flavor formation in rice.

Interestingly, the recent study reported by Bullard and Holguin (1977) was not initiated from a traditional flavor chemistry standpoint but was an attempt to better understand raw rice volatiles in hopes of formulating a rat bait composed of important rice volatiles.

This last study clearly demonstrates that numerous volatiles can be effectively isolated and separated from a produce thought to be relatively bland and thus similar techniques could be quite easily applied to other cereal grains. Efforts of this type are needed to supply informative and useful data currently lacking so that the flavor chemist can more easily and completely understand this important portion of flavor chemistry.

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